

# Understanding of the wrinkles formation during the coating functionalization of lightweight fibrous material: a multiscale approach

Florian Le Gallic

# ► To cite this version:

Florian Le Gallic. Understanding of the wrinkles formation during the coating functionalization of lightweight fibrous material: a multiscale approach. Chemical and Process Engineering. Université Grenoble Alpes [2020-..], 2022. English. NNT: 2022GRALI091. tel-04048638

# HAL Id: tel-04048638 https://theses.hal.science/tel-04048638

Submitted on 28 Mar 2023  $\,$ 

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## THÈSE

Pour obtenir le grade de

# Université Grenoble Alpes

## DOCTEUR DE L'UNIVERSITÉ GRENOBLE ALPES

École doctorale : I-MEP2 - Ingénierie - Matériaux, Mécanique, Environnement, Energétique, Procédés, Production

Spécialité : MEP : Mécanique des fluides Energétique, Procédés

Unité de recherche : Laboratoire de Génie des Procédés pour la Bioraffinerie, les Matériaux Bio-sourcés et l'Impression Fonctionnelle

Compréhension des phénomènes physiques relatifs à l'apparition de plis générés lors de la fonctionnalisation de surface par enduction des matériaux fibreux de faible grammage : une approche multiéchelles.

Understanding of the wrinkles formation during the coating functionalization of lightweight fibrous material: a multiscale approach.

Présentée par :

## Florian LE GALLIC

Direction de thèse :

Raphaël PASSAS Ingénieur HDR, Université Grenoble Alpes Céline MARTIN Maitre de Conférences, Grenoble INP

Directeur de thèse

Co-directrice de thèse

#### Rapporteurs :

**Dominique Knittel** Professeur des Universités, Université de Strasbourg **Paulo Jorge Tavares Ferreira** Maitre de Conférence, Universidade de Coimbra

Thèse soutenue publiquement le 5 décembre 2022, devant le jury composé de :

| Dominique Knittel   | Rapporteur              |
|---|-------------------------|
| Professeur des Universités, Université de Strasbourg      |                         |
| Paulo Jorge Tavares Ferreira                              | Rannorteur              |
| Maitre de Conférences, Universidade de Coimbra            | Парропеці               |
| Pascale Balland   |                         |
| Professeure des Universités, Université Savoie Mont-Blanc | Examinatrice            |
| Ana Paula Costa   |                         |
| Maitre de Conférences, Universidade da Beira Interior     | Examinatrice            |
| Jean-Claude Roux  |                         |
| Professeur des Universités, Grenoble-INP                  | Président - Examinateur |
| Raphaël Passas  |                         |
| Ingénieur HDR, Grenoble-INP - Agefpi                      | Directeur de thèse      |
| Céline Martin   |                         |
| Maitre de Conférences, Grenoble-INP                       | Co-directrice de thèse  |
|   |                         |

Invités :

The necessaries of life for man in this climate may, accurately enough, be distributed under several heads of Food, Shelter, Clothing, and Fuel; for not till we have secured these are we prepared to entertain the true problems of life with freedom and a prospect of success.

Henry David Thoreau in Walden, 1854

# Remerciements

L'ensemble de ce qui est présenté dans cette thèse a été réalisé au sein du laboratoire LGP2 de Grenoble, qui a su m'accueillir, me supporter, m'encourager, m'héberger, me fournir l'ensemble des dispositifs numériques et expérimentaux et auprès duquel j'ai eu l'occasion de faire de nombreuses et belles rencontres ces dernières années. Merci à l'IMEP-2, Tec 21 et la Region Rhône-Alpes pour le financement.

Je tiens tout d'abord à remercier mes 2 encadrants Céline et Raphaël. Merci pour les conseils, la gentillesse, le temps, la bienveillance, l'humanité et la compassion (au sens de « la force secrète de son étymologie » comme l'a si bien dit Kundera). Merci de m'avoir formé à la recherche par la recherche, d'avoir soutenu ma future carrière sans chercher à gonfler les vôtres et merci d'avoir prouvé que la recherche académique peut permettre de s'élever ensemble et non l'un par rapport à l'autre. Soyez les moteurs du changement en montrant à la nouvelle génération de chercheurs l'intérêt du management bienveillant ; et puisse ces derniers oublier leur h-index dénué de sens, pour produire une science de qualité, non de quantité, sociétale et accessible.

Les travaux menés et présentés dans ce manuscrit n'auraient pas pu être réalisés sans l'aide des supports scientifiques et techniques du laboratoire. Ainsi merci à Maxime, Cécile, Karine et Bertine pour le concours apporté à ce projet. Je pense également aux services techniques et informatiques ainsi qu'à Stéphane et Mikaël. Des collaborations internes et externes au laboratoire ont été réalisé. Merci donc à Jérémie Viguié et Denis Curtil du LGP2 pour leur aide exceptionnelle concernant la partie expérimentale autour du pilote et de la mise en place de la D.I.C ainsi que la mécanique du flambement. Pour les collaborations externes, je remercie Pierre Caulet (Ahlstrom-Munksjö), Nicolas Jacques (IRDL Brest), Pierre Vacher (USMB), Axel Le Nozahic (SWM), Romuald Leon (SWM), François Bonnel (CMTC), Georges Kapelsky (SIMAP) et Mamadou Toungara (ENETP, Bamako) pour le concours apporter à ce projet. Enfin merci aux étudiants que j'ai encadrés, notamment Cédric Dumont, Julien Dufieux, Elsa Rozzi et Romain Dubuis

Enfin, il est bien plus facile de travailler dans un lieu et une ambiance propice au travail : il est important pour moi de mentionner le bon esprit, l'optimisme et la motivation des doctorants et post-doctorats et que j'ai eu la chance de côtoyer ces dernières années. Les longues discussions, les sympathiques conversations tenues durant les pauses cafés/thés et les points de cultures générales ou les échanges scientifiques font partis intégrants des très bons moments passés en votre compagnie. Se reconnaîtront, entre autres, Maxime Teil, Arnaud, Loreleï, Mathieu, Bastien, Gabriel, João, Lorette, Amélie, Fanny, Khawla, Clémentine, Julia, Emilien, Laura et Julie. J'ai une pensée toute particulière pour Claire, qui a finalement reconnu avoir été mon encadrante de stage et qui est aujourd'hui une formidable amie ; ainsi que pour Marlène, ayant commencé sa thèse en même temps que moi (à quelques mois près...) : merci pour ta présence rassurante et réconfortante (sans t'en rendre compte), sans oublier ton humour et tes conseils.

Au moment où ces lignes sont écrites, j'ai déjà eu l'opportunité de soutenir la thèse. C'était un moment que j'attendais avec beaucoup d'impatience (non sans stress) pour la richesse des échanges scientifiques. J'ai été servi et suis aujourd'hui ravi du moment passé où j'ai pu considérer de nombreuses perspectives pour la suite du projet. Merci encore aux rapporteurs, Paulo Ferreira et Dominique Knittel pour leur travail de relecture du manuscrit, leurs rapports et nos discussions. Et merci également à mes trois examinateurs, Ana Paula Costa, Pascale Balland et Jean-Claude Roux, pour les échanges notamment sur la partie mécanique de la thèse, qui m'ont beaucoup intéressé.

Pour terminer, même s'ils sont moins concernés par les travaux présentés ici, j'aimerais remercier l'ensemble de mes amis, de mes proches et de ma famille pour leur soutien. Je pense notamment à mes amis de Bretagne Clémentine, Noémie, David, Gwen et Agathe, ainsi qu'à mes amis de l'ENSTIB et du Moulin Simon, Lucas et Franck. J'ai une pensée toute particulière pour Margaux qui a toujours été là pour me réconforter, m'aider et je souhaite à tout le monde de rencontrer une aussi merveilleuse personne au moins une fois dans sa vie. Enfin, je remercie mes parents, Marie-Hélène et Sylvain, qui m'ont toujours soutenu et encouragé pour aller dans la voie qui me plaisait le plus.

# Abbreviations and Notations

# Latin letters

### Lowercase letters

- a Web span (m)
- $a_{mn}$  Amplitude (m)
- $a_y$  Described transition between the first Newtonian plateau and the power law zone

 $b_{w,tan}$  WSD y-intercept (MPa)

b Web width (m)

c Constant  $(m^5)$ 

$$d_{c-IR}$$
 Distance between the coating station and the IR dryer inlet (m)

 $d_e$  Drop diameter (m)

 $d_{particle}$  Particles diameter (m)

 $d_s$  Drop diameter measured a distance  $d_e$  of the drop bottom (m)

dA Elementary surface  $(m^2)$ 

dW Elementary work to increase a surface area of dA  $(N \cdot m)$ 

exp Exponential function

f Constant

g Gravitational acceleration (9.81  $m \cdot s^{-2}$ )

 $h_{jurin}$  Liquid height in a single in capillary, determined by Jurin's law (m)

- $h_s$  Measuring height (mm)
- h Liquid height in a single in capillary (m)
- i Number of wrinkles (used by Hashimoto)
- $k_c$  Buckling coefficient
- $k_{jp}$  Transverse buckling wave number
- $k_n$  Constant used by Puntel
- $k_{odw}$  Flow consistency index  $(Pa \cdot s^{n_{odw}})$ 
  - $k_p$  Wave number

 $k_s$  Inverse of a characteristic diameter  $(m^{-1})$ 

 $k_{Wr}$  Shape parameter Weibull law

| $l_{c,jp}$      | Characteristic length (m)  |
|-----------------|--|
| $l_{cm}$        | Wrinkling wavelength   |
| $l_{res}$       | Resonance length (m)   |
| $l_{x,jp}$      | longitudinal buckling wavelength,  |
| m               | Number of wrinkles in longitudinal direction of a tensile test   |
| $m_0$           | Initial mass (g)   |
| $m_{binder}$    | Mass of starch used as a binder (g)  |
| mc(%)           | Moisture content of paper $(\%)$   |
| $m_{f}$         | Final mass (g)   |
| $m_{particles}$ | Mass of uncooked starch particles in the coating color (g)   |
| $m_{wa,eq}$     | Mass at equilibrium (g)  |
| $m_{wa}(t)$     | Mass of water absorbed into porous media (g)   |
| $m_{water}$     | Mass of water (g)  |
| n               | Number of wrinkles in transverse direction of a tensile test   |
| $n_a$           | Severity of water absorption   |
| $n_c$           | Flow behaviour in Cross's law  |
| $n_e$           | Factor of severity of the Young's modulus decay  |
| $n_{kp}$        | Number of wrinkles used by Puntel  |
| $n_{odw}$       | Flow behaviour in Ostwaeld-de-Waele's law  |
| $r_{cap}$       | Capillary radius (m)   |
| $r_{particle}$  | Particles radius (m)   |
| $r_w$           | Wenzel's roughness factor  |
| $t_1$           | Transition time between inertial and visco-inertial regime (s)   |
| $t_2$           | Transition time between visco-inertial and purely viscous regime (s) $% \left( {{\mathbf{x}}_{i}} \right)$ |
| $t_{95}$        | Time value at inflection point of the DPM curve (s)  |
| $t_c$           | Contact time between paper and water on the coating pilot (s)  |
| $\mathbf{t}$    | Time (s)   |
| $t_{f}$         | Paper thickness (m)  |
| $t_{max}$       | Time value at the highest transmission value in DPM $(s)$  |
| $t_{wet}$       | Wetting time (s)   |
| $w_{mn}$        | Out of plane displacement (m)  |
| $x_c$           | Filler ratio in paper  |
|                 |  |

# Capital letters

| A, B  and  D                   | Constants   |
|--------------------------------|---|
| $A_{cm}$                       | Wrinkling amplitude used by Cerda (m)                                 |
| $A_e$                          | Coefficient depending upon the intermolecular vibration $(Pa\cdot s)$ |
| $A_{e0}, a_e \text{ and } b_e$ | Constants   |
| $A_n$                          | Constant  |
| $A_p$                          | Cross-sectional area of pores $(m^2)$                                 |
|                                |   |
|                                |   |

| $A_{s,eq}$           | Plateau value of the aborptiveness $(g_{water} \cdot m_{paper}^{-2})$ |
|----------------------|---|
| $A_s$                | Water absorptiveness of paper $(g_{water} \cdot m_{paper}^{-2})$      |
| $A_{Wr}$             | Amplitude in Weibull law $(\mu m^2)$                                  |
| $D_{iso}$            | Web bending stiffness for isotropic materials $(N \cdot m)$           |
| $D_T$                | Tortuosity fractal dimension  |
| $D_{xx}$             | Web bending stiffness in x-direction $(N \cdot m)$                    |
| $E_a$                | Activation energy $(J \cdot mol^{-1})$                                |
| $E_{CD,max}$         | Maximum value of Young's modulus following CD (GPa)                   |
| $E_{CD,min}$         | Minimum value of Young's modulus following CD (GPa)                   |
| $E_{CD}$             | Young's modulus in CD (GPa)   |
| $E_{MD,max}$         | Maximum value of Young's modulus following MD (GPa)                   |
| $E_{MD,min}$         | Minimum value of Young's modulus following MD (GPa)                   |
| $E_{MD}$             | Young's modulus in MD (GPa)   |
| $E_{w,tan}$          | WSD tangent modulus (MPa)   |
| $E_{tan}$            | Elastic tangent modulus (GPa)   |
| $E_x$                | Young's modulus in x-direction (GPa)                                  |
| $E_z$                | Young's modulus z-direction (GPa)                                     |
| ${ m E}$             | Young's modulus for isotropic materials (GPa)                         |
| $F_{dw}$             | Strength measured during a Du Noüy ring or Wihelmy plate test (N)     |
| $G_{xz,Baum}$        | Shear modulus in the $xz$ plane (GPa)                                 |
| G                    | Grammage $(g \cdot m^{-2})$   |
| Н                    | Shape factor used in pendant drop method                              |
| J                    | Proportionality factor  |
| $K_c$                | Penetration or spreading constant $(s^{-1})$                          |
| $K_p$                | Strain plateau in WSD test $(\%)$                                     |
| $L_{dw}$             | Length considered during a Du Noüy ring or Wihelmy plate test (m)     |
| M                    | Energy emittance $(W \cdot m^{-2})$                                   |
| $N_x$                | Force in x-direction per unit length $(N \cdot m^{-1})$               |
| $N_z$                | Force in z-direction per unit length $(N \cdot m^{-1})$               |
| R                    | $8.314J \cdot mol^{-1} \cdot K^{-1}$                                  |
| Re                   | Reynolds number   |
| $\mathrm{R}^2$       | Coefficient of determination  |
| $S_{bs}$             | Bending stiffness $(mN \cdot m)$                                      |
| $S_{DPM}$            | Maximum slope measured in DPM (% of transmission $\cdot s^{-1}$ )     |
| $S_p$                | Cross-sectional area of the porous media $(m^2)$                      |
| S                    | Dimensionless coefficient used in Richardson-Zaki law                 |
| $\operatorname{Sdr}$ | Developped interfacial areas ratio (%)                                |
| $T_{cr}$             | Critical web tension $(N \cdot m^{-1})$                               |
| $T_{heating}$        | Heating temperature (°C)  |
| $T_{measured}$       | Measured temperature (°C)   |

Tension in x-direction  $(N \cdot m^{-1})$  $T_x$ Т Fluid temperature (K)Particle speed calculated using Richardson-Zaki law  $(m \cdot s^{-1})$  $V_{Richardson-Zaki}$ Particle speed calculated using Stokes lax in a shear-thinning fluid  $(m \cdot s^{-1})$  $V_{shear_thinning}$ Particle speed calculated using Stokes law  $(m \cdot s^{-1})$  $V_{Stokes}$ Web speed  $(m \cdot s^{-1})$  $V_{web}$ Adhesion work (or Dupré's Energy)  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$  $W_A$ W function of Lambert  $W_{lbt}$ 

# Greek letters

#### Lowercase letters

| $\beta$ | Web | shape | factor |
|---------|-----|-------|--------|
|---------|-----|-------|--------|

- $\delta_{\alpha_r}$  Relative error (%)
- $\delta_p$  Shape factor proposed by Benevante (m)
- $\varepsilon_c$  Porosity (%)
- $\varepsilon_s$  Sensor emissivity
- $\varepsilon_x$  Strain in x-direction (%)
- $\varepsilon_z$  Strain in z-direction (%)
- $\eta$  Dynamic (or apparent) viscosity  $(Pa \cdot s)$
- $\eta_{\infty}$  Viscosity of the second Newtonian plateau(at high shear rates)  $(Pa \cdot s)$
- $\eta_0$  Viscosity of the first Newtonian plateau(at low shear rates)  $(Pa \cdot s)$
- $\gamma_{lg}$  Liquid surface tension  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma_{lq}^d$  Dispersive part of the liquid surface tension  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma_{lq}^p$  Polar part of the liquid surface tension  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma_{sg}$  Surface Free Energy (SFE) of a solid  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma_{sg}^d$  Dispersive part of the Surface Free Energy (SFE) of a solid  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma^p_{sg}$  Polar part Surface Free Energy (SFE) of a solid  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\gamma_{sl}$  Solid-liquid interfacial energy  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$
- $\dot{\gamma}$  Shear rate  $(s^{-1})$
- $\kappa_s$  Measuring angle (°)
- $\lambda_a$  Mass constant to model paper disc stacking (g)
- $\lambda_c$  Cut-off value (mm)

$$\lambda_c^{-1}$$
 Shear rate at which shear thinning behaviour appears  $(s^{-1})$ 

- $\lambda_s^{-1}$  Absorptiveness value at middle height (in  $g_{water} \cdot m_{paper}^{-2}$ )
- $\lambda_{Wr}$  Scale parameter in Weibull law
  - $\mu$  Friction coefficient
- $\nu_{iso}$  Poisson's ratio for isotropic materials
- $\nu_{xz,Baum}$  Poisson ratio calculated with Baum's method
  - $\nu_{xz}$  Poisson's ratio for transverse strain in the z-direction

- $\nu_{zx}$  Poisson's ratio for transverse strain in the x-direction
- $\varpi$  Constant
- $\phi$  Volume fraction in particle (%)
- $\phi_A$  Fraction of surface of a chemical compound A
- $\phi_B$  Fraction of surface of a chemical compound B
- $\phi_p$  Inclination angle of a capillary tube with respect to the horizontal plane (°)
- $\phi_f$  Angle between the tensile test direction and MD (°)
- $\rho$  Mass density of suspending fluid  $(kg \cdot m^{-3})$
- $\rho_{fiber}$  Volumetric mass density of fiber  $(g \cdot cm^{-3})$
- $\rho_{filer}$  Volumetric mass density of filler  $(g \cdot cm^{-3})$ 
  - $\sigma$  Stephan-Boltzmann constant  $(5.6697.10^{-8}W \cdot m^{-2} \cdot K^{-4})$
- $\sigma_{e,iso}$  Normalized stress for isotropic materials (Pa)
- $\sigma_{e,ortho}$  Normalized stress for orthotropic materials (Pa)
  - $\sigma_{x,cr}$  Critical tensile stress in x-direction (Pa)
    - $\sigma_x$  Tensile test in x-direction (Pa)
  - $\sigma_{z,cr}$  Critical compressive stress in z-direction (Pa)
    - $\sigma_z$  Stress in z-direction (Pa)
    - $\tau$  Characteristic transition time between inertial and viscous regime (s)
    - $\tau$  Shear stress (Pa)
    - $\tau_1$  Time constant (s)
    - $\tau_2$  Time constant (s)
    - $\tau_a$  Time constant (s)
    - $\tau_{cr}$  Critical shear stress (Pa)
    - $\tau_d$  Time constant (s)
    - $\tau_p$  Correction factor of tortuosity
  - $\theta_{c,A}$  Contact angle of a compound A (°)
  - $\theta_{c,B}$  Contact angle of a compound B (°)
  - $\theta_{c,i}$  Initial contact angle (°)
  - $\theta_{c,eq}$  Contact angle at equilibrium (°)
    - $\theta_c$  Contact angle (°)
    - $\theta_c^*$  Corrected contact angle for a rough/heterogeneous surface (°)
  - $\theta_{cr}$  Critical misalignment angle (°)
  - $\theta_{Wr}$  Position parameter in Weibull law
    - $\xi_1$  Anisotropy factor of paper
    - $\xi_2$  Constant

#### Capital letters

- $\Delta \rho$  Difference fluid and particle volumetric mass density  $(kg \cdot m^{-3})$
- $\Delta T$  Work done by forces acting in the middle plane of the plate  $(N \cdot m)$
- $\Delta t_f$  Increase in the paper thickness (m)

- $\Delta U$  Strain energy of bending  $(N \cdot m)$ 
  - $\Delta$  Constant
- $\Phi_{binder}$  Cooked starch mass fraction (wt%)
- $\Phi_{particles}$  Mass fraction of uncooked starch grains in the coating gel (wt%)
  - $\Pi_p$  Perimeter of pores, respectively (m)
  - $\Sigma r^2$  Sum of the squared deviations
  - $\Theta_{t,0}$  Initial tensile stiffness  $(kN \cdot m^{-1})$
  - $\Theta_t$  Tensile stiffness  $(kN \cdot m^{-1})$

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# Chapter

# General Introduction

# Context

Since its creation, paper as a material has constantly evolved to meet society's needs. Currently, research focus in the reduction of grammages with constant mechanical characteristics and the functionalization of papers in order to obtain specific surface properties (roughness, oil and moisture barrier, oxygen and water permeability, etc.) for the reduction of the environmental foot printing of the paper industry. These characteristics can be obtained by coating paper surface with suitable aqueous coating color. The quality of the coating obtained depends on the triplet: paper/coating color/coating process. Once the coated paper obtained, important properties must be controlled: water absorption, basic weight, surface and hydro-expansion. For the coating color, the rheological properties, dry matter content and chemical nature must be considered. As for the process, the main parameters are the quantity of coating color transferred, the travel time from coating to drying, the drying conditions, the web tension and the rollers alignment.

When coating very lightweight papers, wrinkles may appear at the exit of the coating area (Figure 1.1) which, after drying and depending on the nature of the coating color, may be irreversible and may cause non-conformities and downgrading of the products.

Here, a coupling between water absorption, which reduces the mechanical properties of paper, and buckling phenomena, possibly due to shear, misalignment and tension, has to be studied.



Figure 1.1: Conformed (left) and non-conformed (right) paper.

Firstly, water coming from the coating sauce weakens the mechanical fibre network properties.

Secondly, the loading imposed by the web tension (used to tension the paper during the process) may be non-uniform across the web. This may be due to roll misalignment. This non-uniform distribution of the load could generate secondary compressive stresses perpendicular to the paper transport direction and lead to an out-of-plane deformation: this is buckling. Then passing to a web span to another it becomes winkle (on the roller). If the buckled paper passed over the roll it will create creases. Buckling could also just be" tension buckling" if the buckling criterion is low.

A question then immediately comes to mind: "what is a wrinkle?" Wrinkling is a most common and costly web defect encountered in the manufacturing and converting of lightweight grades of paper, film and textiles. It is so common, that a lot of synonyms existed: baggy lane, creases, troughs, soft/hard wrinkles ... In this study, the following terms will be used as follows [1]:

- $\rightarrow$  A web trough is an out-of-plane deformation of the web that occur between rollers in web-handling system (= web buckled in web span)
- $\rightarrow$  A **baggy web** is a web with one edge stretched and the other floating
- $\rightarrow$  A web wrinkles is an out-of-plane deformation of the web that is transferred over rollers from one web span to the next (= web buckled on roller).
- $\rightarrow$  A web creases is permanent deformation from wrinkling

Figure 1.2 represented the evolution from troughs to creases.



Figure 1.2: From troughs to creases on the RK coating pilot of the LGP2 laboratory.

This project is taking place within the MatBio and BioChip teams, of the LGP2 laboratory, in Grenoble (France). It is also a continuation of a collaboration with INSA Lyon, supported by the LGP2 (Roll and Fun project, 2018) as the part of the development of a paper-based thermal insulator. The targeted objective of this former project was to produce paper-based thermal insulation continuously. However, the paper wrinkling issue after coating and drying remains. It should also be noted that this theme of dimensional variations linked to the hydro-expansion of fibrous supports and out-of-plane deformation is a recurrent problem to manufacture fibrous products.

# Objectives of this PhD thesis

Thus, the main objective of this PhD thesis is to fully understand the mechanisms underlying the wrinkle appearance during the roll to roll coating process. The final goal is to limit or totally avoid wrinkles appearance when depositing a functional layer on the surface of lightweight papers. This project is also based a multi-scale study of the physical phenomena involved and their fundamental understating/approach. The understanding and technological resolution of this challenge can subsequently lead to the development of new functionalities for Roll to Roll technology. To achieve the project goal, three major objectives will have to be achieved, each being a results chapter, listed below and illustrated Figure 1.3.



Figure 1.3: Visual abstract presenting the manuscript organisation.

- → Chapter 4 knowledge of the paper behaviour when coated : This first results chapter will focus on understanding the water absorption phenomena of GHDS 35 paper. The paper wettability will be studied, taking into account its roughness. Then the water absorption will be analysed using 3 techniques: Cobb, PDA and "Paper discs stacking". This chapter will also deal with the coating sauce, focusing on the starch cooking, rheology and the sedimentation phenomena that can occur with starch particles.
- $\rightarrow$  Chapter 5 understanding of the wrinkle formation mechanics throughout a multi-scale approach: The second chapter of results will strongly deal with the wrinkles mechanics. Through static and dynamic observation of the wrinkling/buckling phe-

nomenon, observations will be made during tensile tests by using Digital Image Correlation (D.I.C) and tests on a coating pilot. The wrinkles produced on the latter will be characterised a posteriori on macroscopic and microscopic scales. Models from the literature will be used to better understand the phenomena.

 $\rightarrow$  Chapter 6 - instrumentation of the coating pilot and development of a driving assistance tool: The last chapter of results will present the instrumentation of the coating pilot in the first place. The study of the temperature sensor and its monitoring during the process will be the focus of the first part of this chapter. The second part will focus on the realisation of a control map tool, in order to better master the process. The papers coated in the laboratory will also be presented, as well as their characteristics.

Theses 3 objectives (and chapters) will be preceded by a literature review (**Chapter 2**) and a presentation of the materials and methods used in this project (**Chapter 3**).

# Scientific valorisation and presentation

The work presented in this manuscript was presented during 5 conferences through posters, oral presentations and one conference article:

- → Le Gallic & al. Highlighting of the factors influencing a non-contact infrared temperature measurement during a paper coating process,  $25^{th}$  TECNICELPA, Coimbra (Portugal), March 2021 (oral presentation)
- $\rightarrow$  Le Gallic & al. Study of the rheological properties of a starch-based coating color for the production of a multilayer paper insulation, 7<sup>th</sup> EPNOE International congress, Nantes (France), October 2021 (poster presentation)
- $\rightarrow$  Le Gallic & al. Control of wrinkling phenomenon during surface functionalization process: example of coating in paper industry, CODEGEPRA 2021, Grenoble (France), November 2021 (poster and oral presentation)
- $\rightarrow$  Le Gallic & al. Approaching Young's modulus changes during aqueous coating, CIADICYP 2022, Girona (Spain), June 2022 (oral presentation)
- $\rightarrow$  Le Gallic & al. Wrinkles formation and origins: from theory of web handling to coating pilot scale experimentation, 17<sup>th</sup> Fundamental Research Symposium, Robinson College, Cambridge (United Kingdom), September 2022 (oral presentation and conference article)

# Chapter 2

# Literature review

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This chapter will be dedicated to a literature review of the different topics discussed in this thesis. First, the paper as a material will be reviewed: origin, manufacture, structure and surface. The coating processes will then be discussed, firstly on the coating color (pigments, binders, formulation and sedimentation) before focussing on the coating techniques and web handling that can be found during the coating process. The third part will deal with the phenomena of paper wettability and the absorption of liquids, including water by paper. The rheology, of starch in particular, will be discussed. Finally, the fourth and last part of this chapter will focus on the buckling phenomena that can occur on webs, such as paper, through two phenomena: tension buckling and shear wrinkling.

## 2.1 Paper

#### 2.1.1 Paper origin and composition

Paper is first and foremost fibres from trees or annual plants, growing around the world in fields or forests. So to begin this chapter, let's take a quick look at the origins of paper in terms of raw materials. Forest, according to FAO (Food and Agriculture Organization) is a land spanning more than 0.5 hectares with trees higher than 5 meters and a canopy cover of more than 10 percent, or trees able to reach these thresholds in situ. It does not include land that is predominantly under agricultural or urban land use. Forests cover 31% of the total land area

of the world. The Forests of Former USSR, South America (mainly Brazil), and Asia-Oceania (mainly China) alone accounts for more than half of the total world's forest area.

Although, large scale tree plantation and natural expansion has significantly reduced the net loss of forests in the previous decade but deforestation rate is still alarming. Deforestation in Africa, Oceania and Latin America was the main cause for the net loss of forests in the previous decade due to deforestation are mainly social and economic politics. In Africa the main cause of deforestation is the dependence of its population on wood as a source of energy. Moreover, in South-East Asia, some companies does not hesitate to chop natural forest for paper production and to replace the destroyed forest hectares with arable lands with palm trees for the production of palm oil, leading to the destruction of biodiversity and single-wood species forest (case of Asian Pulp and Paper companies in Indonesia (APP) [2][3].

From the Neolithic period onwards, humans have shaped the forest, its boundaries and its landscape to cope with the increasing settlement of the population. Since the industrial revolution, everything has accelerated and since 1950, wood is exploited more and more throughout the world. Global industrial groups appeared, polarising the resource and making it a major strategic issue [4].

Wood is an oriented composite and plant-based material. Its fields of use are determined by its behaviour when subjected to physical or chemical treatment but also by its quality which is linked to its macroscopic, microscopic structure and its chemical constituents: cellulose (40-50%), hemicellulose (20-25%) and lignin (25-30%) [5]. Looking more specifically at its structure, wood can be defined as a set of plant cells that settle into an organized and dynamic complex with a certain rigidity. The cell wall of these plant cells is composed of three different parts (Figure 2.1) [6][7]:



Figure 2.1: From living cell to wood fibre [8].

- $\rightarrow$  The middle lamina, which corresponds to the cement between the cells. Its thickness is from 0.5 to 1.5 µm. It is essentially made up of pectins and lignin;
- $\rightarrow$  The primary wall, which corresponds to the outer layer of the cell. It has a thickness of 0.1 µm. It is essentially made up of cellulose micro-fibrils, hemicellulose and pectins;
- $\rightarrow$  The secondary wall, which is the inner wall of the plant cell. This wall is subdivided into 3 layers: the outer layer S1, the middle layer S2 and the inner layer S3. Its constitution is similar to the primary wall but it contains more lignin;

The wood constituents are distributed differently within the middle lamina, the primary wall and the secondary wall. This distribution of the polymers present in the cell varies according to the plant studied (Figure 2.2).



Figure 2.2: Distribution of principal chemical constituents in softwood cell wall layers [9].

The primary wall represents 1% of the relative thickness of the cell wall. The outer layer is between 10 and 20% of the thickness. The middle layer S2 is the major part of the cell wall with 70 to 90% of the wall thickness. Finally the inner layer S3 is between 2 and 8% of the thickness. In the different walls representing the wood, fibre are made of cellulose micro-fibrils. This micro-fibrils are not oriented in the same direction in function of the layer considered and the wood species. To determine this Micro-Fibrils Angle (MFA), the Page method could be used [10]. In general, the primary wall has randomly MFA. The S1 layer MFA is between 50 and 70°. For the S2 layer, MFA is from 10 to 30° and for S3 layer from 60 to 90°. Note that a 0° MFA mean a vertical fibril. In the paper industry different types of wood are used:

- $\rightarrow$  Softwood (pine, fir, spruce, etc.), which contains long cellulosic fibres (2 to 4 mm), which give papers good mechanical properties.
- $\rightarrow$  Hardwood (birch, beech, aspen, hornbeam, eucalyptus, etc.), which contains shorter fibres (0.6 to 1.5 mm), which provide opacity and printability.

#### 2.1.1.1 Cellulose and hemicellulose

Cellulose is the most abundant polymer on earth. It is estimated that 50 billion tons of cellulose are produced annually, 80% of which comes from wood. It is also present in annual plants such as cotton, hemp or flax as well as in algae, fungi and bacteria. Cellulose consists of the repetition (homopolymer) of a molecular unit, cellobiose, with a size of 1.025 nm. Two cellobiose units are linked by a  $\beta$ 1-4 bond. The degree of polymerization (DP) of cellulose (i.e. number of units) is on average 10000 in wood, which corresponds to a fiber of about 5  $\mu$ m. Cellobiose itself consists of 2 units of  $\beta$ -D-glucopyranose (Figure 2.3). Hemicellulose is an amorphous polymer



Figure 2.3: Cellobiose (between brackets) and 2  $\beta$ -D-glucopyranose units (which composed cellobiose unit) [11].

with a lower DP and molecular weight than cellulose (DP<200). Unlike cellulose, hemicellulose is a heteropolymer with ramifications. The main types of hemicelluloses are xylans which are 5-carbon sugars and gluco-mannans which are 6-carbon sugars. Hemicelluloses are different between hardwood and conifers.

#### 2.1.1.2 Lignin

Lignin is the second largest constituent of wood by weight: 20 to 30%. It is a non-linear, amorphous, water-insoluble polymer of phenolic nature, i.e. it is based on a phenol group in the constituent units of lignins. Lignins are heteropolymers whose constituents are not always the same: there are therefore an infinite number of lignins.



Figure 2.4: The 3 lignin precursors for plants (from left to right): p-hydroxyphenyl unit, guaiacyl unit and syringyl unit [12].

Indeed, there is a great variability due to the botanical origin, the essence and the nature of the cells. It should be noted that there is more lignin in conifers than in hardwoods. Lignins are mainly composed of 3 types of constituent units: p-hydroxyphenyl units (H unit), guaiacyl units (G unit) and syringyl units (S unit) (Figure 2.4). These units also allow differentiation between coniferous, hardwood and herbaceous plants.

#### 2.1.1.3 Interaction between lignin and cellulose

Wood is a composite. Cellulose is the wood's framework and plays the role of axial reinforcement: it is a structural element of wood. Lignin is the matrix of this material. It cements the fibres together, fixes and waterproofs the cell. It also participates in the mechanical maintenance as a glue between the cells. It is a protective barrier against microbial and fungal attacks, against physical or chemical attacks: hydrophobic and antioxidant properties thanks to the phenol group. Hemicelluloses are intended to be an agent of compatibility between lignin and cellulose [6][13].

#### 2.1.1.4 The others components of wood

In the other components, 2 families are present: extractables (organic) and ashes (mineral). These are secondary metabolites: they do not contribute to the growth, and therefore to the mechanical properties of the wood. However, they are the ones that bring color, odour, repellent, antifungal and antioxidant properties to the wood. The main families of extractives are lipids, phenolic compounds and carbohydrates [11][14].

#### 2.1.2 Paper making process

A sheet of paper or cardboard is made from cellulose fibres. These fibres are mainly extracted from wood or coming from recycled paper and cardboard. They are of various origins: industrial (processing scraps, industrial and commercial packaging, unsold newspapers, office products...) and household (old newspapers, household packaging...). Auxiliary materials may be added during the manufacture of paper (mineral fillers, additives, etc.) to improve the characteristics of the paper [15].

#### 2.1.2.1 A short history of paper

The first signs written by cavemen were written on stone, bone, then on wood, metal and clay. It is with the Egyptians that papyrus, extracted from a reed, appeared. It competed with parchment, developed in Minor Asia, from washed and sanded calf and goat skins. In the year 105 A.D., paper was discovered in China. Taso-Lun, Minister of Agriculture, designed a paper pulp made from old rags, bark and nets reduced to pulp [16]. In France, it was not until the  $13^{th}$  century that the first archival documents written on paper appeared, but it was not until the  $14^{th}$  century that the first French paper mills were built.

On January 18, 1799, Louis-Nicolas Robert (1761-1828), a young inspector at the Essonnes paper mill, obtained a patent for his invention: the first continuous paper machine, which made it possible to produce more paper at lower prices. In 1803, Didot Saint Léger, Bryan Donkin and the Fourdrinier brothers operated the first English paper machine in Frogmore (Kent). Around 1850, the first machine for making multi-ply cardboard appeared. In 1856, Edward C. Haley filed the first patent in England for corrugated paper used in particular for making hats. The first French corrugating machine is installed in 1888 in Limousin[3][16]. Today, paper technologies are constantly evolving, contributing to the development of industry, the dissemination of knowledge and the packaging of consumer products. It is also, in France and in 2018, 5.7 billion turnover (paper and cardboard), know-how and many jobs. As for the production of paper, cardboard and pulp, it has grown steadily over the last 10 years. However, the relocation of some companies to Asia or South America has transformed the landscape of the paper industry. Between 2007 and 2017, China has become the worlds leading producer of paper and cardboard (115766 thousand tons in 2017 against 73500 in 2007), thus overtaking the USA (72279 thousand tons in 2017 against 83664 in 2007).

#### 2.1.2.2 Pulp manufacturing

The manufacture of pulp consists of separating the cellulose fibres from wood and/or from paper and cardboard to be recycled. This separation can be obtained either by mechanical means or by the action of chemical reagents. Mechanical or thermo-mechanical pulps are obtained by destructuring of the wood combined with the action of water and temperature. It is carried out using grinding wheels for logs and defibrators for shavings. The heating and the mechanical friction action allow the wood to be broken down into fibres, this is called wood defibration. The pulp obtained is very heterogeneous (heaps of fibres, logs, individual fibres, fine elements). Additional grading and refining steps are necessary to produce a pulp with homogeneous properties. Steam treatments prior to the defibering operation are carried out for thermo-mechanical pulps (TMP). This softens the lignin in the wood, facilitating the separation of the fibres. In the case of chemical-thermo-mechanical pulps (CTMP), chemical agents are used at temperatures above 100°C up to 180 °C to further improve fibre separation [17], like sodium hydroxide for example.

Chemical pulps are obtained by cooking wood at high temperatures (between 130 and 180°C depending on the process) and under pressure in digesters in the presence of chemicals, called cooking liquor which can be acidic or basic. Lignin will be preferentially removed although cellulose and hemicellulose will also be degraded. Fibers are separated from each other in a blow tank with limited mechanical action (Figure 2.5) [18]. There are different types of process and therefore different types of pulp obtained: sulfite/bisulfite cooking, organosolv cooking, alkaline cooking (kraft process), free sulphur cooking (soda process).

Mechanical pulps are called high yield pulps compared to chemical pulps. In addition, they offer good opacity and good calendering properties. However, their mechanical characteristics are weaker than those of chemical pulps. The color of the pastes manufactured by the processes mentioned above is different. Depending on their use, they require more or less pronounced bleaching. For example, printing and writing papers require a pulp bleaching step.

#### 2.1.2.3 The manufacture and processing of the sheet of paper and cardboard

Mills that do not make their own pulp receive baled pulp from suppliers. Once the fibers cooked, the first step in making the sheet of paper is to suspend the fibres in water. The purpose of disintegration is to disperse and individualized the fibers. This step is facilitated by the hydrophilic nature of cellulose. These fibres are then refined to obtain the properties required



Figure 2.5: An overview of chemical and papermaking process: from logs to customers [19].



Figure 2.6: Example of double disks refiner.

for sheet formation and for the final paper product. This operation consists of conveying the pulp between two discs (one fixed, one rotating), lined with blades (Figure 2.6)[20]. The fibres are hydrated (swelling and softening of the fibre) and fibrillated (partial tearing of the outer wall of the fibre). Refining results in an increase of specific fiber surface area and helps the creation inter-fibre bonds.

This treatment also leads to a cutting of the cellulosic fibres. Finally, the pulp is cleaned, screened and diluted to reduce its concentration. Fillers and chemicals may be added before it arrives on the paper machine.

Before becoming a sheet of paper or cardboard, the pulp travels a long way through the paper machine. The paper machine will be used to continuously produce a material sheet, with a given width, which can be up to 10 m, and corresponding to a well-defined specification (weight, thickness, given physical and optical properties). A paper machine achieves impressive speeds: from 1800 m.min<sup>-1</sup> (newsprint) to 2200  $m \cdot min^{-1}$  (special machines). Some machine builders are even looking to increase speeds up to 2500 m.min<sup>-1</sup> and several pilot paper machines are already running at speeds above 2000 m.min<sup>-1</sup> for light grades (newspaper). The paper machine consists of three main parts: the wet end, the press section and the dry end (Figure 2.7).

In the wet section, fibres are distributed by the headbox at low consistency (2 to 10 g.L<sup>-1</sup>) on one wire (Fourdrinier formation) or between two wires where the sheet is formed and then drained, first by gravity and then by vacuum. In the press section, the sheet is compressed between two cylinders covered with absorbent felt. It is then mechanically dewatered as much as possible. A film-size press (or coating) section could be placed between pre and post-dryingFinally, it is in the dryer section where the remaining water is thermally removed (evaporation). The sheet is dried against internally steam-heated cast iron drums. Calenders could precede winders section. The dryness of the sheet is 20 % after the forming area and about 50 % after the press section. On leaving the dryer, the sheet has a moisture content of between 4 and 9% (by mass). It is stored in roll form [21][22]. It should be noted that a roll at the exit of the machine is more than 40 km of paper and about 2.5 tons, if it is not more.

Before this final rewinding step, which is the end of the paper machine, the sheet can undergo a number of additional in-line or out-line treatments: coating, smoothing, calendering, etc [16].



Figure 2.7: Scheme of a paper machine with size press section and calenders [23]

In parallel to the papermaking process, on-line measurements are carried out on the paper material, most often with the aim of regulation: weight (by beta radiation), paper moisture content (infrared or microwave), paper thickness (by laser, image analysis), filler rate (by Xrays), color, whiteness, gloss, opacity and fluorescence (by optical methods).

## 2.1.3 Structure and surface of paper

Paper products could be divided in 4 categories [24]:

- $\rightarrow$  Graphic papers: these are the supports of communication, literature, knowledge and information.
- $\rightarrow$  Wrapping and packaging paper-cardboard: they protect and preserve large-consumer goods because paper makes their packaging flexible and strong and has a high degree of machinability, whereas corrugated paper used in the manufacture of corrugated cardboard.
- $\rightarrow$  Hygiene papers: also known as "tissue" is the most common paper used in the manufacture of toilet paper, paper towels, handkerchiefs, diapers...
- → Industrial and special papers: different types of application exist such as fiduciary uses (identity papers, bank notes, etc.), specific graphic uses (transfer papers, etc.), industrial uses (laminated paper, abrasive papers, etc.), and other specific uses (cigarette papers, filters, etc.).



Figure 2.8: Possible pore structures in paper, from left to right : surface pore, connected pore and cavity.

First thing to look at on this different kind of paper it is their surface structure. It is often characterized by its roughness. The roughness of typical uncoated paper and paperboard surfaces, when evaluated by profilometry, were found to be within the range of 3 to 5  $\mu m$ . Lower values could be found for coated paper[25]. The most commonly used roughness parameter is the average distance between the peak tops and valley bottoms of the surface  $R_a$ . Paper roughness is determined by fibre morphology, forming and calendering. Paper roughness may be categorized into three length scales [26]:

- $\rightarrow$  Optical roughness: at length scales smaller than 1  $\mu m$ , it is related to surface properties of individual fibres) and to internal cracks of other solid materials;
- $\rightarrow$  Micro-roughness: at 1-100  $\mu m$ , it is related to shapes and positions of fibres and fines in the network structure;
- $\rightarrow$  Macro-roughness: at 100  $\mu$ m-1 mm, is the result of paper formation;

A typical paper surface is porous. At the microscopic scale, there are spaces between the fibers in the paper web. It makes paper a network with fibres of different sizes that are mechanically and chemically linked together. The spaces between the fibres are the paper pores. Paper could also contain mineral fillers retained in the pores. Paper has a random and irregular structure, with pores of different sizes and shapes that could be interconnected. The paper porous structure is often described by a model of capillaries with a certain radius distribution.

Pores start to appear due to stiffness of fibres: it prevents them from bending that they would always touch their nearest neighbours in the thickness direction [26]. Different types of pores can be distinguished in the paper [27] as shown Figure 2.8:

- $\rightarrow$  Pores connected to one side of the paper only;
- $\rightarrow$  Pores connected to both sides of the paper. They may also have branches and interconnections;
- $\rightarrow$  Pores not connected to the overall pore network : they form cavities. There are small cavities within the fibres called intra-fibre pores. The volume occupied by these pores is often negligible compared to the volume of the inter-fibre pores;

The pore network is involved with the fibrous paper structure [26]. Therefore, paper can be described as a two-phase material: a filling phase and a solid phase (Bristow 1986). Paper can be characterized by its porosity, specific surface area, permeability and tortuosity. Paper porosity is the fraction of void in the material in relation to its total volume. In the case of paper containing fillers, it is given by equation 2.1.

$$\varepsilon = 1 - \frac{G}{t_f} \left( \frac{1 - x_c}{\rho_{fiber}} + \frac{x_c}{\rho_{filler}} \right)$$
(2.1)

where G is the paper grammage,  $t_f$  the paper thickness,  $x_c$  the filler ratio in paper,  $\rho_{fiber}$  the volumetric mass density of fiber and  $\rho_{filler}$  the volumetric mass density of filler.

The pore structure could be changed by different factors. Paper is compressible meaning that its pore structure changes when it is compressed, sometimes irreversibly. Paper is hygro-expansive. Thus, pores shape and size change when the paper moisture content changes, due to the fibres swelling and the breaking of the inter-fibre hydrogen bonds when paper becomes wet. The paper structure depends on all the papermaking unit operations: drainage, wet pressing, drying and calendering [26]. The spaces among fibers in a paper web will be greatly affected by the degree of refining of fibers before forming the web. The reduced porosity of paper resulting from refining also can be partly attributed to generation of cellulosic fines, which tend to fill in the spaces among the fibers of paper [25].

The paper apparent density varies according to the web thickness. The surface pores are larger than the pores inside the web. The paper density varies from 200  $kg \cdot m^{-3}$  for common filter paper ( $\varepsilon = 0.87$ ) to 1400  $kg \cdot m^{-3}$  for glazed greaseproof paper ( $\varepsilon = 0.1$ ). The fines affect the thickness density distribution in the web. Paper is anisotropic in the plane and mostly in the thickness. The paper pores are larger in the web plane than in thickness. There is non-uniform fibre orientation distributions and also flocculation affecting porosity [26].

Different characteristics of paper depend of its porosity and pores structure. The specific surface area is the surface area of the pores per unit mass. It depends on the pore size distribution. Permeability is the capacity of a porous medium to let fluids or gaz flow through it in a given direction. Tortuosity is the ratio of the actual distance travelled by a fluid flowing in one direction through the paper to the apparent length of the paper in that direction. Tortuosity accounts for pore shape and inter-pore connections (Clennell 1997). Porosity and specific surface area are determining parameters of the paper permeability. Porosity, pore size distribution and pore tortuosity also control the liquid transport in paper [28]. Note that the paper porosity considers the occluded pores although these do not participate in the fluid flow (gases or liquids). On one hand, porosity and specific surface depend exclusively on the dimensions and number of pores. They do not take into account the possible anisotropy of the porous medium. This information is obtained experimentally with mercury intrusion porosimetry [29]. Recent X-ray microtomographic techniques have also provided a way to non-destructively image the paper structure in three dimensions [30]. Tortuosity and permeability, on the other hand, are directional quantities. They depend on the direction in which the measurement is made. For papers, the permeability in the web plane is greater than the permeability in the web thickness [27].

## 2.2 Sizing and coating process

"Coated papers were manufactured in the USA as early as the first decade of the 19th century. The first coated paper was manufactured principally for labels by hand brushing the coating colors onto paper sheets which were then hung on racks to dry" wrote R. N. Thompson in [31]. Today things have changed a lot in terms of the coating colors used and their formulations, the coating processes and their speed and the use of coated papers. This section aims to provide readers with the key elements to understand the coating process through 3 points: coating color and their components, coating processes and finally web handling techniques.

#### 2.2.1 Coating and sizing color

Aqueous coating for paper or board applications generally contain three distinctive groups of materials besides water: pigments, binders and additives. Surface sizing aims to increase or reduce liquids penetration into papers. It allows the deposition of 1 to  $4 \ g \cdot m^{-2}$  of dry matter on paper. Pigment coating aims to improve the optical properties of paper surface and its topography to improve its printing quality. The most important coated paper grades are lightweight coated where the basis weight of the coated layers (both sides) is less than  $g \cdot m^{-2}$ .

The materials found in coating and sizing as well as the techniques used are presented in the following paragraphs using the following references [32][33][34][35][36].

#### 2.2.1.1 Pigments

**Kaolin clay** - Kaolin clay is by far the largest coating pigment used today. It gives papers an excellent surface finish and good printability. Kaolin clay can be divided into different groups. Airfloat clays are used in filler applications and pre-coat. Delaminated clays are produced by applying mechanical shear force to a clay slurry. Clay stacks are separated into individual platelets. This lamellar structure is used in paper coating for its good coverage quality. Calcined clays are made from hydrous clay exposed to very high temperatures (around 1050°C) in a calciner. The plate-like structure of the clay becomes a voluminous and highly porous structure. It improves the whiteness of kaolin but highly increases porosity and inks/varnishes penetration and then reduces gloss.

**Calcium Carbonate** - This pigment, with rhombohedral shape, can be produced from quarries (Ground Calcium Carbonate (GCC)) or by precipitation (Precipitated Calcium Carbonate (PCC)). GCC is from crushed chalk, limestone or marble obtain by dry or wet process. PCC is produced by reacting calcium hydroxide with carbon dioxide, and produce pigment of high brightness and purity. Depending upon reaction conditions, particles of different shape and crystalline structure are produced: aragonite or calcite crystals (either scalenohedral or prismatic shape). PCC is particularly interesting for its high whiteness and its low degree of yellowing.

**Titanium Dioxide** - This compound is extracted from Ilmenite mines and treated by mechanical crushing followed by sulphuric acid treatment. Titanium dioxide is then precipitated and calcined. Another treatment is possible with chlorine in a furnace. Two abrasive crystalline forms exist for titanium oxide: anatase and rutile. Titanium oxide has very good dispersion properties, high whiteness with an excellent opacifying power, high brightness and blue white shade. Titanium dioxide is used as a complement to others pigments like calcined clays, for premium grades or with unbleached kraft. However, this compound is less and less used.

**Talc** - This is a natural pigment that does not require any special chemical treatment. It is extracted from a quarry and ground to the desired particle size. Talc is used in coating processes for its low hardness and its ability to reduce the abrasiveness of the pigment layers. Talc also allows to obtain a matt coating finish while preserving the gloss of inks and varnishes. Talc slurries have low dry content: around 50 to 60%.

**Plastic pigments -** They are synthetic spherical pigments obtained by emulsion polymerisation of vinyl monomers (styrene). They have several advantages: lowest density of all pigments (density close to 1); high gloss, especially when high temperature calendering; good optical properties; high micro porosity; almost no abrasiveness; particles do not form films and remain globally individualised during their use.

#### 2.2.1.2 Binders and co-binders

Binders are indispensable, although expensive. The main role of binders and co-binders is to ensure cohesion between pigments and adhesion with substrate. Their choice and dosage have direct impact on the dispersion rheology. The products most frequently encountered come from three sources: vegetable (starch or soya proteins), animal (milk casein) or synthetic (latex or polyvinyl alcohols) [35]. In a coating formulation, it represents between 8 and 18% of the layer (by mass) [37][38]. However, they also have certain disadvantages depending on the binders and the chosen process: they could foam, reduce opacity, printability and gloss. Moreover, they may be incompatible with some pigments.

**Starch** - As an adhesive for paper coating, starch was introduced around 1900 [32]. Starch is an abundant renewable resources, particularly used in the paper industry, especially in sizepress sauce and also in this project. Thus, the understanding and knowledge of this material is essential in the present context and requires a more detailed explanation. The general references used to present starch are the following one [34] [37] [39], [40] [41], [42], [43], [32], [33]. Starch is a high molecular weight polymer. It is a mixture of two different chemical compounds: amylose and amylopectin (Figure 2.9). Both are formed from anhydroglucose unit (AGU) which has 3 hydroxyl groups that help the formation of inter- and intra-molecular hydrogen bonds. It gives starch its hydrophilic character, just like cellulose. In the case of starch, the AGU are  $\alpha$ -(1-4) and  $\alpha$ -(1-6) linked. Amylose is a linear polymer with AGU linked by  $\alpha$ -(1-4)-D-glycoside bonds, slightly branched by  $\alpha$ -(1-6) linkages and a DP around 1000. Amylopectin is a highly branched polymer consisting of relatively short branches of  $\alpha$ -D-(1-4) glycopyranose that are interlinked by  $\alpha$ -D-(1-6) –glucosidic linkages approximately every 20 to 30 glucose units. It has a DP of 100,000.



Figure 2.9: Amylose (top) and amylopectin (bottom) structure [40].

Starch comes from various plants: corn and potato are the most commonly used, as well as wheat, rice and tapioca. It is granules with dimensions between 2 and 100  $\mu m$  and it is commercially available as a white dry powder. These granules have a multi-scale structure: granule (2-100  $\mu m$ ), into which growth rings are found (120-500 nm) composed of blocklets (20-50 nm) made of amorphous and crystalline lamellae (9 nm) containing amylopectin and amylose chains (0.1-1 nm). These granules are also insoluble in cold water and find few uses in industry without hydrothermal or thermo-mechanical treatments. Indeed, the polymerised structure of starch presents a large number of secondary bonds, hydrogen bonds between the different chains, making it particularly difficult to access. These hydrothermal treatments are commonly used in the paper industry, food industry or in the case of adhesives. Nonetheless in presence of water excess (water-starch ratios > 1.5:1)[44] heated to at least 60°C, starch grains can absorb water and thus swell, gelatinize, solubilize and turn into a gel when cooled. These 3 stages called sorption, gelatinization and retrogradation are explained below:

- → Sorption: this is explained by the attachment of water molecules on starch hydroxyl groups, through hydrogen bonds. Water firstly breaks weak bonds between hydroxyl groups and continues with the strongest bonds This dilate the macromolecular network: the starch grains swell. Starch grain are capable of absorbing water (0.48–0.56 g/g dry starch) due to their semi-amorphous nature. Hydration (at 25 °C) increases the grains diameter of approximately 10% to 25%.
- $\rightarrow$  Gelatinization: water absorption increases with temperature and starch granules collapse. Amylose and amylopectin solubilize to form a colloidal solution and the granular structure disappears. When the gelatinization temperature is reached, the starch solution viscosity is at its highest because the grains are swollen by the water absorption. Then, viscosity decreases to a minimum value corresponding to the bursting of all the grains.

A feature called the Maltese cross is a characteristic of starch grains as illustrated Figure 2.10. This cross divides the granule into quadrants and it is linked to systematical arrangement of macromolecules grains. This cross disappears during gelatinisation process and is therefore a good indicator to check if starch is fully cooked. The presence/absence of the


Figure 2.10: Maltese cross observed within potato starch granules viewed under plane-polarized light (x120) [42].

Maltese could be checked with polarized light microscopy. Moreover, gelatinization transitions of starches may be measured using Differential Scanning Calorimetry (DSC). Due to the heterogeneous grain structure, starch thermal transitions occur over a temperature range rather than at a defined temperature. Gelatinization generally occurs over a 10 to 15 °C temperature range [41]. For a native normal starch (i.e. amylose content between 20 and 30%), gelatinization temperature is found between 55 and 80 °C.

→ Retrogradation: while cooling and in absence of any starch chemical or thermal modification, amylose and amylopectin macromolecules can reassociate by recreating hydrogen bonds initially destroyed by hydration. This is retrogradation which is the crystallization (or recrystallization) of hydrated starch. Amylose and amylopectin retrograde on very different timescales: amylose crystallization being very rapid (minutes to hours) and amylopectin recrystallization being very slow (days to weeks). For starch pastes with amylose and amylopectin, retrogradation involves phase separation (formation of polymer-rich and polymer-deficient regions). Retrogradation may be monitored via a multitude of techniques (DSC, Fourier-transform infrared spectroscopy and viscometry, etc)[41].

Retrogradation should be avoided as much as possible in the paper industry. The gel produced cannot be pumped, transported and deposited on paper due to its high viscosity. It also leads to a decrease in the binding capacity of starch. Retrogradation is favoured by conditions of low agitation, low temperature and pH < 7.5. Chemical or thermal modifications can prevent or delay this phenomenon. The advantages of using starch in paper making are its relatively low price, the gave stiffness to the coated layer and its good water retention properties in coating formulation.

The operation which leads to the heating of the starch in the presence of water is called "cooking" and takes place in specially designed thermostatically controlled tanks, either in a jet cooker or in a batch cooker. The first one allows a more regular cooking than the second one. Following the starch aqueous suspension viscosity during a specified heating-cooling cycle, in the presence of shear, over a defined analysis time period is very useful. This is called the pasting profile. Heating or cooling rates/temperatures, length of hold and shear rate may all

be varied. It is possible to mention some measured characteristics defined below and illustrated Figure 2.11:



Figure 2.11: Pasting profile of a wheat starch granule suspension over the course of a heating and cooling cycle [44].

- → Pasting time: the point in time, to a given heating rate, where enough starch grains have swelled to measured an initial rise in viscosity (above the original ungelatinized granule slurry). This value is reported in regard to the pasting temperature (i.e minimum temperature needed to cook starch under given conditions) [44].
- → Peak viscosity: it results from a rapid swelling of granules upon gelatinization. Paste composition at the peak is composed of both highly swollen and ruptured granules in a continuous phase of solubilized starch. Peak viscosity is indicative of starch thickening power. Then the starch paste viscosity will decrease due to rupturing of the fragile, swollen grains until a trough viscosity is reached. This value is obtain during a hold period at peak temperature (usually 95 °C) [44].
- → Trough viscosity (hot paste viscosity): is the solubilized starch continuous phase viscosity containing dispersed grains remnants. The "breakdown" is the peak viscosity minus trough viscosity. It indicates the paste relative stability at high temperature and shear conditions [44].
- $\rightarrow$  Setback: is the final viscosity minus trough viscosity. It reflects the extent of amylose recrystallization occurring within a starch paste [44].

Beyond pasting properties, more complete analysis of starch dispersion and/or gel properties may be conducted using uni-axial compression testing and rheometry [36] [45]

**Latex** - They are aqueous dispersions of insoluble high molecular weight polymers obtained by emulsion. Latexes are dispersions of spherical copolymer of controlled sizes particles (like plastic pigments) between 0.1 and 0.2  $\mu m$ , in water with surfactants added for stability. Three classes of latex are used as coating binders: styrene-butadiene (SBR), styrene-butyl acrylate and vinyl acetate homo and copolymer. Latexes do not provide water retention. Soluble binders or soluble co-binders are usually associated with latexes. SBR is the dominant synthetic binder used in paper coating today. It was developed during World War II to replace natural rubber. It is a tough and strong binder. Depending on the styrene butadiene ratio, different glass transition temperatures are obtain resulting in different properties and behaviour during coating [34].Other latexes are also used: PVAc (Polyvinyl acetate), acrylic latex and PVA (Polyvinyl alcohol) [36][45].

**Co-binders** - The role of co-binders is to adjust the coating rheological properties and its water retention. The co-binders are also used as optical brightener carriers while having a certain binding power. The most commonly used co-binders are carboxymethyl cellulose (CMC) and starch; however, soy protein and polyvinyl alcohol can also be found [36].

Water - It represents 35 to 40 % of coating color mass. Being the vector of all others elements, it is a very important constituent of the coating color. Water should be evaporated during drying to let the coating layer being fixed. But water could also lead to different issues during the process: local decreasing of the mechanical properties, curling or wrinkles [38].

# 2.2.1.3 Additives

Coating additives are very common in paper coating processes today [34]. Dispersant are used to make easier pigments dispersion. They could be organic (sodium polyacrylate, the most used) or inorganic (sodium hexameta phosphate). Concerning the viscosity modifiers, they are thickeners (caseinates, CMC, Hydroxyethyl cellulose (HEC), high viscosity starch) or thinners like urea. The water-holding agents, like CMC and some polyacrylates, are used to prevent water in the coating color from penetrating paper too quickly. The lubricants are very useful to increase the production tools life and to improve calendering ability by reducing the abrasiveness of the pigment layer. Calcium stearate is mainly used. Biocides or biostats, like inorganic boron and organo-sulfur molecules, are unavoidable in coating processes to avoid fermentation and bacteria attack. Concerning the pH adjusters, soda ash and ammonia are commonly found is the industry. Repellents are useful to release paper and the most common are silicon compounds. Insolubilizers are used to prevent certain coated products from re-solubilising when in contact with water after coating (in offset printing, for example). This is particularly the case for starch and casein. Glyoxal-based resins are commonly used. Optical brighteners are often used in premium paper grade. They make the coated paper look very white while using stilbene or benzophenone derivates. Dyes are also found to give specific shade to the coated paper. Finally foam control agents are found in coating formulation.

# 2.2.1.4 Formulation and preparation of coating color

The workshop for preparing a coating color is called a "kitchen". Many of the preparation systems are automated, making the operators' task easier. The main components of a kitchen for the preparation of coating color are: storage tanks for the different products, mixers mounted on load cells and cookers. All of this is connected by transport and dosing systems (pipes and pumps) [35].

Whether dry pigments or slurries are used, the order of preparation remains the same: the pigments are first dispersed in water with the addition of dispersant to minimise caking. The binder is then slowly added to avoid rheological shocks, while adapting the stirring speed to avoid binder degradation. The pH is controlled all along the preparation to avoid dispersion problems for example. Finally, the additives are added to the mixture, before it is transported to the coater feed tank. Once the coating color is obtained, different properties are measured to ensure optimal quality: dry matter content, viscosity, pH and water retention. It is sometimes interesting to know some other properties of the coating color such as surface tension, fluid dynamic, elongational viscosity and dynamic surface tension [36].

#### 2.2.1.5 Sedimentation

After formulating a coating color, stability over time is required. A suspension is a heterogeneous mixture of solid objects in a liquid phase. The instability of a suspension could be explain by gravitational attraction which leads to sedimentation of the solid object in the liquid phase. The sedimentation of an isolated spherical particle in an infinite Newtonian fluid is known analytically. A particle speed can be described using the Stokes law (equation 2.2), when the Reynolds number is small  $Re \ll 1$  (equation 2.3).

$$V_{Stokes} = \frac{d_{particle}^2 \cdot g \cdot \Delta \rho}{18 \cdot \eta} \tag{2.2}$$

and

$$R_e = \frac{\rho \cdot V_{Stokes} \cdot d_{particle}}{\eta} \tag{2.3}$$

If the particles number increases sufficiently, it is no longer possible to describe the interactions between all particles. Thus, for high volume fractions in particles (> 5%), Richardson-Zaki [46] law is used and the sedimentation speed as shown equation 2.4 with S = 4.65 + 19.5d/D for a Reynolds number below 0.2.

$$V_{Richardson-Zaki} = V_{Stokes} \left(1 - \phi\right)^S \tag{2.4}$$

In the case of a non-Newtonian fluid, the resolution of the sedimentation problem is more complex. Thus, a simple approach is to introduce the characteristic shear rate created by a particle with a given speed. Using Stokes velocity expression combined with Ostwald-de-Waele's law (described later in the document equation 2.29), the particle velocity is described equation 2.5 [47].

$$V_{shear-thinning} = \left(\frac{2^n \cdot g \cdot \Delta\rho}{9 \cdot k_{odw}}\right)^{1/n} \cdot (0.5r_{particle})^{\frac{n}{n+1}}$$
(2.5)

# 2.2.2 Sizing and coating process

Coating devices are generally referred as "coaters". They are located off or on machine. A coating station has 3 functions: to deposit the coating color on the paper, to remove the coating color excess on the paper and to spread the coating. However, new technologies allows to put the exact amount directly on the paper like curtain coating. In this section, the coating delivery systems will be described first, before focusing on the dosing system [48].

# 2.2.2.1 Coating color application on papers

The main systems used to deposit the coating color on paper are the following ones and are presented Figure 2.12:

**Roller applicator** - It brings the excess coating color on the paper to be coated. It generally soaks in a tank where the coating color is located. Different parameters can be adjusted: height of the coating color in the tank, roller speed, and its distance from a counter roller. In order to avoid evaporation or thickening of the coating color, the roller can be cooled or heated. Above  $1250m \cdot min^{-1}$ , problems with coating color splashing may occur. Note that dwell times (i.e transportation time) are long in roll applicator system [49] [36].

**Short dwell** - This process corresponds to an injection of the coating color tangentially to the coating support and very close to the coating dosing system (generally a blade, described later 2.2.2.2). To dose the coating weight, the blade is mounted on a system of micrometric screws over its entire width, allowing a localized adjustment of the deposited coating color. This type of system has several advantages. Lower excess coating color is deposited with this system and allows the blade or the dosing rod to work at lower pressures, improving runnability. The contact time between paper and excess coating color is minimized. The paper is therefore less weakened by the rewetting which limits breakage. The coating color penetration in the web is also limited. However, at high speeds, vortexes appear in the coating color, before the blade, leading to coating weight heterogeneity on the paper web. In addition, this system is more sensitive to air bubbles and needs a deaeration device [36].

**Curtain coating** - Another system developed is the curtain coating. It is a relatively old coating process, dating from the end of the  $19^{th}$  century. It was first used to coat candies with a vertical slot. In the second part of the  $20^{th}$  century, the slide process was developed to apply simultaneously up to ten photosensitive layers in a single curtain on photographic films and papers. The principle is simple: a vertical plane flow is created with the coating color. The latter is deposited by gravity on the horizontal coating support. The curtain must be stable. Then, flow control is needed as well as viscosity, surface tension control and the absence of air bubbles. This process produces layers with excellent regularity and allows the application of several layers simultaneously. [36].



Figure 2.12: Three different way to deposit coating color on paper.



Figure 2.13: A size press system [50].

**Sizing press** - Surface sizing is a critical unit operation which has significant effects on coater runnability and on the quality of the final coated web. Starch films is typically used to fill in the surface voids in the web, reducing the pore sizes and therefore the fluids penetration rate. This process is made with size press. During this sizing operation the objective is to flood a nip entrance with sizing solution. The paper will absorb some of the solution and the excess is removed in the nip. The overflow solution is collected in pans below the size press and is recirculated to the nip. Three mains size press configurations are possible: vertical, inclined, horizontal as illustrated Figure 2.13 [34][36].

# 2.2.2.2 Metering systems

**Blades** - This is the most developed system and the most installed on industrial coaters (Figure 2.14a). The blade dosing system allows speeds between 1800 and  $2500m \cdot min^{-1}$  with high mass concentration colors (60 to 65%) [51]. To regulate the coating color, the blade pressure on web is adjusted by pneumatic or mechanical systems. Two types of blades are commonly found: bevelled blade and bent-blade. Bevelled blade is made of special hardened steel, with a thickness between 0.25 and 0.65 mm. It is mounted in such a way that only blade end is in contact with the paper surface. These blades are beveled with a grinding angle between 15 and 55°. It allows to deposit between 5 and 13  $g \cdot m^{-2}$  of dry coating color on the web. Bent-blade is mounted in S-shape by a double stop system so as to present one of its faces in flat support. It is not bevelled but their tips are coated with ceramic or metal alloy layer to increase their abrasion resistance. Bent-blade allows to deposit between 10 and 25  $g \cdot m^{-2}$ . The blade support



Figure 2.14: Three different way to meter coating color on paper.

is generally a mechanical system [52][36].

**Rod coater -** The Mayer Coating Company of Rochester (NY) founded in 1905 by Charles W Mayer was the company which developed this system. Rod coaters are more commonly used for pre-coating. (Figure 2.14b) The rod coater rotation is opposite to the web direction [34] and its speed is slow (10 to 30 revolutions per minute). The rod diameter is between 10 and 20 mm. A numbering of the Mayer rods makes it possible to know the mass of coating color deposited. This numbering is a function of the winding (this point will be presented later Table 3.5) With this system, it is necessary to avoid too high web-rod contact pressures otherwise the coating surface is quickly degraded. Rods can be smooth or threaded (by winding), it is also important to adapt the coating color viscosity otherwise pigment particles can clog the rod. In the case of Mayer rod, it is the wire diameter on the rod that controls the final weights. There is long dwell time in these system. [36].

Air knife - There is no contact between the web and the dosing system (Figure 2.14c). The layer thickness obtained is more regular. The coating amount is control by the air pressure, the nozzle gap and the distance from web. However, mastering such a system can quickly become tricky. Indeed, projections of drops occur around the air knife, generating clogging. Moreover, there is also foam formation. This requires regular maintenance of the system. The coating colors are less concentrated (and therefore less viscous) than in the case of metal blade coatings [36].

### 2.2.2.3 Drying systems

Drying is a delicate operation that can lead to quality issues on the final product. Drying consists in removing the water contained in the coating or any other solvent, and the water that has penetrated in the paper. To dry paper, conduction (impingement drying), convection (air float drying and air foil drying) and radiation (infrared drying) are used. Impingement drying use a hood with a controlled hot air circulation and a tunnel with idler rolls that could be heated. In the hood, air blows trough nozzles onto the web supported by rolls. Air speed and the temperature control the drying. The temperature control are made at the hood inlet to avoid danger linked to over-heating [52].

Air float and foil dryers are built in way that air supports the web. With a two sides drying, the foil and float dryers are more effective and smaller compared to impingement dryer. This is mainly found with high and large machine.

The infra-red (IR) dryers are mainly use to warm-up the web before the air dryers. This is due to the property of IR to go deeper into coated material. It is a non contact drying system, with a good heat "penetration" and a higher heat transfer. It takes less place than other system, while improving quality and having a higher energy efficiency (45 to 55 %). IR dryers use either gas or electricity to produced the IR with wavelength from 2 to 5  $\mu m$ . The IR lamps are used with reflectors to minimize energy loss. Nonetheless, it is only really worth it with water based coating [52], [53].

# 2.2.3 Web handling

Coating is an element of what is called "web converting". Web converting is the fact of taking a web and transformed it irremediably to confer it new property. Contrary to web converting, web handling does not seek to modify web. Web handling seeks to preserve all the properties of web. The problems encountered by web handling specialists are mostly geometric: for example a flat web that becomes wrinkled and unusable. In this part, some aspects of web handling will be discussed. The references used in this part are: [54][55], [56] [57][58]. For further information, the reader is invited to consult David Roisum's books on the subject: *The mechanics of web handling* [54] and *The mechanics of rollers* [55].

### 2.2.3.1 Unwind and Rewind

Unwinder and rewinder have some common functions. They must support the paper reel during the process. To do so roll spool, expanding shaft or expanding cores could be used. In these devices mechanical or pneumatic systems perform the expansion of shafts. Unwinders control the required web tension (must remain constant) with mechanical brake or motorized brakes and can guide the web.

# 2.2.3.2 Spreading devices

Spreaders are required on most web processes to prevent or remove wrinkles, to widen a web or to separate slit during winding. It exists a wild diversity of spreading system. One of the most important things in web handling is the "Normal entry law" [59] "A web will seek to enter a downstream roller at a right angle to the roller's axis at the point of first contact. If the web is not entering at right angles, it will move sideways at an ever decreasing rate". This law is valid only if there is no slippage between web and rollers and describes web behaviour at guides, winders and misaligned rollers. Keeping this law in mind, three different spreading mechanism can be presented: the concaved spreader roller, the bowed spreader roller, the D-bar spreaders. Other way to spread web exist: dual bowed roller spreader, pos-Z spreader, expander roller, edge pull web stretchers, compliant cover rollers, grooved spreader roller,... but will not be presented in this document.



Figure 2.15: Three different way to spread web on roll to roll system [60].

**Concave spreader roller -** This spreader is a roller whose diameter at the ends is slightly greater than at the center (cf. Figure 2.15a. In its ideal configuration, the diameter profile of the roller is cut as an arc of a circle. Notice that spreading effects can appear on any roller, due to very small diameter changes. Concave roller has constant rotational speed (rpm) on its width. However, it has a varying surface speed  $(m.min^{-1})$  depending of roller diameter at every position. Thus, concave roller surface speeds is higher at the extremities than at the roller center. This surface speed difference lead to ingoing web tension distribution that is shaped similarly to the speed profile, leading to spreading.

**Bowed spreader roller-** The bowed spreader has a curved stationary axle upon which a rotating sleeve is mounted in bearing sets (cf. Figure 2.15b). The web center travels exactly in MD (Machine Direction), while edges travel perpendicular to the roller axis at the edges. The MD velocity distribution is maximum at the machine centreline and decreases toward the edges, which creates an outward rotation of the web. The CD (Cross Direction) velocity is zero at the centreline and increases as it progresses to the edges, which causes an outward lateral displacement of the web and thus spreading.

**D-bar spreaders-** It takes its name from the characteristic "D" cross-section of the bar as illustrated Figure 2.15c. D-bar's shape can be adjusted by intermediate jacks. With this adjustment, local baggy or wrinkled spot can be spread. The problem, however, is that the bar soon ends up looking like a snake after several adjustments, which affects spreading uniformity.

**"Free" spreader -** A "free" spreader uses Poisson's contraction. As a web is stretched under increasing tension, it necks-down in width. This decrease in width may translate into flatter webs or better slit separation. However, increasing tensions will increase the propensity to web breaks. Moreover, when tension is increased in some span, it becomes difficult to reduce tension further downstream without causing wrinkle.

**Flattening** - Usually all that is need to flatten a web is to lightly wrap a large diameter roller. Caution must be exercised because loss of traction also means a certain loss of web handling control. However, if often is possible to maintain tension and speed match on a flattening roller yet still allow wrinkle to slide outward. In general, wrinkles will tend to begin on the most highly wrapped rollers in a system.



Figure 2.16: The four guiding technologies [56] [56].

## 2.2.3.3 Guiding equipment

Lateral misalignment have a lot of different causes: material properties, roller misalignments, unmaintained machines, environmental conditions and processing conditions. It leads to telescoped rolls, badly wound rolls or web thickness variations. Moreover changes in roller drag and air entrainment between the web and roller can also cause lateral misalignment. So, web guiding help to improve the process runnability by deliberately changing rotation axis of the guide roller and conduct the web to different positions.

Web guides are mainly electro-mechanical devices that automatically control the web position. There are 3 main components in web guiding system : sensors, controller and guide mechanism. Sensors are used to spot the current web position. The type of sensor used is usually based on the web type and process. The controller reads the sensor information and determines the required correction for the guide mechanism. The controller then commands the actuator to move the web material to the desired position. To guide a web, there are different techniques presented below.

Web edge guiding is usually referred to guiding on a single web edge. This is the most common type of web guiding. This method is suitable when the web width does not change during and between runs. Center guiding is used when the web edges are uneven or if the web width changes during or between runs. The center line of the web is guided using two sensors, one on each web edge. Line guiding may be used on web with a printed line, using camera based solution to guide the web. Contrast guiding is similar to line guiding. The web may be guided based on a contrasting feature on the web. A printed contrast or a contrast due to a coating process can be used as the reference for contrast guiding.

Depending on the location where the guiding is required, four different types of guiding technologies are available: displacement guides, steering guides, unwind guides and rewind guides as illustrated Figure 2.16. Displacement guides is the most common web guides used in industry. It includes two rollers on the web guide mechanism that rotate. It enables web displacement with minimal bending stresses on the web. This system is very simple and compact. Nonetheless they are some situations where displacement guides cannot be used: after long span, locations with web wrap constraints and installation with space constraints. To overcome this problem, another steering guides are typically used. The system is made of one or two rollers that travel over an arc. The steering guide bends the web in the entry span to create the lateral motion. The steering depends on different factors: web speed, web stiffness, entry span length,... Moreover, the installation of a steering guide requires a lot of attention to prevent web breakage.

Specific guiding system are used in unwind and rewind. Unwind guides are a type of terminal web guides that align the web fed into the machine. Typically a carriage or a side lay carrying the entire web roll is moved in CD. The carriage is typically mounted on high precision linear bearings with linear actuators that can move the entire system (carriage + roll). An idle roller is also used to stabilize the web to avoid vertical displacement during unwinding caused by the roll diameter changes. Rewind guides are used at the end of a roll to roll system. The web wound on the roller is guided to avoid web telescoping. Rewind guides are similar to unwind guides. The rewind guide chases the web to align the different layers of the wound roll.

Other important parameters have also to be taken in count as roller diameter and roller smoothness that play a critical part in web guiding. Moreover, a proper installation geometry is needed focusing on three important parameters: entry spans, exit span and web wrap around rollers.

#### 2.2.3.4 Tension control and sensing

Different tension control equipments can be used. They must be as close as possible to the point it affects and different web tensions are necessary in a process. The tension must be controlled after unwinding, just before laminating or coating operation, in the drying tunnel and at the rewind area to optimize the web tension control. [56].

**Tension control** To control and regulate tension, two possibilities exist: open loop or closed loop control. Open loop tension control is selected when the cost of a tension control is a consideration. An open loop tension control system has no actual tension feedback. It is based only on a tension set point without feedback or influence from actual conditions and cannot respond to tension disturbances. Tension is regulated using torque control in the drive system. Closed loop tension control incorporated a force measuring sensor or a dancer roll system to control tension. Tension is regulated using speed or torque control in the driving system [56].

There are two options to measure tension. The first one is the load cells; as illustrated Figure 2.17a, which is specifically designed for web tension measurement and transform it into a proportional electrical signal. The majority of load cell designs use strain gauges as sensing element and are mounted in pairs, supporting an idler roll. It forms a full Wheatstone bridge. The strain gauges are attached to a mechanical structure that deflects when a tension force is applied. The other option is the dancer roll as shown Figure 2.17b. It is a moving preloaded idler arm. Its force and positioning is derived from web tension. Pivoting dancers are the most common. Dancer roll system requires a position sensor for the dancer position control like optical encoders. Friction should be minimise to avoid correction delay so low friction bearing can be used and dancer mass should be as low as possible to minimize inertia effect. Dancer rolls are also used in accumulators systems because of their storage capability.



Figure 2.17: Tension sensing system [58].

# 2.3 Liquid absorption by paper

Now that the coating processes have been presented, it is necessary to look at the physical phenomena that can occur during these processes. The first that may come to mind is the absorption of water that may be in the coating color. Thus, this section will look at the liquid absorption of paper.

## 2.3.1 Paper wettability

When a coating color is applied to paper, it does not immediately penetrate the fibrous network. There is a first contact because the coating color wets the paper. It is on this first point that this sub-section will concentrate: the paper wettability.

#### 2.3.1.1 Surface tension

The cohesive forces between the molecules in a liquid are responsible of the surface tension. Molecules in a liquid are subject to equal attractive forces in all directions, whereas those on the surface of the liquid have less interactions (Figure 2.18. This lack of bonding leads to liquid surface tension phenomena. An energy model helps to obtain an equation describing surface



Figure 2.18: Surface tension appearing at the interface of gas (G) and liquid (L).

tension: "when increasing the free surface area by an elementary amount, molecules must be transferred to the surface. The elementary work dW to increase the surface area of dA" is then written:

$$dW = \gamma_{lq} \cdot dA \tag{2.6}$$

With  $\gamma_{lq}$  the liquid surface tension  $(J \cdot m^{-2} \text{ or } N \cdot m^{-1})$ .

#### 2.3.1.2 Contact angle on homogeneous surfaces

A drop of liquid deposited on a perfectly smooth horizontal solid surface, chemically homogeneous, adopts at equilibrium a conformation depending on the interactions between the liquid, the solid and the gas phases. At equilibrium the system minimises its energy and in the case of partial wetting, the drop takes a spherical shape if the liquid volume is small. In this case, Young's equation (equation 2.7) expresses the contact angle formed at the intersection of the three phases of the system:

$$\cos(\theta_c) = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{lg}} \tag{2.7}$$

with  $\gamma_{sg}$  the surface free energy (SFE) of the solid in equilibrium with the liquid vapour,  $\gamma sl$  the solid-liquid interfacial energy and  $\gamma_{lg}$  the surface tension of the liquid in equilibrium with its vapour. The Young-Dupré's equation could also be written as equation 2.8:

$$W_A = \gamma_{lq} \cdot \left[1 + \cos(\theta_c)\right] \tag{2.8}$$

where  $W_A = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$  and it corresponds to the adhesion work (sometimes called Dupré's energy) in  $J \cdot m^{-2}$  or  $N \cdot m^{-1}$ .

Different models are used to determine the SFE. The most known are the Fowkes method, the Owens, Wendt, Rabel and Kaelble (OWRK) method and the Van Oss-Chaudhury-Good method.

**OWRK method-** A model (equation 2.9), in which a dispersion term is combined with a polar term, has been considered by researchers [61][62]. Using just two probe liquids, such as di-iodomethane and water, different surfaces can be classified with respect to their dispersion and polar nature. The strength of this approach is that by using water as a probe, the method is very useful in applications where hydrogen bonding may be important [25].

$$\gamma_{lg} \cdot [1 + \cos(\theta_c)] = 2\sqrt{\gamma_{sg}^d \cdot \gamma_{lg}^d} + 2\sqrt{\gamma_{sg}^p \cdot \gamma_{lg}^p}$$
(2.9)

The OWRK method is used more frequently in practice than the Fowkes method. Then the OWRK will be used in this study.

**Fowkes method** - Fowkes assumed that the SFE of a solid (and surface tension of a liquid) is a sum of independent components, associated with specific interactions considering the dispersion, polar, hydrogen, induction and acid-base components, respectively. The Fowkes method follows a similar way to the OWRK method. However, this method can only be used for fully dispersive system [63].

**Van Oss and Good method** - The Van Oss and Good method goes further than the OWRK method. The SFE is divided into a disperse part along with a Lewis acid part and a Lewis basic part. According to the Lewis acid-base theory, polar interactions take place when an electron acceptor (+) impinges on an electron donor (-) [63].

#### 2.3.1.3 Contact angle on heterogeneous surfaces

Wettability and contact angle concepts all assume a smooth and uniform surface. Nonetheless real case are not perfect: cellulosic surfaces are no exception to the rule. Roughness and chemical defects are easily found. More precisely, it is the wetting hysteresis that reflects the presence and action of surface heterogeneities on the wetting. This wetting hysteresis is defined as the difference between a maximum contact angle reached during an increase in drop volume (advance contact angle) and a minimum contact angle reached during a decrease in drop volume (receding contact angle). Two models describe the behaviour of liquids on surfaces with roughness or chemical heterogeneities but only apply when the drop size is large compared to the scale of the surface roughness.

**The Wenzel's model** - Wenzel in 1936 was the first researcher who focused on he roughness contribution in wetting[25], [64], using a geometrical argument based on a roughness factor  $r_w$  as shown in equation 2.10.

$$r_w = 1 + \frac{Sdr}{100} \tag{2.10}$$

where Sdr is the developed interfacial area ratio and corresponds to the area's additional surface contributed by the material texture as compared to the planar definition area. The Sdr of a completely level surface is 0. Thus, the Young's equation needs a correction as shown in equation 2.11 [65] [66].

$$\cos(\theta_c^*) = r_w \cdot \cos(\theta_c) \tag{2.11}$$

where  $\theta_c^*$  is the corrected contact angle for a rough and/or heterogeneous surface. Wenzel's equation normally only applies to systems with no hysteresis. This would normally exclude most industrial surfaces in general and paper in particular [67]. Even in cases where contact angle hysteresis is observed, average value between advancing and a receding angle can be taken, and then applies the Wenzel equation to the result [25]. Wenzel equation is pretty accurate when

applied to hypothetical surfaces having regular roughness. Different experiments have been made to verify Wenzel's model [25].

The Cassie and Baxter model - Cassie and Baxter proposed in 1944 [68] the expression of a drop contact angle on a chemically heterogeneous surface. In the case of a bicomponent heterogeneous surface (compounds A and B), the expression of the resulting contact angle is given by equation 2.12 :

$$\cos(\theta_c^*) = \phi_A \cdot \cos(\theta_{c,A}) + \phi_B \cdot \cos(\theta_{c,B}) \tag{2.12}$$

where  $\phi_A$  represents the fraction of surface of chemical compound A for which the contact angle has a value  $\theta_{c,A}$  on a surface consisting exclusively of this compound, and  $\phi_B$  the fraction of surface and the corresponding contact angle  $\theta_{c,B}$  for compound B.

## 2.3.1.4 Techniques to determine liquid surface tension

**Du Noüy ring** A maximum force  $F_{dw}$  occurs when the lamella, produced when a ring (Figure 2.19a) moves through a liquid phase boundary, is aligned vertically to the ring plane. This maximum correlates with the surface tension  $\gamma_{lg}$  according to equation 2.13.

$$\gamma_{lv} = \frac{F_{dw}}{L_{dw} \cdot \cos(\theta_c)} \tag{2.13}$$

The wetted length  $L_{dw}$  of the ring is the sum of the inner and outer ring circumference. Platinumiridium is used as the material for the ring, as this alloy is optimally wettable due to its very high surface free energy and therefore generally forms a contact angle  $\theta_c$  = 0° with liquids. The material is also chemically inert and easy to clean.

Wihelmy plate - When a vertically suspended plate is in contact with a liquid surface or interfaceas shown Figure 2.19b), a force  $F_{dw}$  acts on this plate as shown equation 2.13. The difference here is that  $L_{dw}$ , the wetted length of the plate, is equal to its perimeter. To measure the force  $F_{dw}$ , the plate is attached to a force sensor of a tensiometer. The material used for the Wilhelmy plate is the same as for the Du Noüy ring. With the Wilhelmy method, a dynamic contact angle could be measured by slowly immersing and then withdrawing the tested solid. It also enables to measure SFE from different materials using liquids with known properties.

**Jurin's law** - During the wetting of the internal walls of a capillary, the spreading of the liquid on the walls imposes a curvature on the fluid which induces a depression and thus the rise of the liquid in the capillary (capillary rise). It is this depression which is responsible for the spontaneous imbibition of porous media. It is possible to calculate the equilibrium height  $h_{jurin}$  reached by the liquid when the hydrostatic forces (weight of the liquid) compensate the capillary forces. This relation is the Jurin's law, firstly described in 1718 [69] [70], and presented equation 2.14.

$$h_{jurin} = \frac{2\gamma_{lg} \cdot \cos(\theta_c)}{\rho \cdot g \cdot r_{cap}}$$
(2.14)



Figure 2.19: Surface tension measuring systems.

where  $\rho$  the density of the liquid  $(kg \cdot m^{-3})$ ,  $r_{cap}$  (m) the radius of the tube, and g the acceleration of gravity (9.81  $m \cdot s^{-2}$ ).

**Pendant drop method** - This method is based on the shape of drops at equilibrium as illustrated Figure 2.19c. Small drops tend to be spherical because the surface tension effects depend on the surface area of the drop (sphere = minimum surface area). As the hydrostatic pressure is dependent on height, the curvature of the drop interface also changes in the vertical direction. When equilibrium is reached, the liquid surface tension ( $\gamma_{lg}$ ) of a liquid can be determined using equation 2.15.

$$\gamma_{lv} = \frac{\Delta \rho \cdot g \cdot d_e^2}{H} \tag{2.15}$$

where  $\Delta \rho \ (kg.m^{-3})$  is the density difference between the liquid in the drop and the surrounding phase, g = 9.81  $m.s^{-2}$ ;  $d_e$  (m) is the drop equatorial diameter and H is a shape factor.  $H^{-1}$ is a function of  $d_s/d_e$ , where  $d_s$ , is the diameter measured at a distance  $d_e$  from the bottom of the drop. The values of  $H^{-1}$  were determined empirically. This method cannot be used for volatile liquids.

### 2.3.2 Water absorption in paper

Now that the coating color has wetted the paper, it can penetrate the fibre network. This sub-section will therefore look at the absorption of liquids, including water, by the paper.

### 2.3.2.1 The Lucas Washburn law

Liquid transports in porous material are possible with the presence of a driving potential. These driving potentials may be multiple at a same time [71]. Generally, penetration of a liquid into a porous substrate takes place by capillary flow into pores. The classical liquid transport model is

based on Lucas (1918) and Washburn (1921) works [69] [72] [70]. Before focusing on the Lucas - Washburn model (LW), it is important to present the prerequisites [25]:

- $\rightarrow$  the capillaries are cylindrical and have uniform diameter;
- $\rightarrow$  the walls are perfectly smooth;
- $\rightarrow$  the contact angle of the liquid with the solid surface is constant, even when the liquid front is moving;
- $\rightarrow$  the liquid flow is laminar;
- $\rightarrow$  the liquid is Newtonian;
- $\rightarrow$  the capillary is connected to an unlimited tank of the pure liquid.

The kinetics of spontaneous ascent in a tube of radius  $r_c$  less than the capillary length has been studied by many authors such as Washburn [73], Quéré [74] and Fries [72]. They have highlighted different regimes during a capillary ascent and defined transition times between these different regimes. Fries [72] writes a momentum balance on the system composed of a tube of radius  $r_c$  and a reservoir containing a fluid with characteristics of density  $\rho$ , dynamic viscosity  $\eta$ , liquid/gas surface tension  $\gamma_{sl}$  and static contact angle between the fluid and the solid wall  $\theta_c$ . This balance is a complex equation which is usually simplified, leading to equation 2.16

$$\rho \cdot \frac{dh}{dt} \frac{d^2h}{dt^2} = -\frac{8\eta}{r_c^2} \cdot h \cdot \frac{dh}{dt} + \frac{2\gamma_{lg} \cdot \cos(\theta_c)}{r_c} - \rho \cdot g \cdot h$$
(2.16)

Because it is rare that all of these assumptions are strictly true, the approach of Lucas and Washburn can be regarded as an approximation in most practical cases. The LW model, presented equation 2.17 links the height or the depth of liquid penetration into the materials with different parameters.

$$h = \left(\frac{\gamma_{lg} \cdot r_{cap} \cdot \cos(\theta_c)}{2\eta}\right)^{0.5} \cdot t^{0.5}$$
(2.17)

where  $r_{cap}$  is the capillary radius (m),  $\eta$  is the fluid viscosity ( $Pa \cdot s$ ) and t is the time (s). Two important points have to be highlighted. Firstly the penetration depth is proportional to the square root of time. Second, the penetration is driven by the contact angle between the liquid and the solid. Therefore, the contact angle between the liquid and the solid is a key criterion to determine if capillary penetration is possible [75]. Experimental results indicate that this model can be used to describe the average large-scale time evolution of liquid penetration also in more complex capillary systems and in porous media such as paper [76].

## 2.3.2.2 Limits and modifications of the Lucas-Washburn law

The analytical solution of the LW equation and some experimental results showed a good consistency but also some limitations in the following situations:

- $\rightarrow$  porous medium is simplified as a combination of many idealized capillary pores with the shape of parallel cylinders;
- $\rightarrow$  the capillary imbibition model considers one-dimensional (1D) flow in straight tubes;
- $\rightarrow$  the interconnection of pores is not considered and their complex geometries of pore have to be taken into account;
- $\rightarrow$  the static contact angle and tube radius are presumed known;
- $\rightarrow\,$  the tortuosity is neglected, and the actual flow channel is replaced with a straight-line fluid motion;
- $\rightarrow$  the liquid velocity into the material channels will not necessarily be uniform; [25]. Roberts et al. [77] revealed that some channels within a paper web may be entirely bypassed as liquid chooses "easier" and unblocked channels;
- $\rightarrow$  the swelling of cellulose materials can constrict the open areas of pore cross-sections [71];

This is why other researchers set out to solve the equation under other hypotheses. A capillary ascent can thus be successively described by: an inertial regime, a visco-inertial regime, a viscous regime and a visco-gravitational regime. Quéré has studied the cas of inertial regime[74]. To establish the solution associated with this regime, the terms related to viscous and gravitational forces are neglected in the differential equation. The following solution expressing the fluid height in the porous medium as a function of time is shown in equation 2.18.

$$h(t) = t \sqrt{\frac{2\gamma_{lg} \cdot \cos(\theta_c)}{\rho \cdot r_c}}$$
(2.18)

In this case, the ascent rate is constant. This law remains correct for a limited time interval beyond which the viscous forces are no longer reasonably negligible. Fries [72] defines transition times between regimes corresponding to the instants beyond which the deviation between the solutions in each regime is greater than 3%. The transition time  $t_1$  between the inertial regime and the visco-inertial regime is thus defined by equation 2.19.

$$t_1 = 0.1856 \cdot \tau \tag{2.19}$$

where  $\tau = \frac{\rho \cdot r_c^2}{8\eta}$  is commonly defined as the characteristic transition time between the inertial and the viscous regime. Concerning the visco-inertial regime, only the influence of gravity is neglected. Bosanquet [73] obtains the following solution presented equation 2.20.

$$h(t) = \sqrt{\frac{\gamma_{lg} \cdot \cos(\theta_c)}{2\eta} \left(t - \tau \left(1 - \exp\left(-\tau \cdot t\right)\right)\right)}$$
(2.20)

The transition time  $t_2$  between the visco-inertial regime and the purely viscous regime is defined by Fries [48] by the following relation:

$$t_2 = 16.921 \cdot \tau \tag{2.21}$$

The viscous regime is the one described by Lucas and Whasburn. The solution given by this law at short times is not representative of real physics. When t tends to zero, the impregnation rate then tends towards infinity. It is essential for very short times to consider inertial effects as Quéré. Finally, Fries studied the visco-gravitational regime. They defined a limit fluid height beyond which it is essential to consider gravitational effects. This limiting fluid height corresponds to 10% of the equilibrium height given by Jurin's law (equation 2.14). It enables the calculation of the capillary imbibition process for a longer time than is the case in the classical LW equation [72].

$$h(t) = \frac{2\gamma_{lv} \cdot \cos(\theta_c)}{\rho \cdot g \cdot r_{cap} \cdot \sin(\Phi_p)} \cdot \left\{ 1 + W_{lbt} \left[ -exp \left( -1 - \left( \frac{\rho^2 \cdot g^2 \cdot r_{cap}^3 \cdot t \cdot \sin^2(\Phi_p)}{16\eta \cdot \gamma_{lv} \cdot \cos(\theta_c)} \right) \right) \right] \right\}$$
(2.22)

where  $\sin(\Phi_p)$  is the is the inclination angle of the capillary tube with respect to a horizontal plane and  $W_{lbt}$  is the Lambert function. At the end of this visco-gravitational regime, equilibrium between capillary pressure and hydrostatic pressure is reached. The equilibrium height is given by Jurin's law. A discussed limitation of these models concerns the contact angle considered. In all these laws, it is the static contact angle  $\theta_c$ . This choice can be questioned especially in the first moments of a capillary rise. It may be wise to couple these models with the laws expressing a dynamic contact angle.

Other works more related to paper could be cited. Bristow [71] was able to measure water penetration at considerably shorter contact times. The non-linearity between the obtained sorption values and the square root of contact time was explained by the concept wetting delay: there is a wetting time,  $t_{wet}$ , before the water starts to penetrate into the paper. After this wetting delay, the water sorption was suggested to follow the square root relationship indicated in the Washburn model. Bristow explained that swelling must be taken into account when water transport phenomena in cellulosic material is discussed. He separated the total water sorption into a pore sorption part describing the transport in the existing pores, and a fibre sorption part depending on the water taken up by the fibre material. Hoyland [71] proposed a modified LW model taking into account the thickness variations of paper :

$$h(t) = \sqrt{\frac{\gamma_{lv} \cdot r_{cap} \cdot \cos(\theta_c \cdot (t - t_{wet}))}{2\eta}} - \varpi \Delta t_f$$
(2.23)

where  $\Delta t_f$  is the increase in the thickness at time t and  $\varpi$  is a constant. Research in recent years has been conducted to investigate the capillary-driven flow in porous systems by modifying and extending the LW model.

Finally, more general works concerning the modelling of capillary-driven flow in porous systems could be quickly presented. Adding various correction factors into the microstructure of rocks, including tortuosity and pore shape, [78] modified the LW equation adding a pore shape factor  $\delta_p$  presented equation 2.24.

$$\delta_p = \frac{2\sqrt{\pi \cdot A_p}}{\Pi_p^2} \tag{2.24}$$

where  $A_p$  and  $\Pi_p$  denote the cross-sectional area and the perimeter of pores, respectively. The

mass m of the absorbed water into porous media can also be expressed as follows:

$$m(t) = \varepsilon_c \cdot S_p \cdot \rho \cdot \sqrt{\frac{\gamma_{lv} \cdot r_{cap} \cdot \delta_p \cdot \cos(\theta_c)}{2\tau_p \cdot \eta}}$$
(2.25)

where  $\varepsilon_c$  and  $S_p$  are porosity and the cross-sectional area of the porous media, respectively.  $\tau_p$  a correction factor of tortuosity. On the basis of tortuous streamline with fractal characteristics, Cai et al. [78] modified and extended the classical LW equation. They demonstrated that the more tortuous the streamline, the longer the time it takes to reach a given height. It can be expressed with equation 2.26:

$$\frac{dh}{dt} = \frac{(2r_{cap})^{2D_T - 1} \cdot \gamma_{lv} \cdot \cos(\theta_p)}{8\eta \cdot D_T \cdot h^{2D_T - 1}} - \frac{(2r_{cap})^{2D_T} \cdot \rho \cdot g}{32\eta \cdot D_T \cdot h^{2D_T - 2}}$$
(2.26)

where  $D_T$  is the tortuosity fractal dimension.

Many models exist to approximate the absorption of liquid by porous materials. They integrate more or less components of the fluid or the material, in order to approach a behaviour as realistic as possible. However, some of the characteristics used are not always easy to acquire. Thus, in this study, we will remain close to the classical LW theory, and will not complicate the model.

#### 2.3.2.3 Measure the penetration of liquid into paper

There are different methods for measuring the absorption/penetration of liquids in papers. Six methods will be presented: some are regularly found in the literature, others are more innovative.

**Cobb index** - The measurement of water absorption by the Cobb method (according to ISO 532-5) consists of wetting one side of a paper with a given quantity of water for a given time on a given surface (key parameter). The measurement obtained is given in  $g_{water} \cdot m_{paper}^2$ . This value depends on the height of the water column used and the water/paper contact time. The test is only valid if there is no leakage during the test.

**Bristow wheel -** Developed by Bristow in 1967 [71], this method consists of attaching a strip of paper to a wheel with a rotation speed between 0.01  $cm \cdot s^{-1}$  and 10  $cm \cdot s^{-1}$ . Above this wheel, a small reservoir containing the test liquid is attached. At a given moment, the tank is brought into contact with the paper. The liquid then flows onto the paper through a slit of 1 mm wide under the reservoir. This test therefore allows a paper of known speed to be wetted with a known volume of liquid. It gives access to the depth of penetration of the liquid into the paper for different application times.

**Scanning absorptometer -** This absorptometer is based on the Bristow's method [79]. During a scanning absorptometer measurement, liquid is supplied from a scanning head moving along a spiral path on paper as illustrated Figure 2.20. The speed of the head moving over the paper surface is kept constant over a certain part of the paper sample. The head speed could



Figure 2.20: Scanning absorptometer apparatus [79]



Figure 2.21: Salminen apparatus [71].

be increased , enable the system to measure the liquid penetration at different contact times (between 10 ms and 10 s). The total absorbed liquid is obtained in  $ml.m^{-2}$ .

Salminen apparatus [71] - This device was designed with the possibility to measure liquid penetration at different pressure and temperature, with high contact time possibility. It consists of a liquid applicator with a slit opening, a liquid flow measurement through the slit opening, a backing roll and a web velocity control system (cf. Figure 2.21). The web velocity and the time needed for the penetration of a given liquid volume into the paper are measured. The liquid sorption per area unit and the contact time between liquid and paper are obtained with this method.

**DPM**[75], [79] - This test enable to determine liquid penetration at very short time using the evaluation of ultrasound transmitted through paper thickness during wetting. The sample is fixed on a sample holder with double-sided tape. When the test starts, the sample holder is immersed into the test liquid (water here). When the immersion is complete, a high frequency (1 or 2 MHz), low energy ultrasound signal is transmitted through the sample in thickness direction.

During all the test, the transmitted signals are recorded over time. There are two types of sample holders: a flat sample holder where backside is completely covered with the tape; a grooved sample holder where the sample is not in contact with the tape in the grooves. The typical curves obtained by PDA are shown in Figure 2.22. The abscissa corresponds to the measurement time. The ordinate indicates the transmission rate of the transmitted signal. By convention, the maximum transmission point is set to 100%. The curve shows an increasing transmission at the beginning of the measurement. This is followed by a decreasing one. During the first phase, many air bubbles get stuck in the paper. They are gradually replaced by the liquid in the tank. This wetting phase is proportional to the roughness of the paper. Thus, the test starts with a lot of liquid-air-paper interaction to then give way to liquid-paper interactions only.



Figure 2.22: Parameters for the evaluation of DPM measurement proposed by Waldner and Hirn [75].

The change of behaviour can be materialized by the time  $t_{max}$ , corresponding to the highest transmission and it is often interpreted as the wetting time. The decreasing phase appears when the wetting is realized and the air in the paper is driven out little by little from the paper. The intensity of the transmitted signal then decreases with time. The slope of the decreasing phase is proportional to the penetration speed. The time  $t_{95}$  defined on the Figure 2.22 corresponds to the inflection point of the curve and the index  $S_{DPM}$  is the maximum slope (in % of transmission  $\cdot s^{-1}$ ). This method is very practical to determine the wetting time  $t_{max}$  however it does not allow to quantify the exact quantity of absorbed liquid contrary to other methods (Cobb and Bristow wheel for example).

**Karppinen method** - Based on diffuse light reflection from paper, Karppinen [80]studied the penetration of different liquids: water, mineral oil and pure isopropanol into paper samples. Their method could identify the individual wetting behaviour of different paper qualities and different wetting agents. In practice, this method is well suited for dynamic testing of paper wetting featuring up from 10 ms single droplets applied on paper.

## 2.3.3 Rheology of coating colors

Starches differ significantly in physicochemical, rheological, thermal and retrogradation properties. Potato starch exhibits higher swelling power, solubility, paste clarity and viscosity than wheat, rice or corn starches. Morphological characteristics, such as shape and size of the starch granules, are also different. Gelatinization temperatures and gelatinization enthalpies from different sources are also different depending on the origin. Potato starch shows a higher tendency for retrogradation than cereal starches [81]. In another study, Sing et al [82] also showed that even within the same starch botanical source (potato), the impact of cultivars could modify



Figure 2.23: Picture of the measurement device proposed by Karppinen [80] and its schematic presentation.

the properties during cooking and use. Via DSC measurement, they shown that starches with higher crystallinity have higher transition temperatures as well as gelatinization enthalpy. This is linked to a higher degree of crystallinity, providing structural stability and makes the granules more resistant to gelatinization. Moreover, starches with long branched chain length in amylopectin molecules have higher gelatinization enthalpy, meaning that more energy is required to gelatinize.

Rheology of paper coatings is a key factor influencing runnability, water retention and coating holdout [33]. For example viscoelastic coating baths have an impact on the porosity of coating layer and carboxymethyl cellulose slows water penetration in paper. In addition, in the previous section dealing with liquid absorption in papers, the viscosity of the penetrating fluid is taken into account in the physical models. In this subsection, the rheology fundamentals necessary for this project will be presented as well as the techniques for measuring fluid viscosity. Starch being used in this project, a given part fill also focused on the rheological behaviour.

#### 2.3.3.1 Fundamental rheology tools for this project

Viscosity can be defined as the resistance of a fluid to flow and can be related to the internal friction in the fluid, [83]. Dynamic viscosity  $\eta$  ( $Pa \cdot s$ ) (sometimes named apparent viscosity) can be defined (equation 2.27).

$$\eta = \frac{\tau}{\dot{\gamma}} \tag{2.27}$$

where  $\tau$  is the shear stress (*Pa*) and  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ). Different parameters could impact fluid viscosity. For all liquids and pastes,  $\eta$  decreases when temperature increases. The thermal agitation destroyed fluid order at short distance. The liquid viscosity variation with temperature can be described approximately by the Eyring law as presented equation 2.28 below:

$$\eta = A_e \cdot exp\left(\frac{E_a}{R \cdot T}\right) \tag{2.28}$$

where  $A_e$  is a coefficient depending upon the intermolecular vibration  $(Pa \cdot s)$ ,  $E_a$  is the activation energy  $(J \cdot mol^{-1})$ , R is equal to  $8.314J \cdot mol^{-1} \cdot K^{-1}$  and T is the fluid temperature (K) [84]. The chemical fluid nature and the concentration of solute are also influencing factors. The fluid nature (mass fraction or volume fraction), aspect ratio of suspended particles impact

fluid behaviour. The viscosity of liquids increases slightly with pressure but this is often negligible except in applications such as lubrication. The influence of time, combined with that of the shear stress, can impact fluid viscosity: this is thixotropic and antithixotropic fluids.

The variation of viscosity with the shear stress allows the discrimination of fluids according to their rheological behaviour. Thus, three categories of fluid are made: Newtonian fluids, non-Newtonian fluids dependent or not of time and viscoelastic fluids.

**Newtonian fluids** - For a Newtonian fluid the viscosity  $\eta$  is constant regardless of the shear rate  $\dot{\gamma}$ .

Shear thinning or pseudoplastic fluids - These are non-Newtonian fluids. Their viscosity decreases when shear rate increases. Two Newtonian plateaus can exist at low and high shear rates but may be difficult to observe experimentally. Several empirical equations have been proposed to describe the rheological behaviour of shear thinning fluids. The most used is the Ostwald-de-Waele model, described equation 2.29, where the constant  $n_{odw}$  is the flow behaviour index (dimensionless) and  $k_{odw}$  is the flow consistency index ( $Pa.s^{n_{odw}}$ ).

$$\eta = k_{odw} \cdot \dot{\gamma}^{n_{odw}-1} \tag{2.29}$$

In the case of shear thinning fluid,  $n_{odw} \in [0; 1[$ . If  $n_{odw} = 1$ , the fluid is a Newtonian fluid. The other widely used model is the Cross model. It considers three area : a high viscous Newtonian plateau, a shear thinning transition and a low viscous Newtonian plateau as presented equation 2.30.

$$\frac{\eta_0 - \eta}{\eta - \eta_\infty} = \left(\lambda_c \cdot \dot{\gamma}\right)^{n_c} \tag{2.30}$$

where  $\eta_0$  and  $\eta_\infty$  are the viscosities of the first (at low shear rates) and second (at high shear rates) Newtonian plateaus.  $\lambda_c$  is a time homogeneous constant and  $\lambda_c^{-1}$  is the shear rate at which shear thinning behaviour appears.  $n_c$  has the same dimensionless meaning that  $n_{odw}$  in the Ostwald-de-Waele model. When  $\eta_\infty \ll \eta \ll \eta_0$  then this model is like a power law model [85]. There is also the Carreau-Yasuda model presented equation 2.31 where  $n_c$  and  $\lambda_c$  have similar significance that in the Cross law.

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \left[1 + (\lambda_c \dot{\gamma})^{a_y}\right]^{\frac{n_c - 1}{a_y}} \tag{2.31}$$

where  $a_y$  is a dimensionless parameter describing the transition between the first Newtonian plateau and the power law zone [86]. If  $a_y = 2$ , the model is called the Carreau model. The Carreau Yasuada model is used to fit data from a fluid that has 2 Newtonians plateau and with a power law region in between. The parameter  $a_y$  adjusts the transition from the Newtonian plateau into the power law region. In fact, the Carreau-Yasuda model is an extension of the Carreau model. The advantage over the Carreau model is that it is continuous for all shear rates  $(\dot{\gamma} \ge 0)$ .

It can be said that, under the flow conditions prevailing during the coating process, coating

colors exhibit a non-Newtonian viscoelastic behaviour [49]. These non-Newtonian behaviour of paper coating color is due to the presence of particles in the coating formulation [33].

**Shear thickening fluids** - The apparent viscosity of these fluids increases with shear stress. They can have an initial and final Newtonian domain. An equation of the Ostwald-de-Waele type can represent this behaviour. The difference with shear thinning fluid is that  $n_{odw} > 1$  in equation 2.29. They are sometimes called dilatant fluids because an increase in fluid volume can occur at high stresses

Viscoplastic fluids or threshold fluids - They are characterized by a threshold shear stress  $\tau_c$  below which the flow is impossible. A first approach to this behaviour is the Bingham (1922). However, it does not take into account the shear thinning behaviour that a fluid can exhibit beyond the threshold flow. The Herschel-Bulkley equation (1926) can then be used. It models properly paper coating flow behaviour at shear rates below 1000  $s^{-1}$  [33].

Thixotropic fluids - Thixotropic fluids are fluids that are dependent on both shear stress (i.e. non-Newtonian) and time. A thixotropic fluid, starting from a state of rest for a sufficiently long period, sees its viscosity decreasing with time and its structure changing under the application of a constant shear rate. The rheogram of a thixotropic fluid shows a hysteresis. The area of the hysteresis loop is related to the shear history. Hysteresis loop consists of a complete flow curve for a thixotropic materiel, obtained by measurements on a rotational viscometer, showing for each shear rate value two values of shearing stress: one for increasing shear rate and one for decreasing shear rate [32]. Note that thixotropy is quite common in paper coating formulations [33].

**Viscoelastic fluids** - A viscoelastic fluid is a material that has both viscous and elastic properties. The quantities characterizing these properties are dependent on the time of solicitation.

### 2.3.3.2 Rheology of starch

Nuru et al [87] exhibited the shear thinning behaviour of a sage starch paste as well as the relation of this behaviour with temperature. Again, they showed that shear rate, starch concentration and temperature influence rheological properties. With their results, they proposed a single relation to link starch gel dynamic viscosity  $\eta$  with these 3 parameters (cf. equation 2.32)

$$\eta = A \cdot \dot{\gamma}^B \cdot C^D \cdot exp\left(\frac{E_a}{R \cdot T}\right) \tag{2.32}$$

where A, B and D are constants. This relation is a mixed between power law model and Eyring law. Concerning the rheological characteristics of starch paste, it depends on many factors: chemical structure of starch, modification, starch concentration, pasting conditions (temperature, shear rate and heating rate) and storage conditions (temperature and time) [88]. The viscosity profile of native and modified starch is given in Figure 2.24. It shows the shear thinning behaviour of starch gel. Moreover, it is shown that the lower the starch concentration, the lower the viscosity at a given shear rate. Such behaviour will therefore be expected in this study. There is an overall viscosity reduction in the modified starch, but there is no change in the shear thinning property.



Figure 2.24: Viscosity profile of native and modified starch as a function of shear rate [89].

Doublier, in 1981 [90] also worked on the impact of concentration on rheology properties. With a study of wheat starch pastes flow behaviour trough different concentrations (0.3 to 8%), it has been showed that flow curves indicated a non-Newtonian and shear thinning behaviour whatever the concentration but at different scale. Shear-thinning happens due to the disentanglement of the polymer network. These curves have also a Newtonian limit viscosity between 0.3% and 1.5%. Above this concentration, the flow curves could be described by an Ostwald-De Waele equation over a limited range of shear rates. Concerning the impact of temperature Figure 2.25 shows that the higher the temperature, the lower the viscosity  $\eta$ .

In a recent publication, van der Sman et al [91] shown that much of the rheological behaviour of concentrated polysaccharides, as starch, is governed by the ratio  $T_g/T$ . They showed that the Carreau-Yasuda model well describes the flow curves. In this model presented earlier equation 2.31, inverse of critical shear rate represents a fundamental relaxation time, which is dependent on both temperature and moisture content. Furthermore, for linear polymers it is found that this relaxation time also depends on polymer molar weight. Nonetheless, other components impact the rheological properties of the coating color and make the rheological behaviour not totally predictable [92] [93].

The viscosity of starch paste determines the thickening power of starch for various applica-



Figure 2.25: Starch viscosity as a function of temperature [87].

tions. After cooling and storage, and depending on the starch botanical origins, the starch paste do not act the same. Wheat and maize starch pastes (at 6%, w/w) can form gels with a defined shape and exhibit a viscoelastic property. In the other hand, waxy maize, tapioca, and potato starches remain as pastes or form rather weak gels at higher concentration [88].

### 2.3.3.3 Techniques for measuring rheological properties [94] [83]

There are different techniques for measuring rheological properties in different configurations. In this project, only the parallel plate cone plane and capillary configurations will be presented (Figure 2.26). Regardless of the basic geometry, the rheology equations assume non-slip of the fluid at the wall. Techniques exist to detect slip or fracturing of the fluids during testing. In fact, during rheology measurements, the onset of slip means that there is a loss of contact between the sample and the tool. The adhesion condition is a prerequisite for the interpretation of rheometric tests. Thus, the measurement becomes dependent on the study conditions. Within the sample, the flow is no longer controlled and the shear state becomes unknown [95].

**Parallel-plate viscosimeter** A plate of known radius is rotated at angular speed parallel to a fixed plate of the same radius. Unlike the cone-plane system, the velocity gradient is not constant between the two plates and is even less suitable for low viscosity liquids. The stress value is taken for the maximum radius value.

**Cone-plane viscosimeter** A cone with a known half-angle at the apex, is rotated under the action of a constant torque (or at constant angular velocity). A fixed plane is in contact, without friction, with the top of the cone; this plane is placed perpendicular to the axis of the cone. The cone rotation speed is measured, or the cone torque. No correction is necessary provided that measurements are not made at very high speed (turbulence). This method has the advantage of allowing a uniform gradient and shear stress between the cone and plate, a wide measurement range and the use of a small volume of fluid required. However the device is difficult to use with low viscous or low surface tension liquids.



Figure 2.26: Three different rheometer techniques.

**Capillary rheometer** - To fully characterize the rheology of coating colors, the tested shear rates are from 0.01 to 1 000 000  $s^{-1}$  which is complicated to obtain. Nonetheless, capillary rheometer can be a powerful tool for characterizing the high-shear behaviour of coating colors. A correction should be applied with this method to correct inertial effect[33].

# 2.4 Buckling and wrinkling of paper

## 2.4.1 Tension buckling and fluting

# 2.4.1.1 Tension buckling from the mechanistic point of view

Anisotropic membranes with fibrous textures are omnipresent both in organisms and manufacturing like biofilms, skins, biological tissues, woven fabrics, paper and composite materials [96]. They are made of a deformable matrix and fibres with some privileged directions. Zhu et al. [97] experimentally showed that an orthotropic film remains flat when stretched in the highstiffness direction, while wrinkles occur when it is stretched in the low-stiffness direction (Figure 2.27). Liu et al. [96] showed that the degree of orthotropy and the shear modulus significantly affect wrinkling orientation and stability boundary for orthotropic, elastic films during uniaxial stretching.

One of the first theory used is the tension-field theory, first introduced by Wagner [96]. It assumes membrane have infinitely low bending stiffness. This theory was used to model operations on the human skin performed by plastic surgeons for example [96]. However, more sophisticated plate/shell theories that account for both stretching and bending contributions to elastic strain energy are required to predict wrinkling phenomena. Thus the small-strain wrinkling of stiff sheets was used. Friedl et al [98] [99] first uncovered that a stretched rectangular sheet induces transverse compression somewhere which leads to wrinkles. A model of a simply supported plate buckling under uniform membrane loads is proposed to obtain analytical information. Assuming that lateral compression  $\sigma_z$  and global tension are proportional, we have:  $\sigma_x$ :  $\sigma_z = J \cdot \sigma_x$ . The analytical expression of critical longitudinal stress  $\sigma_{x,cr}$  as a function of the aspect ratio  $\frac{a}{b}$  and proportionality factor  $J \leq 0$  is proposed equation 2.33.



Figure 2.27: Deformation at different tensile strains during tensile test of highly orthotropic films in low stiffness direction. Each line represents a different sample width (name W here). Each column is a different strain rate. The red rectangles are configurations where out of plane displacement appear [97]

$$\sigma_{x,cr} = -\frac{\pi^2 \cdot Et_f^2}{12(1 - \nu_{iso}^2)} \left[ \frac{\left(\frac{n}{a}\right)^4 + 2\left(\frac{mn}{ab}\right)^2 + 4}{J\left(\frac{m}{b}\right)^2 + \left(\frac{n}{a}\right)^2} \right]$$
(2.33)

where  $t_f$  is the film thickness, E the Young's modulus,  $\nu_{iso}$  is Poisson's ratio and m, n are the half-buckled wave numbers along the longitudinal and transverse directions of the test, respectively. Furthermore, to simply determine the critical condition, Friedl et al.[98] provided a diagram (Figure 2.28) of the dimensionless buckling coefficient  $k_c$  to calculate the critical tensile stress based on equation 2.34

$$\sigma_{x,cr} = k_c \cdot E\left(\frac{t_f}{b}\right)^2 \tag{2.34}$$

Cerda and Mahadevan [100] studied the instability problem of webs/plates with two opposite edges clamped and subjected to uniform tension (Figure 2.29).

They determined the transverse wrinkling wavelength  $l_{cm}$  and amplitude  $A_{cm}$  by minimizing bending and stretching energies. They showed that wrinkling is fully linked to geometry. They considered that the film is subjected to a longitudinal stretching strain  $\varepsilon$ . The condition of transverse inextensibility is  $(A_{cm}/l_{cm})^2 \sim \mu_{iso} \cdot \varepsilon$ . Thus, they minimized the energy of the system and it leads to the wrinkling wavelength (equation 2.35) and amplitude (equation 2.36).

$$l_{cm} = 2\sqrt{\pi} \left(\frac{S}{T_x}\right)^{0.25} a^{0.5}$$
(2.35)



Figure 2.28: Critical buckling coefficient according to Friedl et al. versus the length/width ratio [98].



Figure 2.29: Example of wrinkles formation, during an uni-axial test, on a polyethylene sample of length a = 250 mm and width b = 100 mm. The thickness  $t_f$  is around 0.1 mm. On the picture, the strain is about 10 % [100].

$$A_{cm} = \frac{\sqrt{2}}{\pi} \left(\frac{\Delta}{b}\right)^{0.5} \cdot l_{cm} \tag{2.36}$$

where  $\Delta = A_n^2 \cdot k_n^2 \frac{b}{8}$  and  $k_n = \frac{2\pi n}{b}$ . Jacques and Potier-Ferry [101] [102] [103] further carried out an analytical calculation from an energy standpoint to explore wavelength selection and mode localization in a long tensile plate. Figure 2.30 illustrates the studied mechanism, in the different stages of wrinkles formation.

The considered problem has no analytical solution, but the critical tensile stress  $\sigma_{x,cr}$  (equation 2.37) and transverse wavelength  $l_{jp}$  (equation 2.38) can be determined.

$$\sigma_{x,cr} = \frac{E\pi^2}{3(1-\mu_{iso}^2)J^2}$$
(2.37)

$$l_{jp} = \frac{2\pi}{k_{jp}} = \sqrt{2|J|l_{x,jp}l_{c,jp}}$$
(2.38)

where  $l_{x,jp}$  is the longitudinal buckling wavelength,  $l_{c,jp}$  is a characteristic length and  $k_{jp}$  is the transverse buckling wave number. Puntel et al [104] showed that the applied critical strain



Figure 2.30: Appearance of wrinkle during sheet conveying. Here  $T_B$  is the critical buckling load and  $T_W$  is the critical wrinkling load [101].

depends on aspect ratios and verified the scaling law obtained by Cerda and Mahadevan [100], providing the critical strain (equation 2.39).

$$\varepsilon_{cr} = \frac{\pi^2 t_f^2}{48(1-\mu_{iso}^2)a^2} \left[ 1 + \frac{a^2}{b^2} \cdot \left( (n_{kp}+2)^2 \left( 1 + \frac{a^2 n_{kp}^2}{b^2} \right) + n_{kp}^2 \right) \right]$$
(2.39)

where  $n_{kp} \in \mathbb{N}$  is related to the wave number  $k_p$ , satisfying  $n_{kp} = k_p - 2$ .

In this study, we will use the  $k_c$  criterion of Zhu et al [97]. Indeed, it is the theory taking into account the orthotropy of paper. Thus, the critical tensile stress can be calculated. However, when some papers deal with isotropic films [100] [99] [104] [98], it is necessary to use a formulation that considers the anisotropy (or orthotropy) of the paper. Thus, based on Zhu et al.[97] work on highly orthotropic films, equation 2.40 can be used.

$$\sigma_{x,cr} = k_c \frac{E_x \pi^2}{12 \left(1 - \xi_1 \nu_{xz}^2\right)} \cdot \left(\frac{t_f}{b}\right)^2 \tag{2.40}$$

where equation  $\xi_1$  (2.41) is the anisotropic coefficient and  $\xi_2$  (equation 2.42) a coefficient depending on the Poisson's ratios and  $\xi_1$ .

$$\xi_1 = \frac{E_z}{E_x} \tag{2.41}$$

$$\xi_2 = \frac{4\left(1 - \nu_{xz}\nu_{zx}\right)}{1 + \nu_{xz} + \frac{1 + \nu_{xz}}{\xi_1}} + \nu_{zx} + \nu_{xz}\xi_1 \tag{2.42}$$

Thus,  $k_c$  can be isolated in equation 2.43.

$$k_{c} = \left\{ \frac{3\xi_{1} - 1 + 2\xi_{1}^{2}\nu_{xz}}{\xi_{1} + 1 + 2\xi_{1}\nu_{xz}}\beta^{2} + \xi_{1} \left[\beta^{-2}n^{2}\left(n+2\right)^{2} + n^{2} + \left(n+2\right)^{2}\right] \right\}$$
(2.43)

where  $\beta = \frac{b}{a}$ . However, this relationship is only valid when the plate is clamped at its ends, contrary to the assumption made by Good where the plate, i.e. the paper, is simply supported and thus generates a different behaviour with respect to the Poisson's effect. Moreover, Juner's work is also based on the Föppl-von Karman equation and must therefore be used with the assumption of its complexity in mind [105]. In all these previous studies, webs were modelled as plates subjected to uniform biaxial loads, which did not conform to the practical stress distributions in the webs. Some works try to used stress function to approach case where tension field are not uniformly distributed [106] [107] [108].

#### 2.4.1.2 Tension buckling from the paper maker point of view

Wrinkles, web weaving, fluting and cockling are commonly seen in any web transport systems, such as paper machine, winder, converting machine, and printing press (cf. Figure 2.31). Paper is a viscoelastic, time-dependent material, greatly influenced by water, tension and heat. The paper web tension - coating color - heat interaction have complex effects on the paper material. Thus, linked to these four parameters, two effects have been highlighted concerning buckling appearence: Poisson effect due to web tension and differential shrinkage[109].



(a) Cockling appearance [110]

(b) Typical fluting pattern [111]

Figure 2.31: Highlighting of cockling and fluting appearence on paper.

In a coating process, paper is fixed by rollers at both ends. Cross Direction (CD) shrinkage is then restricted. Web tends to buckle and out of plane displacement appears when the tension is high enough. Moreover, when web tension is not uniform across the paper width it also leads to buckling by secondary compression stress in CD as a result of the Machine Direction (MD) web tension. It lead to the formation of troughs to minimize the stress in thickness direction. This tension wrinkling occurs when thin materials are stretched under constraint. Tension wrinkles disappear when the tension is released if the elastic limit was not reached. In coating process, paper is subjected to variations due to its contact with water and heat during the drying. Both of them decrease the elastic limit. However, the tension used in coating process is high enough to exceed the elastic limit, especially when the paper is wet. If the tensile buckling is not corrected before drying, it will stay on the final product. Paper may wrinkle by tension only but adding heat creates a sharper and narrower fluting pattern than tension alone [112][113][110][114].

Another factor is the non-uniform CD moisture profile often seen at dry end of papermaking process: areas where the moisture content is high have lower web tension. The elastic stiffness in MD is usually 3 times larger than that in CD. In addition, the hygroexpansion coefficient of paper in CD is usually 3 times larger than in MD. So, if fluting is driven by hygro-strains, changing the direction of paper fiber increases the critical moisture change, needed to initiate fluting, approximately by a factor of 9. Differential shrinkage between printed and non-printed areas in printing process could be a reason of fluting. They postulated that image areas lose less moisture during drying as the ink layer prevents moisture from evaporation. Coffin[115] predicted the wavelength of fluting and showed that with this theory, tension is an important factor determining the fluting wavelengths [116][117][111].

Paper may take up and lose moisture during the coating process causing important hygroexpansion or shrinkage in paper. These mechanisms tend to predict much larger wave length of fluting than what were observed in printing. However, if paper is assumed to be non-uniform, local buckling can occur [118]. One example of non-uniformity is local variations of fibre orientation (its direction and degree). This structural variation could trigger local variations of hygroexpansion, and thus local buckling . Cockling is, on the other hand, more random features without any specific orientation direction. Fundamental mechanisms of fluting and cockling are still somewhat controversial. Cockle can be created by producing local variations of drying "histories". If paper sheet has some wet and dry areas during drying, these areas develop residual strains differently, and then buckle after drying is completed, causing cockles [119].

## 2.4.2 Shear wrinkling of a web in a roll-to-roll process

The study of wrinkles on a moving web is not new. The theory setting out the foundations for studying this problem was proposed by Leonhard Euler, around 1750, who formulated a first theory of beams by defining the elastica, a medium or neutral fiber that deforms in bending without contracting or compressing. The study of plate bending returned during the 19<sup>th</sup> century with the studies of Young, Laplace, Poisson, Navier, Cauchy, Fourrier, Germain, Lamé and Clapeyron. In 1888, Love used the assumptions of Gustav Kirchhoff, themselves inspired by the Euler-Bernoulli assumptions for beams, to found a theory of thin plates. The plate theory was consolidated by Rayleigh (1877), von Kármán (1910), Timoshenko (1921), Reissner (1945) and Uflyand (1948).

It is important to note that in the literature, the Timoshenko's theory of elastic stability is frequently found and cited as well as Föppl–von Kármán equations that described large deflections of thin flat plates. The physical validity of these last equations stay questionable [105]. It is then possible to draw a parallel between a plate and a web. It is known in the web handling industries that web shear wrinkles come from misaligned rollers. Therefore, many investigators formulated the prediction model of wrinkles for isotropic webs with constant Young's modulus in MD and CD.

The plates buckling theory considers the webs as plates with low bending stiffness. Analyses have been done using the energy methods or numerical methods such as finite element anal-

| Parameters           | Variation  | Wrinkle risk | Impact                                      |
|----------------------|------------|--------------|---|
| Web span             | $\searrow$ | ****         | ***** on critical misalignement an-         |
|                      |            |              | gle 📡                                       |
| Web thickness        | $\searrow$ | ****         | * on critical misalignment angle $\nearrow$ |
|                      |            |              | **** on the critical web tension $\searrow$ |
| Friction             | 7          | ***          | *** on the critical web tension $\searrow$  |
| Web Poisson's ratios | $\searrow$ | *            | * on the critical web tension $\searrow$    |
| Web Young's Modulus  | $\searrow$ | ****         | ** on the misalignment angle $\searrow$     |
|                      |            |              | **** on the critical web tension $\searrow$ |

Table 2.1: Prediction of web wrinkles proposed by Martz [126](high arrow: increase, low arrow: decrease, \*\*\*\*\*: very important impact, \*: low weak)

ysis [120] [120] [103] [121]. Shelton [59] studied the boundary conditions of webs transported through misaligned rollers: webs were modelled as Euler beams, and the normal entrance law was proposed to determine the boundary conditions. Then, the stress distribution in the web could be obtained. Furthermore, based on Shelton's studies, many other buckling analyses of webs have been done and published. For example, a series of studies were carried out in the Web Handling Research Center (Oklahoma State University, USA). In 1989, experimental investigations show that two types of wrinkling failures can exist in webs subjected to shear due to roller misalignment [122]. Good et al. [123] presented a buckle prediction model for isotropic webs with roller misalignment, which reliably forecasted the web behaviour. However, anisotropic materials such as paper, have different Young's modulus in MD and CD. Moreover, in the case of paper-webs, the web air permeability could impact wrinkles formation. Accordingly, Good and Beisel analysed the mechanism of buckling of anisotropic PET rolls. Hashimoto [124] proposed a theoretical modelling of paper-web wrinkling generation due to misalignment of roller and also considers web speed and web tension. It is completed with experimental verifications.

Beisel [125] studied the buckling phenomenon caused by the imperfect structure of rollers, such as coin or concave profile of rollers. Moreover, Good and Beisel [125] used the biaxial loaded plates buckling criterion to study the buckling of the web caused by the misalignment of the roller. These theories have been used by Martz in his PhD thesis [126] where he also proposed a table that sums up the impact of each process parameters (Table 2.1).

Kim Lin and Mote [107] [108] studied the critical buckling loads of webs with all edges simply supported and subjected to non-uniform tension. Tang et al. [106] proposed a theoretical calculating process for the elastic buckling of webs transported through a pair of misaligned rollers, by making use of the plate buckling theory and determining the stress distribution of webs by using the Timoshenko beam theory.

**Theoretical models:** Webs are composite membranes and plate structures that react to compressive stresses until they reach the critical buckling stress [127] [123]. Wrinkles in web are caused by the compression exceeding the critical buckling stress (when plates don't shorten but bend) and can be loaded in three directions. In this case, the focus is made on wrinkles, with machine direction web tension, induced by lateral shearing forces in the web, and the wrinkles

that result are called "shear wrinkles" (Figure 2.32a). Timoshenko proposed a solution for the buckling stresses for a rectangular plate [128]. It allows tension on two opposing sides and compression on the other two opposing sides.



Figure 2.32: Buckling generation by shearing and impact of friction force .

Assuming that the plate is slightly buckling under the forces applied in its middle plane and then to calculate the magnitudes that the forces must have in order to keep the plate in such a slightly buckled shape. The solution uses the energy method. It states that when the work done by forces acting in the middle plane of the plate  $\Delta T$  becomes larger than the strain energy of bending for any shape of out of plane deflection  $\Delta U$ , the plate is unstable and buckling occurs [122]. Thus, to find the critical buckling load, the work done by the forces is set equal to the strain energy in bending as shown equation 2.44.

$$\Delta U = \Delta T \tag{2.44}$$

Isotropic materials (Timoshenko's theory) [128]: Introducing forces  $N_x$ ,  $N_z$ , the Poisson's ratio for an isotropic material  $\nu_{iso}$ , the web bending stiffness  $D_{iso}$  and out of plane displacements w, it leads to equation 2.45.

$$-\frac{1}{2} \iint \left[ N_x \left( \frac{\partial w}{\partial x} \right)^2 + N_z \left( \frac{\partial w}{\partial z} \right)^2 \right] dx dz = \frac{D_{iso}}{2} \iint \left\{ \left( \frac{\partial^2 w}{\partial x^2} + \frac{\partial^2 w}{\partial z^2} \right)^2 - 2\left( 1 - \nu_{iso} \right) \left[ \frac{\partial^2 w}{\partial x^2} \frac{\partial^2 w}{\partial z^2} - \left( \frac{\partial^2 w}{\partial x \partial z} \right)^2 \right] \right\} dx dz \quad (2.45)$$

Assuming that x-direction is MD and z-direction is CD,  $w_{mn}(x, z) = w$  (equation 2.46) could be described as the solution of linear partially differential equation and  $a_{mn}$  is the amplitude [24].

$$w_{mn}(x,y) = a_{mn} \sin\left(\frac{m\pi x}{a}\right) \sin\left(\frac{n\pi z}{b}\right)$$
(2.46)

It is assumed that the edges of the plates are simply supported. b is the web width (mm), a the web span (mm). The number of half waves in the x-direction is m, and in z-direction in n. Thus, combining the previous equation, dividing by the web thickness  $t_f$  and introducing the

stress yield  $\sigma_x$  and  $\sigma_z$ , it leads to equation 2.47 and equation 2.48.

$$N_x \left(\frac{m\pi}{a}\right)^2 + N_z \left(\frac{n\pi}{b}\right)^2 = D_{iso} \left[ \left(\frac{m\pi}{a}\right)^2 + \left(\frac{n\pi}{b}\right)^2 \right]^2$$
(2.47)

$$\sigma_x m^2 + \sigma_z \left( n \cdot \frac{a}{b} \right)^2 = \sigma_{e,iso} \left[ m^2 + \left( n \cdot \frac{a}{b} \right)^2 \right]^2$$
(2.48)

where  $\sigma_{e,iso}$  is a normalized stress [128] presented equation 2.49.

$$\sigma_{e,iso} = \frac{\pi^2 D_{iso}}{a^2 t_f} \tag{2.49}$$

Setting m = 1 because only one-half wave appeared in MD direction, equation 2.48 become equation 2.50.

$$\sigma_x + \sigma_z \left( n \cdot \frac{a}{b} \right)^2 = \sigma_{e,iso} \left[ 1 + \left( n \cdot \frac{a}{b} \right)^2 \right]^2 \tag{2.50}$$

Equation 2.50 is the basic equation for failure criteria used to indicate if wrinkling appeared on the web. Finally, after some calculation, for an isotropic plate, it leads to the critical normal stress necessary to generate wrinkles  $\sigma_{z,cr}$ , where *i* is the number of half waves for a specific web span that is wrinkled (equation 2.51).

$$\sigma_{z,cr} = \frac{b^2}{i^2 a^2} \left[ \sigma_{e,iso} \left( 1 + \frac{i^2 a^2}{b^2} \right)^2 - \sigma_x \right]$$

$$(2.51)$$

**Orthotropic materials:** In a similar way, by taking into account the anisotropy of paper, with a thickness  $t_f$  (mm),  $\sigma_{z,cr}$  is given by [15] according to equation 2.52.

$$\sigma_{z,cr} = \frac{b^2}{i^2 a^2} \left[ \sigma_{e,ortho} \left( 1 + \xi_1 i^4 \frac{a^4}{b^4} + \xi_2 i^2 \frac{a^2}{b^2} \right) - \sigma_x \right]$$
(2.52)

where  $\sigma_{e,ortho}$  is the normalized stress for orthotropic plates given equation 2.53.  $D_{xx}$  is the web bending stiffness in x-direction given equation 2.54.  $\sigma_x$  is the stresses generated by the web tension  $T_x$ , given equation 2.55.

$$\sigma_{e,ortho} = \frac{\pi^2 D_{xx}}{a^2 t_f} \tag{2.53}$$

$$D_{xx} = \frac{E_x t_f^3}{12 \left(1 - \nu_{xz} \nu_{zx}\right)} \tag{2.54}$$

$$\sigma_x = \frac{T_x}{t_f} \text{ with } T_x \text{ the web tension}$$
(2.55)

 $E_x$  and  $E_z$  are the elastic modulus (MPa) in x-direction (loading direction and web transport direction) and z-direction (transverse direction),  $\nu_{xz}$  is the Poisson's ratio for transverse strain in the z-direction  $\varepsilon_z$  when stretched in the x-direction, where  $\varepsilon_x$  is the strain in x-direction.
Since the ratio  $\frac{E_z}{E_x}$  is defined as  $\xi_1$ , the Poisson's ratios in the same plane are related due to the symmetry of the stiffness matrix as presented equation 2.56.

$$\nu_{xz} = \frac{-\varepsilon_z}{\varepsilon_x} \text{ and } \nu_{zx} = \xi_1 \nu_{xz} \tag{2.56}$$

To define the interger i, equation 2.57 must be true.

$$\sigma_{e,ortho} \left[ 1 - i^2 (i+1)^2 \xi_1 \frac{a^4}{b^4} \right] < \sigma_x < \sigma_{e,ortho} \left[ 1 - i^2 (i-1)^2 \xi_1 \frac{a^4}{b^4} \right]$$
(2.57)

It is possible to determine the maximum critical shear stress that the web must withstand  $\tau_{cr}$  (equation 2.58) and link it with the tram error  $\theta_{cr}$  (°) (also called misalignment angle) (equation 2.59) according to equation 2.46, invoking Castigliano's second theorem:

$$\tau_{cr} = \sqrt{\sigma_{z,cr}^2 - \sigma_x \sigma_{z,cr}} \tag{2.58}$$

$$\theta_{cr} = \frac{6\tau_{cr}a^2}{E_xb^2} \tag{2.59}$$

Another point to consider is the friction between the paper and the surface of the roll. Indeed, this friction will determine the web tension T at which wrinkles may or may not appear. This critical tension value  $T_{cr}$  is inversely proportional to the value of the friction coefficient  $\mu$ . Thus, as presented by Hashimoto [124], a simple empirical model, leading to equation 2.60.

$$T > T_{cr} = \frac{2t_f^2}{\mu b} \sqrt{\frac{E_x E_z}{3\left(1 - \nu_{xz}\nu_{zx}\right)}}$$
(2.60)

# Chapter 3

# Materials and methods

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This chapter will present the materials and techniques used in this project. The four papers used will be presented as well as the chemicals used to perform contact angle tests. The techniques for preparing and characterising the starch gel and the coating color will be presented. Finally, all the equipment and techniques used to produce the coated paper and to characterise it (with or without coating) will be detailed.

# 3.1 Materials

#### 3.1.1 Papers

In this project, four different papers are tested. The common point between them is the low or very low grammage they have. General characteristics of these papers are:

- → GHDS 35 and GHDS 40 are one-side coated glossy papers used for flexible packaging, made with hardwood and softwood. The coated side is made of calcium carbonate, kaolin and SBR Latex. GHDS 35 is a 35 g.m<sup>-2</sup> paper and GHDS 40 is a 40 g.m<sup>-2</sup> paper. Compared to GHDS 40, GHDS 35 provides a 12.5% weight reduction enabling a lower environment footprint impact. It also has good performance during lamination, printing and converting. Main applications include pouches or sachets, for food and non-food end-uses such as sugar, coffee, aromatic herbs or dehydrated products. These papers are suitable for extrusion with PE or lamination with alufoil and PET. They can be printed after lamination with flexo and helio printing. There lower basis weight also facilitates sealing process according to the manufacturer.
- → CPRAW is a notebook paper, i.e. a paper for rolling cigarettes. This grade is made of 100% chemical unbleached softwood pulp. The pulp is highly refined and no fillers are introduced into the paper. With its very low grammage of 14 g.m<sup>-2</sup>, the CPRAW paper has very little opacity. This paper has not been treated for wet strength and it is not waterproof.

#### 3.1. MATERIALS

→ CPBS is a cigarette paper used in cigarette making machines. It is composed of a mixture of so-called textile pulps (linen pulp and hemp pulp), bleached eucalyptus pulp and calcium carbonate as fillers. With its very low grammage of 23.5 g.m<sup>-2</sup>, this paper is laid: the drip roller on the flat table is marked with a striped pattern that leaves a watermark in the paper, characteristic of cigarette papers. This paper has not been treated for wet strength and it is not waterproof.

An important point was mentioned: the project was supposed to be done only with GHDS 35. However, it was necessary to order new GHDS 35 reel, but the manufacturer had stopped production and offered GHDS 40. In addition, an opportunity emerged at the end of the project to have one CPRAW reel and one CPBS reel with another manufacturer. This is why the project studies were mainly carried out on GHDS 35.

#### 3.1.2 Starch

The starch used is a STABILYS A025-thermally modified potatoes starch from Roquette (France). It is a white and odourless powder. It has a pH of 6.2 in a 20 %wt water suspension. Its relative density is 0.5 and its solubility in water is 350 g.L<sup>-1</sup>. The median grain size is 18.7  $\mu$ m accord to manfufacturer (NFX 11-666 standard). The formulation used in this project is then made of a starch gel (starch cooked in water), at different mass fraction, with uncooked starch particles, at different mass fraction.

#### 3.1.3 Chemicals used for contact angle measurement

Liquids used for contact measurements are: Hexadecane (CAS: 544-76-3) and 1-Bromonaphtalene (CAS: 90-11-9) are from Fischer Scientific. Glycerol (CAS: 56-81-5) is from Sigma Aldrich. Ethanol (>99.8%) (CAS: 64-17-5) is provided by Honeywell. Ethylene Glycol (CAS: 107-21-1) is from Acros Organics. Home-made distilled water is used. The surface tensions, dispersive and polar components of these test liquids are given Table 3.1.

| Tested liquid     | $ \begin{array}{c} {\bf Surface \ tension} \\ ({\bf mJ.m^{-2}}) \end{array} $ | $egin{array}{c} \mathbf{Polar} \ \mathbf{component} \ \mathbf{(mJ.m^{-2})} \end{array}$ | $egin{array}{c} {f Dispersive} \ {f component} \ {f (mJ.m^{-2})} \end{array}$ |
|-------------------|---|---|---|
| Distilled water   | 72.8  | 51  | 21.8  |
| Glycerol          | 64  | 30  | 34  |
| Hexadecane        | 27.5  | 0   | 27.5  |
| Ethylen glycol    | 48  | 19  | 29  |
| 1-Bromonaphtalene | 44.6  | 0   | 44.6  |

Table 3.1: Surface tension, polar and dispersive components of liquids used during contact angle measurements [63].

# 3.2 Coating color

In this project, a difference will be made between the starch gel and the coating color. Starch gel is starch cooked in water. The coating color consists of starch gel with uncooked starch grains added.

#### 3.2.1 Preparation of the starch gel

In order to prepare the coating color, a cooking robot (Moulinex Companion XL) is used. The temperature is adjustable from 30 to 150 °C by steps of 5 °C. Several rotation speeds are available but are given in arbitrary units. Figure 3.1 shows the blade used for mixing during cooking. The blades are 50 mm high with a base diameter of 160 mm and a top diameter of 170 mm. They are inclined at 45° and the percentage of empty space is about 35 %. It is also possible to set the cooking time. The cooking parameters are chosen following the advice of the supplier: 30 min of cooking at 95 °C at the slowest robot speed at a mass concentration 15 wt% and 20 wt%



Figure 3.1: Blade used to cook and blend starch gel in cooking robot.

The cooked starch mass fraction  $\Phi_{binder}$  in the starch gel is calculated as presented in equation 3.1.

$$\Phi_{binder} = \frac{m_{binder}}{m_{binder} + m_{water}} \tag{3.1}$$

where  $m_{binder}$  is the mass of starch used as a binder and  $m_{water}$  is the mass of water used for the coating color.

The mass fraction of uncooked starch grains in the coating gel  $\Phi_{particles}$  is calculated according to equation 3.2 using  $m_{particles}$  as the mass of uncooked starch particles in the coating color:

$$\Phi_{particles} = \frac{m_{particles}}{m_{binder} + m_{water} + m_{particles}}$$
(3.2)

#### 3.2.2 Devices and methods for characterising the coating color

The starch and the starch gel are characterised following a wide range of techniques to have different useful information for the project: rheological behaviour, water absorption and surface properties.

#### 3.2.2.1 Determination of the starch grain sizes

To confirm the supplier specifications, starch particles sizes are measured in water using a laser granulometer (Cilas particle size analyser 1190) based on the Fraunhofer method . During the test, ultrasonic system is on to maximise the dispersion of the particles and avoid aggregates. The obscuration level is set around 15 points to obtain a good measure while slowly adding starch particles. In addition, Scanning Electron Microscope (SEM) pictures of dry starch grains are taken to have additional information about the size and shape of the grain. A FEI Quanta 250 (SEM) is used equipped with a field emission gun in ETD (Everhart–Thornley Detector) or SDD (Silicon Drift Detector) mode.

#### 3.2.2.2 Sedimentation studies

To study the behaviour of starch grains in water, a sedimentation study is performed. It will help to know if during the coating process, starch grain could sediment and then lead to heterogeneity when deposited on the paper. It consists in suspending a known quantity of uncooked starch grains in water. Different phases will appear over time which are linked to particles sizes. The test is carried out in a 1 L graduated test tube at 20.5 °C as shown Figure 3.2. After a time



Figure 3.2: Sedimentation test evolution at 2 different times : t and t +  $\Delta$ t.

 $\Delta t$ , sedimentation occurred. With no evaporation,  $h_0$  is total height,  $h_0 = h_1 + h_2$ , where  $h_1$  is the height of the first sedimentation phase and  $h_2$  is the height of the second sedimentation phase. During the study time, the heights of the various phases are measured by taking pictures at different times, using a Sony Alpha 6000 with a 35-70 (f 3.5 -4.5) lens on a tripod.

#### 3.2.2.3 Differential Scanning Calorimetry (DSC)

DSC measurements are performed to characterized the temperature at which starch grains exploded. This helps to ensure a good coating quality while being certain to be at the best cooking temperature. This is done with a DSC Q100 (TA Instruments, NewCastle) filled with liquid nitrogen cooling system. A suspension of starch in water ( $\Phi_{binder} = 20 \text{ wt\%}$ ) is placed in a hermetically sealed pan. Each sample is heated from 5 °C to 145 °C with a heating rate of 10 °C.min<sup>-1</sup>. Measurements are done in duplicate to ensure repeatability. The sample weight was between 15 and 25 mg.

#### 3.2.2.4 Starch gel cooking control

To optimize the starch gel cooking, the cooking is followed by optical microscopy. The aim of the method is to take a sample at different cooking times. A drop of this sample is placed on a microscope slide as shown Figure in 3.3. The microscope used is a Zeiss microscope Axio Imager M1 with AxioVision SE64 software.



Figure 3.3: Highlighting of the cooking evolution of starch particle by optical microscope analysis.

Particular attention is paid to the quantity deposited. Indeed, a too important quantity of starch grains deposited on the slide would lead to obtain several layers of starch grains and would interfere with the observation. While the cooking progressed, less and less grain should be observed. When no more grains are seen, the cooking is done. It is a complementary measure to the DSC.

#### 3.2.2.5 Rotational rheological measurement of the starch gel

To determine the rheological behaviour of the fluids used during coating, rheological measurements are performed. The used device is an Anton Paar MCR 302 rheometer in a cone-plan set up (CP50-1 measuring cone) (Figure 3.4) and with Anton Paar 1.25 software. The measurements are done in a steady state regime and in a saturated moist environment to minimize evaporation.

The starch gels were tested at different shear rates: from 0.1 to 10000 s<sup>-1</sup> and at different temperatures: from 20 to 50 °C. The gap between the measuring cone and the heating plate is set to 102  $\mu$ m. Two starch mass fractions  $\Phi_{binder}$  are tested:  $\Phi_{binder} = 15$  %wt and 20 %wt. An average viscosity value is measured by considering at least 200 points on the stabilisation viscosity plateau. The results will be used to follow the viscosity evolution at different shear rate and temperature. They will be compared with different models from literature.



Figure 3.4: Rotationnal rheological measurement with a cone-plan system.

#### 3.2.2.6 Measure of the starch gel density

To forecast particles sedimentation in starch gel, density characterisation is realized. The experiment will be performed in two stages: the volume of the density probe is determined with a liquid with known density (calibration step), hereafter the density of unknown liquids can be determined as illustrated in Figure 3.5 while recording the mass variation over time and using Archimede's principle. The device used is a Sigma 701 tensiometer from Biolin Scientific with a 12 mm diameter glass sphere. It is needed to heat the starch gel at 40°C to avoid formation of a starch skin link to gelatinization.



Figure 3.5: Density measurement of a 20 %wt starch gel with a glass sphere.

#### 3.2.2.7 Determination of starch gel surface tension

To study the wettability of paper by the starch gel, it is mandatory to know its surface tension. To perform this measurement, the device used is a Sigma 700 tensiometer from Biolin Scientific with Du Noüy ring [129] or Wilhelmy plate . Whatever the chosen probe, it should be cleaned with ethanol and flamed prior to use (temperature > 1000 °C).

The De Noüy ring method uses the interaction of a platinum ring with the surface of the tested liquid, starch gel here. The ring is submerged below the starch gel /air interface. After immersion, the beaker with the starch gel gradually decreased and the ring pulls up the meniscus of the liquid. During all the operation, the force acting on the support is recorded. The Wilhelmy plate method follows the same principle. It utilizes the interaction between a platinum plate



Figure 3.6: Use of a platinum Wilhelmy plate (19.5 mm x 0,12 mm) to measure starch gel surface tension with 5 round-trip cycles.

(the Wilhelmy plate) and the surface of the starch gel as shown Figure 3.6. In this method the position of the probe relative to the surface is significant. As the surface is brought in contact with the probe liquid, the force sensor will detect this by the change in force it experiences (Figure 3.7).



Figure 3.7: Highlighting of the phenomena that occurs during a surface tension measure: (1) the plate is at its "zero" position; (2) the plate is in contact with the liquid, the advancing contact angle can be recorded; (3) the plate continues to go deeper in the liquid; (4) the plate is going back to its "zero" position, the surface tension is measured. The receding contact angle can be recorded [25].

The plate is then wetted to a set depth. When the plate is later returned to the zero depth of immersion, the force is registered. In order to obtain significant value, 10 round trips in the starch gel are performed. Moreover, the starch gel can quickly become very viscous and gelatinize. To avoid this phenomenon, the beaker is set in a thermostatic vessel at 40 °C. The gel has a starch mass fraction of 20 %wt. The test depth is set to 6 mm and the test speed is  $20 \ m \cdot min^{-1}$ .

# 3.3 Devices and methods for characterising the paper

## 3.3.1 Room conditions of tests

Some of the tests shown below were done in conditioned room at  $23.5 \pm 1$  °C and  $50 \pm 5$ HR%. Moreover all the samples are stored at least 24 h in these conditions before any testing. Table 3.2 sum up which tests are done in conditioned room.

| Tosts  | Done in conditioned |
|--|---------------------|
| lests  | room                |
| Thickness and grammage determination                 | Yes                 |
| Mercury porosimetry                                  | No                  |
| Tensile test   | Yes                 |
| Kodak rigidity                                       | No                  |
| Water stretch dynamic analyser                       | No                  |
| Finch's test   | No                  |
| Surface roughness measurement                        | No                  |
| Static contact angle measurement                     | No                  |
| Dynamic contact angle measurement                    | No                  |
| Cobb test  | Yes                 |
| Water absorption by paper discs stack                | No                  |
| Dynamic penetration measurement                      | Yes                 |
| All experiments done in the coating pilot, including | No                  |
| temperature and web tension measurement              | NO                  |
| Digital image correlation during tensile test        | Yes                 |
| Measure of the friction coefficient                  | Yes                 |
| X-ray tomography                                     | No                  |
| Scanning electron microscope                         | No                  |
| Wrinkle profile determination                        | No                  |

Table 3.2: Tests carried out in conditioned or unconditioned rooms

# 3.3.2 Composition and structure

In order to determine the characteristics of the papers used, the following methods are used. The grammages G of the samples are determined in accordance with ISO 536. The thicknesses  $t_f$  of the samples are measured following ISO 534. For thickness and grammage, 10 samples are measured.

The pore size distribution and surface area of the papers are measured using mercury porosimetry from Micromeritics AutoPore IV 9500 V1.09 (located at Institute of Environmental Geosciences, Grenoble). The sample weight are 460 and 470 mg.

# 3.3.3 Mechanical properties

## 3.3.3.1 Tensile test

To carry out the test, an Instron 5965 testing system of 5 kN maximum force (Instron, USA) is used, with an accuracy of 0.5% of the read value. Samples with dimensions of 15 mm width

and 100 mm length are tested with a constant rate of elongation set at 10 mm.min<sup>-1</sup>. For each paper, Cross Direction (CD) and Machine Direction (MD) are tested, 10 times each to have representative average values and standard deviations. The geometry allows to be far enough from the jaws and allows the Poisson effect.

The values obtain using tensile test are also used to determine the Poisson's ratios according to two different methods: an empirical model equation and one from mechanics for orthotropic materials. The empirical model equation is used by Biancolini [130] and was first proposed by Baum [131][132]. This empirical correlation bounds shear modulus and Poisson ratios as presented equation 3.3 and equation 3.4.

$$G_{xz,Baum} = 0.387\sqrt{E_x \cdot E_z} \tag{3.3}$$

$$\nu_{xz,Baum} = 0.293 \sqrt{\frac{E_z}{E_x}} \tag{3.4}$$

 $G_{xz,Baum}$  is the shear modulus in the xz plane,  $\nu_{xz,Baum}$  is the Poisson ratio,  $E_x$  is the Young's modulus in MD and  $E_z$  is the Young's modulus in CD.

The other method comes from the constitutive equations of mechanics for an orthotropic material and is proposed by Viguié [133]. Thus, the experimentally measured  $E_{tan}$  can be expressed as presented equation 3.5.

$$\frac{1}{E_{tan}} = \frac{1}{E_x} \cdot \cos^4 \phi_f + \left(2 \cdot \frac{-\nu_{xz}}{E_x} + \frac{1}{G_{xz}}\right) \cdot \sin^2 \phi_f \cdot \cos^2 \phi_f + \frac{1}{E_z} \cdot \sin^4 \phi_f \tag{3.5}$$

In order to obtain  $G_{xz}$  and  $\nu_{xz}$ , it is necessary to measure the tangent modulus of paper sample  $E_{tan}$  at a same strain.  $E_{tan}$  is the slope, in the elastic domain, of the network versus strain plot obtained during the tensile test. The fibres in the sample are not aligned with the measurement direction:  $\phi_f$  is the angle between the tested direction and MD. Once all the moduli are measured, a fitting between the experimental values and the modelled values is performed by the least squares method.

#### 3.3.3.2 Kodak rigidity

The "Kodak rigidity" method enables the determination of the bending stiffness of a test piece clamped at one end by measuring its vibrational resonant length. The vibrational resonant length of a material, in one direction, when it is subjected to vibration of a given frequency depends on its bending stiffness in that direction and its grammage. To determine the bending stiffness of the sample, a resonance method is used following the ISO 5629 standard as shown Figure in 3.8. The bending stiffness S (mN.m) is obtained as presented 3.6.

$$S_{bs} = 20 \cdot \left(\frac{l_{res}}{100}\right)^4 \cdot \frac{G}{100} \tag{3.6}$$

where  $l_{res}$  is the resonance length (mm). However, this method leads to a high dispersion coefficient for the  $l_{res}$  values even if the precision the precision is around 0.1 mm.



Figure 3.8: The resonance method. Resonance corresponds to maximum deflection  $\delta$  and w to the out of plane displacement [134].

#### 3.3.3.3 Water Stretch Dynamics analyser (WSD)

The device comes from Emtec Electronic GmbH (Leipzig, Germany). It consists of measuring the elongation of the paper while it is in contact with water on one side only as explained in Figure 3.9. The paper sample has a width of 60 mm for a length of 210 mm and the water surface is about 55 x 70 mm<sup>2</sup>. The duration of the test is 120 s and the strain measurement starts as soon as the paper is in contact with water. This test is carried out at constant stress (assuming negligible variations in paper cross-section). MD and CD are tested as coated and uncoated face in contact with water.



Figure 3.9: WSD (Water Stretch Dynamics analyser) test principle.

For each combination, 4 different forces could be applied using an adjustable lever arm to

create the torque: 1, 1.5, 2 and 2.5 N. For each chosen force, a combination is tested 5 times.

#### 3.3.3.4 Finch's test

The Finch's test is used to measure the tensile strength of paper after a 20 s immersion in water. The sample is wrapped around a horizontal dry rod and blocked in the upper jaw. The wrapped part is immersed in water and removed from it. Then the tensile test begin. It follows the ISO-3781 standard. The test is performed with a 15 mm width paper strip. The strip is cut to have a length between the dry horizontal rod and the upper jaw of 150 mm as presented Figure 3.10.



Figure 3.10: Finch's test principle.

The immersed length of the strip should be between 25 and 50 mm. The test is performed at a speed of 10  $m \cdot min^{-1}$ . The samples are tested 10 times in the MD and in the CD.

#### 3.3.4 Water absorption and wettability

#### **3.3.4.1** Surface roughness

The roughness is determined using the Alicona InfiniteFocus (Alicona, Alicona Imaging GmBH, Raaba, Austria). It is an optical system which takes pictures of a sample at different heights and then reconstructs a 3D view of the sample from the stack of taken images. It is used for dimensional measurements, surface analysis and characterisation and allows measurement of textures and profiles, according to ISO 25178 standard. In the present study, the measured value is the  $S_{dr}$  (Developed Interfacial Area Ratio). It is expressed as the percentage of additional surface area contributed by the texture, as compared to an ideal plane, the size of the measurement region. To obtain the  $S_{dr}$  value it is necessary to apply a cut-off filter to separate micro-roughness, roughness, waviness and form as explained Figure 3.11.



Figure 3.11: Highlighting of the different scales that could be measured while focusing on surface roughness.

The cut-off value is chosen from the RSM (mean spacing of profile irregularities of primary profile). It follows the DIN EN ISO 4288, ASME B46.1 standards and Table 3.3 indicates the link between the RSM and the cut-off value $\lambda_c$ .

| Periodic profile RSM (mm) | Cut-off filter $\lambda_c$ (mm) |
|---------------------------|---------------------------------|
| $0.013 < RSM \le 0.04$    | 0.08                            |
| $0.04 < RSM \le 0.13$     | 0.25                            |
| $0.13 < RSM \le 0.4$      | 0.8                             |
| $0.4 < RSM \le 1.3$       | 2.5                             |

Table 3.3: Cut-off values as a function of periodic profile RSM

#### 3.3.4.2 Static contact angle: Sessile Drop Method

To know the behaviour of the liquid drop on the papers studied in this thesis and to determine their Surface Free Energy (SFE), the sessile drop technique is used. By placing a droplet of liquid with a known surface energy, the contact angle over time is recording. While knowing the surface energy of the prob liquid, the SFE is determined following the Owens, Wendt, Rabel and Kaelble (OWRK) method [61] [62]. The use of several different probe liquids is required. In the present case, hexadecane, 1-bromonaphtalene, glycerol, ethylene glycol and home-made distilled water are used.

The tested paper is placed under the needle tip of a syringe which deposited 5  $\mu$ L liquid droplets on the sample as shown Figure 3.12. To minimize shrinkage, the paper sample is fixed with tape at its two edges. The "static" contact angle of the droplets is measured over 1 minute with an acquisition frequency of 20 frames per second. Due to the device, there is an initial time of 3 to 10 s between probe liquid-paper contact and the start of the measurement. The optical system used is the OCA 20 goniometer from Dataphysics Instruments GmBH, Filderstadt, Germany. The device provides a  $\pm 0.2^{\circ}$  reading accuracy. Then, the movie obtained is analysed with SCA 20 OCA Control software (Dataphysics Instruments GmBH, Filderstadt, Germany) to determine the contact angle of the drop on the paper over time. 5 tests are done for each



Figure 3.12: Evolution of a contact angle over time during a sessile drop method test.

liquids : it enables to drown a average curve for each liquids.

#### 3.3.4.3 Dynamic Contact Angle (DCA)

This technique is used to measure the receding and advancing contact angle and to demonstrate hysteresis-like behaviour of a material during its entry and exit into a liquid [25]. The DCA method follows the same principle as the surface tension measurement of a liquid. The difference lies in the object of the measurement. In the surface tension measurement, the properties of a liquid are determined with a Wilhelmy plate or a de Noüy ring, with a known materials (platinum). In the DCA technique, the liquid is known and the material characteristics (plate) are unknown.

In the present case, the paper samples are cut to have a width of half an inch (12.7 mm). The length of the sample must be greater than 15 mm in order to be sufficiently wetted. However, for DCA test, it is necessary to have symmetry of the material and the same surface everywhere. Therefore, to minimise the problems associated with asymmetry of the samples, two pieces of paper are stuck together, with the same two sides facing outwards, using double-sided tape as shown Figure 3.13.



Figure 3.13: Size and organisation of a typical paper sample for DCA measurements.

It must be kept in mind that the tape will influence the behaviour of the sandwich: it is the perimeter  $P = 2 \cdot width + 2 \cdot thickness$ , of the sample that is considered in determining the contact angles. So, to minimise the impact of the tape, the following condition is imposed on the double side tape thickness  $t_{dst}$  (equation 3.7).

$$2t_{dst} \le 0.01P \tag{3.7}$$

For this test, 5 up and down cycles are done per sample. The test liquids are water and/or starch gel. The test speed is 5  $m \cdot min^{-1}$  and the immersion depth of 3 mm.

#### **3.3.4.4** Cobb test

The Cobb test follows the ISO 535 standard. The principle of this test is to measure the amount of water that a paper can absorbed during a given time, on a given surface. To do so, the apparatus showed Figure 3.14 is used. A 150 mm square sample is set and blocked under a metallic ring. This ring is locked to avoid water leaks.



Figure 3.14: Cobb test principle

The tests are done at different contact times in a conditioned room with conditioned paper at 23.5  $\pm 1$  °C and 50  $\pm 2$  % HR. The Table 3.4 sum up the used contact time.

| Trial time (a) | Symbol    | Water excess     | Drying start time |
|----------------|-----------|------------------|-------------------|
| I la time (s)  | Symbol    | removal time (s) | (s)               |
| 30             | Cobb 30   | $20 \pm 1$       | $30 \pm 1$        |
| 60             | Cobb 60   | $45 \pm 1$       | $60 \pm 2$        |
| 120            | Cobb 120  | $105 \pm 1$      | $120 \pm 2$       |
| 300            | Cobb 300  | $285 \pm 1$      | $300 \pm 2$       |
| 1800           | Cobb 1800 | 1755 to 1815     | $1800 \pm 15$     |

Table 3.4: Test duration for Cobb tests according to ISO 535 standard.

To determine the water absorptiveness of paper  $A_s$   $(g_{water} \cdot m_{paper}^{-2})$ , the equation 3.8 is used.

$$A_s = \frac{m_{wet} - m_{dry}}{S_{paper}} \tag{3.8}$$

where  $m_{wet}$  is the wet mass, in grams of the tested sample,  $m_{dry}$  is the dry mass, in grams, of the tested sample and  $S_{paper}$  is the tested area (0.01  $m^2$ ).

#### 3.3.4.5 Water absorption by paper discs stack

Capillary rise or Washburn method can be done by using force tensiometer and a special type of sample holder. The measurement set up is shown in Figure 3.15. The sample holder is a cylinder with holes in its base, filled up with 15 mm diameter paper discs. It is immersed into water and the amount of water absorbed into the paper bed is measured against time. One side of the tested paper is coated, the other not: thus, every discs of one trial are set coated side face up or face down.



Figure 3.15: Setting up the water absorption measurement by stacking paper discs on top of each other and immersed it in water.

Different tests are carried out with different numbers of discs. Note that a paper disc has a mass of 7 mg and the balance has a precision of 1 mg. Thus, with only one disc, the measurement is already at the edge of the precision of the apparatus. The immersion depth is set to 0.50 mm, the sampling interval to the minimum (around 10 Hz). The measure lasted 30 min maximum and between 1 and 100 paper discs are used during one trial.

#### 3.3.4.6 Dynamic Penetration Measurement (DPM)

This test enable to determine liquid penetration at very short time using the evaluation of ultrasound transmitted trough paper thickness during wetting. The sample is fixed on a sample holder with double-sided tape. When the test starts, the sample holder is immersed into the test liquid (water here). When the immersion is complete, a high frequency (1 or 2 MHz), low energy ultrasound signal is transmitted through the sample in thickness direction as explained Figure 3.16).

During all the test, the transmitted signals are recorded over time. There are two types of sample holders: a flat sample holder where backside is completely covered with the tape; a grooved sample holder where the sample is not in contact with the tape in the grooves. Three tests are carried out with the flat sample holder (2 with coated side in contact with water and 1 with uncoated side) and 3 others on the grooved sample holder (2 with coated side in contact



Figure 3.16: DPM measurement principle [75].

with water and 1 with uncoated side).

#### 3.3.5 Coating process

#### 3.3.5.1 Coating pilot

The coating laboratory pilot used is from RK Print, UK. This laboratory driver is versatile as it allows different types of techniques to be used for coating flexible films such as plastics or paper. In this study, the material used is paper and the coating technique chosen is the Mayer bar coating. Figure 3.17 represents a simplified diagram of the pilot. Appendix A shows a complete diagram with dimensions.



Figure 3.17: RK laboratory coating pilot.

The coating section consists of a tank for the coating color. This is where an applicator roller dips to collect the coating color. The color is deposited on the paper by contact. In order to ensure good contact between the paper and the applicator roller, a pressure roller is placed upstream of the coating zone so that the paper is pressed properly against the applicator roller (Figure 3.18.



Figure 3.18: The coating station with the different coating tools.

It is once the color has been applied to the paper that the Mayer bar comes into play. The purpose of the Mayer bar is to metering the coating color onto the paper web, to remove excess color from the paper. Rods are available in a wide variety of wire sizes to give a range of coating weights. Table 3.5 sum up the rod characteristics.

| Cada | Wire diameter | Wet film thickness |
|------|---------------|--------------------|
| Code | (µm)          | $(\mu m)$          |
| .002 | 0.05          | 4                  |
| .003 | 0.08          | 6                  |
| .006 | 0.15          | 12                 |
| .012 | 0.30          | 24                 |
| .020 | 0.51          | 40                 |

Table 3.5: Link between Mayer rod characteristics and the thickness of the wet film deposited.

Different widths of applicator rollers are available: 230, 290, 300 and 310 mm. Two pneumatic vane motors drive either the applicator roller and the Mayer bar. The working pressure of the motors is between 3.5 and 4 bars.

To dry after coating, an infra-red drying ramp is installed on the web path. This ramp consists of 5 independent infra-red lamps, each with a power of 500 W. Therefore, the total available power is 2.5 kW. Two hot air dryers are installed just after the infra-red dryer to complete the drying process. These dryers can heat the air up to 200 °C and are temperature-controlled (unlike the infra-red dryer).

The drive part consists of a variable speed DC main drive motor rated at 0.56 kW coupled

to a 10:1 ratio worm gearbox giving a final web speed from 5 to 50  $m \cdot min^{-1}$ . A toothed belt transmission connects the core holder and a pneumatic clutch. The pneumatic clutch is connected to the motor by an angle gear. The working pressure of the pneumatic clutch is between 1.5 and 4 bars. The roller preceding the winding is a speed measuring roller. This control has been installed during this project because it hasn't been available previously.

On the unwinding section, the used paper reel should have an intern diameter of 76.2 mm (3 inch) to be used on the coating pilot. The minimum web width is 220 mm and the maximum width is 305 mm. The unwinding station is equipped with a manually adjustable brake for controlling the web tension.

#### 3.3.5.2 Temperature measurement

In order to carry out the various tests about temperature measurement, sensors from Micro-Epsilon (CT-SF15-C1) were used [135]. The spectral wavelength range of these sensor is 8 to 14  $\mu$ m. The measuring temperature range is -50 °C to 600 °C, for non-metallic materials. The optical resolution of the sensors is 15:1 (ratio between sensor-object distance and spot size at the focus point). Their accuracy is ±1 °C, with a given response time of 150 ms. Note that the electric heating time is 10 min. The emissivity of the sensors can be adjusted between 0.1 and 1. Finally, the sensors can operate in working environments between -20 °C and 180 °C. The emissivity of the paper is considered equal to 0.95.

Figure 3.19 is the test bench set up in order to carry out different tests. It consists of a flat base on which a Peltier device is placed and used as a heating source. A sample of paper of  $30 \times 30 \text{ mm}^2$  is fixed on the plate. On the base, a rail is fixed on which the sensor can move. The rail can be tilted in a perpendicular plan to the base, allowing to change the angle between the sensor and the paper sample.



Figure 3.19: Non-contact IR temperature measurement system.

The impact of the measuring height  $h_s$ , the measuring angle  $\kappa_s$  and the sensor emissivity  $\varepsilon_s$  are studied. The measuring height  $h_s$  varied from 70 to 300 mm, the measuring angle  $\kappa_s$  varied from 0 ° to 60 ° and the emissivity  $\varepsilon_s$  from 0.1 to 1.0. All the tests are made at different temperatures: from ambient temperature 21.3 °C to 190 °C.

Once the IR temperature sensors characterised, the goal is to see where, on the paper width, after an IR dryer on a coating pilot, it is the most relevant to fix the sensor. In order to do so a thermal camera (FLIR - i7) is used to obtain the various images presented in this document. With a resolution of 140 x 140 pixels, the camera works on a spectral wavelength range from 7.5 to 13 µm. The camera measurement accuracy is  $\pm 2$  °C and can take measurements between -20 °C and 250 °C. The images are taken at the output of an infra-red dryer fixed on a coating pilot (Figure 3.20).



Figure 3.20: R pictures taking with Flir-i7 (Web speed: 5  $m \cdot min^{-1}$ .

The images are taken in such a way that the whole width of the paper (300 mm) is visible. About the image processing, the Fiji software is used in order to obtain the different temperature profiles for each picture. The web speed varies from 5 m.min<sup>-1</sup> to 40 m.min<sup>-1</sup>. All the 5 lights of the IR dryer are switch on. The web tension is set to 20 N.m<sup>-1</sup>. The temperature of the pilot room varies from 15 to 35 °C and the relative humidity from 30% to 65%.

#### 3.3.5.3 Web tension measurement

In order to measure the paper web tension, a web tension measuring roller is installed on the coating pilot. The system comes from Erhardt & Leimer. First, a PD30 sensor roll is mounted on the coating pilot. This measures the radial forces that the web exerts on the sensor roller in the direction of measurement. The sensor roller consists of a roller in contact with 2 Wheatstone bridge-type force sensors. These measuring elements are formed as double bending bars on which the extension measuring strips are placed. Switched together, they form a measuring bridge. A mechanical lock also protects the system from overloading. The second component of the tape tension measurement is a DC62 tape tension regulator from the same supplier. This system allows the signal measured by the PD 30 roller to be recovered and the web tension to be accessed in real time via the DC62 display. This system would also allow the installation of

a web tension control via a brake fixed on the core holder of the master reel.

#### 3.3.6 Wrinkles and buckling

#### 3.3.6.1 Digital Image Correlation (DIC)

The wrinkle formation mechanism is reproduced on an Instron 5965 tensile testing machine to recover displacement and deformation information thanks to 2D and 3D image correlation. Sony Alpha 6000 with a 35-70 (f 3.5 - 4.5) lens is used for 2D image correlation and two Canon EOS 1200D DSLR (Digital Single-Lens Reflex) cameras with Canon EFS 24mm 2.8 STM lenses for 3D stereo-correlation (3.21.



Figure 3.21: DIC system installed on the tensile test (left) and on the coating pilot (right).

The software used for the tensile is 7D (developped by Pierre Vacher, from Université Savoie Mont-Blanc). For the DIC study, speckled samples are used. The sample are tested in CD and MD. In the 7D software, an area of interest is defined per set of photos. The algorithm for correlating images is a combination of Harris and Pyramid algorithms. In addition, to carry out the DIC tests, a random speckle is printed on the industrially coated side. These speckles are needed to make difference between each studied point on the samples. The printing is carried out with a Xerox laser printer at a resolution of 600 DPI. Printed papers are also characterised and compared with non-printed papers.

#### 3.3.6.2 Friction coefficient

The surfaces to be tested are placed together in plane contact and under apparent uniform contact pressure. The forces needed to initiate sliding (the static friction force) and to slide the surface relative to each other (the kinetic friction force) are recorded. This follows ISO-15359 standard.

#### 3.3.6.3 X-Ray tomography

A sample of a wrinkled paper and coated with the starch gel is sent to the company Novitom for X-ray tomography on a line at the ESRF (European Synchrotron Radiation Facility) in Grenoble. The sample has a thickness of approximately 35  $\mu$ m. The voxel resolution is 0.7  $\mu$ m on each direction.

#### 3.3.6.4 SEM

SEM pictures of wrinkle and non-wrinkle paper are taken to have more information. A FEI Quanta 250 tungsten SEM is used for the microscopic observation.Both secondary and backscattered electrons are used to perform the images.

#### 3.3.6.5 Wrinkle profile determination

The roughness is determined using the Alicona InfiniteFocus (Alicona, Alicona Imaging GmBH, Raaba, Austria) (cf.3.3.4.1). For the wrinkle characterisation, a wrinkle paper is set under the objective and then pictures are taken in order to obtain the profile of the paper as Figure 3.22.



Figure 3.22: Example of result that could be obtain with Alicona InfinteFocus device.

# 3.4 Conclusion

The different techniques used in this project were presented in this chapter. They will be used in the following chapters presenting the results of this project. The techniques of rheology, sedimentation, wettability and water absorption will be used first in the following chapter. Then, techniques related to the mechanical behaviour of papers will be used. Finally, the process aspects will be discussed, with the related techniques, in the last results chapter of this document.

# Chapter

# Absorption of the coating color by papers

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In this first chapter of results, the preparation of the coating color and its characterisation (as well as its compounds) will be presented. It is fundamental insofar as it plays an integral part in optimising the coating process. In a second step, the phenomena of wettability and water absorption by the paper will be discussed. These are important insofar as they are involved in the coating process and can impact the mechanical properties of the paper. Please note that, in this chapter, only the GHDS 35 paper have been tested.

### 4.1 Properties of the coating color

Before looking at the penetration of liquids into the paper, it is important to know the fluids used. This section will focus on the starch gel especially dealing with its cooking, the sedimentation of starch particle in water and the rheology of the coating color under different conditions.

#### 4.1.1 Preparation of the coating color

#### 4.1.1.1 Control of starch cooking

In order to prepare the coating color used in this project, it is necessary to cook the starch in water to make a starch gel. The cooking of the starch gel must be optimal in order to ensure an explosion of all the starch grains in the water. For this purpose two techniques presented in the materials and methods section are used. The first one is an optical microscopy of the cooking of the grains. The second method is the use of DSC. Both methods aim to determine the temperature at which the explosion of the starch grains is effective.

Thus, different images were taken by optical microscopy in order to follow the cooking of the starch in water. The images presented Figure 4.1 were made with a concentrated starch gel at 15% wt at different temperatures.

When the suspension is cooked at 40.0  $\pm 0.1$  °C. The slide is covered with starch grains, and on different planes: a superposition of grains is visible. The image 4.1b shows a suspension being cooked at 54.5  $\pm 0.1$ °C. Black areas surrounding the starch grains are visible but remain very few. The image 4.1c was taken for a suspension at 64.0  $\pm 0.1$ °C. The number of grains in the picture is much lower than in the two previous pictures. Moreover, the image is blurred: this is due to the heat of the fluid, leading to a movement of the particles. The image 4.1d is the suspension being fired at 75.0  $\pm 0.1$ °C. It has even less visible starch particles compared to the previous image. Shapes in the background are still present. However, these are misshapen and difficult to identify. The last image (Figure 4.1e) is the suspension at 86.0  $\pm 0.1$ °C. It is very blurred. It corresponds to a moving fluid without any particle shape. The suspension is cooked and has become the desired coating color. Then it is possible to say that the cooking and the total explosion of the grains takes place at a temperature between 75.0  $\pm 0.1$ °C and 86.0  $\pm 0.1$ °C.

In order to obtain more precise information about the temperature required to explode the grains, another technique was used: DSC. The latter was also presented in the materials and methods section. The measurements were carried out with a starch suspension in water at an initial mass fraction of 20%wt. A triplicate was performed. The curves of the measurements are shown in Figure 4.2.

The measured heat flow is plotted as a function of the sample heating temperature. The reader will immediately notice the difference between the "starch 20%wt\_1" curve and the "starch 20%wt\_2" and "starch 20%wt\_3" curves. We spoke of the initial mass fraction: this corresponds to the mass fraction in the container where the suspension was made. Although care was taken to have a homogeneous mixture, the samples taken for measurement are of about ten milligrams. It is therefore possible that during the sampling carried out for the "starch 20%wt 1" measurement, the mass fraction of the sample was greater than the original





(e) 86.0  $\pm 0.1^{\circ}$ C





Figure 4.2: Measured temperature by the IR sensor (°C) versus the heating temperature (°C) and measuring height  $h_s$  (mm) (standard deviation:  $\pm 1$  °C). 3 trials were carried out.

mass fraction. However, this was beneficial. Indeed, the curves of the "starch 20%wt\_2" and "starch 20%wt\_3" measurements seem to be smoothed: no clear peaks appear because the water smoothed the measurement. Nevertheless, it is still possible to observe a slight variation of the slope for a temperature close to 72°C.

The "starch 20%wt\_1" measurement shows two very distinct peaks. The first is at 67.61°C. The second is at 82.62°C. It is quite common to find a gelatinization temperature between 55 and 80°C in the literature [41]. Our values are therefore consistent on this point. It is still necessary to understand the appearance of two peaks and not just one. In the work of Singh et al 2008 [82], a second smaller peak is also observed for the sample named K.Sindhuri. The reasons for the presence of two peaks could be related to the difference in gelatinization temperature between amylose and amylopectin or to the presence of crystalline zones with long chains, thus requiring more energy to be destroyed [82]. For the samples "starch 20%wt\_2" and "starch 20%wt\_3", the peak values, although smoothed by water, are 73.92°C and 71.22°C respectively.

If we now compare the results of the optical and DSC measurements, some points can be highlighted. First of all, a first phenomenon seems to appear at around 75°C as observed by microscopy. The DSC measurements allow us to locate this first change more precisely at 70.91  $\pm 3.16$  °C. A second phenomenon appears around 82°C.

Thus, in order to ensure optimal cooking of the starch gel, the said cooking will be carried out at a temperature of 95°C, for 30 minutes in order to allow the temperature of the robotcooker to rise sufficiently. In addition, the cooking will be done under agitation. However, the latter cannot be measured. Indeed, the food processor used is normally intended for domestic use, so the control of the speed of rotation of the stirring blade has been simplified. In order to obtain more information about the cooking of the starch gel, the investment in a RVA (Rapid Visco Analyser) device would have been a plus. This would also have allowed a comparison with many results in the literature.

#### 4.1.2 Rheology of the starch gel

Rheology has a significant role in this project. Indeed, this science allows to have access to different information concerning a fluid subjected to different constraints. The knowledge of the viscosity of the starch gel is therefore necessary for 3 reasons:

- $\rightarrow$  To optimise the coating process by knowing the rheological behaviour of the fluid at different shear rates and temperatures
- $\rightarrow\,$  To study the sedimentation of starch particles in the starch gel in the coating color storage tank
- $\rightarrow$  To evaluate the penetration of water in the starch gel in order to quantify the evolution of the mechanical properties of the paper during coating.

This rheological study will be divided into two parts. The first one will focus on the evolution of the viscosity of the starch gel as a function of the shear rate. The second part will be dedicated to the impact that temperature can have on the viscosity of starch gel.

#### 4.1.2.1 Shear rate dependency of the starch gel viscosity

The objective of this section is to study the rheological behaviour of the starch gel of this project. Through the literature review, it can be said that starch gels are shear thinning fluids, i.e. their viscosity decreases as the shear rate increases. In addition, the starch mass fraction of the gels also affects the rheological behaviour.

Figure 4.3 shows the evolution of the viscosity of starch gels at 15%wt (orange) and 20%wt (black), at different temperatures: 20°C (triangle), 35°C (cross) and 50°C (square). It was not possible to go beyond 50°C because the water in the starch gels evaporated despite the precautions taken (moisture saturation of the measurement environment). The gels dried out and became brittle starch films. Note that each mean value was calculated with at least 100 points. Standard deviations were determined but are not shown in Figure 4.3 because they are small. The highest coefficient of variation is equal to 5.96% and is obtained for  $\dot{\gamma} = 1 \ s^{-1}$  and  $\eta = 42.17 \ Pa \cdot s$  for a starch mass fraction of 15% at 35°C.

First of all, we note the unquestionable decrease in viscosity as a function of the shear rate, whatever the temperature or the mass fraction. The impact of the mass fraction on the viscosity should also be noted. Indeed, at the same temperature and shear rate, the 20%wt gel is more viscous than the 15% gel. This is consistent with the information presented in the literature review (see Figure 2.24). A higher stress is required to disentangle a more concentrated polymer network.

Tests were carried out from 0.1 to 30,000  $s^{-1}$  but when  $\dot{\gamma} > 10,000s^{-1}$  starch gels are ejected from the measuring plate due to the centrifugal force generated. At very low measurement rate



Figure 4.3: Evolution of starch gel viscosity versus shear rate, for different starch mass fraction, at different temperature.

| Code                      | Temperature [°C] | $\Phi_{binder}$ [wt%] | $n_{odw}$ [-] | $k_{odw}$ (Pa.s <sup>n</sup> ) | $R^2$ |
|---------------------------|------------------|-----------------------|---------------|--------------------------------|-------|
| $20^{\circ}\text{C-}15\%$ | 20.00            | 15%                   | 0.10          | 42                             | 0.991 |
| $35^{\circ}\text{C-}15\%$ | 35.00            | 15%                   | 0.13          | 32                             | 0.998 |
| $50^{\circ}\text{C-}15\%$ | 50.00            | 15%                   | 0.27          | 5                              | 0.980 |
| $20^{\circ}\text{C}-20\%$ | 20.00            | 20%                   | 0.04          | 187                            | 0.992 |
| $35^{\circ}\text{C}-20\%$ | 35.00            | 20%                   | 0.09          | 104                            | 0.950 |
| $50^{\circ}\text{C}-20\%$ | 50.00            | 20%                   | 0.23          | 18                             | 0.996 |

Table 4.1: Parameters obtained for the OdW model.  $\Phi_{binder}$  is the cooked starch mass fraction.

the rheometer is extremely sensitive to external disturbances (footsteps, closing doors) and these appear on the rheograms. These events are not negligible and have a negative impact on the stabilisation of the system. Moreover, with heating, the starch gel dries out before stabilisation (Figure 4.4). For these reasons, no stabilisation plateau could be detected although stabilisation seems to occur at high shear rates. Therefore the Cross and Yasuda models will not be used. The Ostwald-de-Waele model will be kept.

In order to see whether the experimental results can be modelled by the Ostwald-de-Waele model, the least squares method (LSM) is used. The problem variables are  $n_{odw}$  and  $k_{odw}$ , respectively the flow behaviour index and the flow consistency index. In order to determine these two variables, the Generalized Reduced Gradient (GRG) algorithm is used. The results of the modelling are presented in Table 4.1 based on 6 sets of experiments (3 temperatures and 2 mass fractions). The coefficients of determination  $R^2$  (a measure of the quality of the prediction of a linear regression) are very good: all greater than or equal to 0.950, and for the modelled by the Ostwald-de-Waele (OdW) model. For each of the 6 sets, the flow behaviour index  $n_{odw}$  is strictly between 0 and 1. This means that the shear thinning behaviour has been well modelled. In addition,  $n_{odw}$  increases when the temperature increases. Conversely, the  $k_{odw}$  coefficient



Figure 4.4: Evolution of viscosity of a starch gel at 15%wt, at 50 °C and  $\dot{\gamma} = 0.1 \ s^{-1}$ . The starch dried and now stabilization of the viscosity appears.

| Shear rate | $\mathbf{E}_{\mathbf{a}} \ (J \cdot mol^{-1})$ | $\mathbf{A_e} \ (Pa \cdot s)$ | $\mathbf{R}^2$ |
|------------|--|-------------------------------|----------------|
| 10         | 8968   | 39.16                         | 0.78           |
| 100        | 8325   | 5.42                          | 0.99           |
| 1000       | 8674   | 1.53                          | 0.95           |
| 10000      | 16102  | 0.08                          | 0.94           |

Table 4.2: Parameters obtained for the Eyring model.

decreases with increasing temperature.

It also appears that temperature plays a significant role on the viscosity of starch gels. Indeed, at identical concentration and shear rate, the viscosity of the gels decreases when the temperature of the latter increases. However, it will be noted that the experimental points for the temperatures of 20 and 35°C are merged several times (always at fixed concentration). The impact of temperature will be discussed in the next section.

#### 4.1.2.2 Temperature dependency of viscosity

As mentioned earlier, the temperature of the starch gels tested seems to impact the viscosity of the gels. This point was presented in the literature review and is not new. This kind of behaviour is regularly modelled by Eyring type law and it will be applied to the present case. Figure 4.5 shows the evolution of the viscosity of a 20%wt starch gel as a function of temperature, at different shear rates.

In the figure, it can be seen that for a given shear rate, the viscosity decreases with an increase of the temperature. The Eyring law will be used to model the experimental behaviour presented Figure 4.5. The LSM method combined with the GRG algorithm was also used as before. The results are presented in Table 4.2.

Few remarks could be done. First of all, the  $R^2$  obtained for shear rate equal to 10  $s^-1$  is 0.78. This is low compared to the other values (0.94, 0.95 and 0.99). The reason for this low



Figure 4.5: Evolution of starch gel viscosity versus temperature at different shear rate for 20%wt starch gel.

value may be the long stabilisation time at  $\dot{\gamma} = 10 \ s^{-1}$ , allowing the gel to dry and thus leading to a wider spread of viscosity values. The second point to address concerns is the values of the activation energies, which are low except at  $\dot{\gamma} = 10000 \ s^{-1}$ . In fact, the activation energy of water, which is a simple molecule easy to move, is 15.6  $kJ \cdot mol^{-1}$ . For  $\dot{\gamma} = 10000 \ s^{-1}$ , the hypothesis made is that at high shear rates the starch and water in the gel separate and the behaviour studied is similar to water. Dolz et al (2004)[136] showed the dependence of  $A_e$  and  $E_a$  on shear rate for biopolymer emulsions. In the present case we do not have emulsions but we try this model anyway (equation 4.1).

$$A_e = A_{e0} + \frac{a_e}{(b_e + \dot{\gamma})^2} \tag{4.1}$$

where  $A_{e0}$ ,  $a_e$  and  $b_e$  are constants. The obtained values are :  $A_{e0} = 8.40 \cdot 10^{-4}$ ;  $a_e = 87.62$ ;  $b_e = 29.93$  with  $R^2 = 1$ . The maximum value of  $A_e$  could be related to  $\eta_0$  (zero shear viscosity). The decay follows the shear-thinning behaviour of the fluid [137], the model is therefore correct.

To conclude this section, let us consider the use of these models and experimental results for the process. It has been shown that starch gels are shear thinning fluids. Their behaviour is also impacted by the gel mass fraction of starch and the temperature. In the context of a coating process, the best compromise between all these parameters must be found. A fluid that is too viscous will be difficult to apply to the paper. On the other hand, if its viscosity is too low, it will run, splash and leave traces. Thus, the gel must not be cold. A coating at 20°C should therefore be avoided. Moreover, if the fluid is too hot, the water contained in it will evaporate and modify the mass fraction of the gel. It is therefore necessary to try to coat between 35°C and 40°C. Rheological modifiers could have been used but it was not is the project philosophy (using the less components and as much as possible bio-sourced). The coating speed will impact the shear rate that the gel will undergo during coating, and consequently the viscosity. In this case it is difficult to know the exact shear rate. However, the speeds are known at all times (provided there is no slip between the sheet and the roller). The speed of the web is between 5 and 40  $m \cdot min^{-1}$ . The speed of the applicator roller is considered to be zero (this is not the case in reality but the applicator roller has no speed control). The distance between the sheet and the applicator roller during the application is difficult to measure. It is assumed that this distance is  $10^{-4}$  m (close to the air gaps found in industry: speed in industry 1800  $m \cdot min^{-1}$ , shear rate:  $10^5$  to  $10^6 s^{-1}1$  by fast calculation air gap between 30 and 300  $\mu m$ . We therefore choose  $100 \ \mu m$ . Thus, knowing the air gap and the sheet speed, the shear rate can be estimated at  $1666 \ s^{-1}$  at  $10 \ m \cdot min^{-1}$  and  $6666 \ s^{-1}$  at  $40 \ m \cdot min^{-1}$ . As first approximation, the shear rate will be set at  $3000 \ s^{-1}$ . At this shear rate, the viscosities of the gels are of the order of 0.03  $Pa \cdot s$  for a 15% wt gel and  $0.07 \ Pa \cdot s$  for a 20% wt gel. To favour the binding power of the gel and limit the quantity of water in it, the 20% wt gel is chosen for the rest of the project (except in specific cases).

The original project of this thesis was to produce a starch gel in which starch particles are suspended to form the coating color. However, no study was carried out on starch gel with uncooked starch particles in it. Indeed, the suspension of uncooked starch particles in the starch gel is not easy to handle and aggregates may appear, causing a problem during the viscosity measurement.

#### 4.1.3 Sedimentation of starch

During the coating process, coating color may stay several minutes on the tank. If the agitation is not enough efficient starch particles can sediment. It is therefore necessary to examine the extent to which these particles sediment in the water first and then in the starch gel, all in order to ensure homogeneity during the coating process. For this we will try to determine the size of the starch particles experimentally. With these data, the sedimentation rate can be calculated with models and compared with experimental results. Depending on the results, a decision will be made to implement a system to prevent sedimentation.

To carry out this study, different information are needed. As presented in the literature review, the Stokes equation refers to the size of the particles but also to the viscosity of the suspending medium. Thus starch particles sizes and starch gel viscosity should be known. For this purpose, a particle size analysis was carried out. SEM photos of the starch particles will illustrate this (Figure 4.7). The other important point is the knowledge of the viscosity of the starch gel. Let us first look at the particle size analysis in order to know the sizes of the particles used. Figures 4.6b and 4.6a show the particle population, by number and volume respectively.

In Figure 4.6b and Figure 4.6a, we have taken care to isolate the small and large particles. For this purpose, we have left the particles sedimented (this already provides an answer concerning sedimentation).

Concerning Figure 4.6b showing the particle population (in numbers), there are some points to discuss. First of all, the heavy particles curve shows 3 peaks: a first one very flattened for a particle diameter close to 15.0  $\mu m$ , a second one at 0.8  $\mu m$  and a third one at 0.2  $\mu m$ . Furthermore, the shape of the curve between 1.6  $\mu m$  and 3.0  $\mu m$  could indicate the existence



Figure 4.6: Population of starch particles, expressed in volume or number, as a function of their diameter. The cross symbols are the experimental values. The dotted lines are used to facilitate reading.

of a fourth peak. The curve for the "Lightweight particles" also shows several peaks: the first is easily identifiable at 2.6  $\mu m$ , the second at 1.2  $\mu m$  and the third at 0.2  $\mu m$ . There also appears to be a fourth peak at 6.0  $\mu m$ , also flattened.

Figure 4.6a showing the population by volume, 3 peaks are identifiable on the curve of the "Heavy particles": at 15.0  $\mu m$ , at 4.0  $\mu m$  and a smaller, almost flattened one at 1.2  $\mu m$ . The lightweight particle curve shows two peaks: the first near 4.0  $\mu m$  and the second at 1.2  $\mu m$ . Thus, it is already possible to identify three different particle sizes. It is not unimportant to find 2 peaks at identical diameters on the curves of "Heavy particles" and "Lightweight particles". This can be explained by the possibility of having small particles that have already sedimented when the heavy particles were collected.

Thus, we see the appearance of many small particles, which had been obscured by the large particles, and which were not identifiable in the volume population figure. Moreover, we note that in figure 4.6b with the population by number, the peaks, whatever the curve, are found at globally similar values:  $0.2 \ \mu m$ , between 0.8 and 1.0  $\ \mu m$  and a possible peak at 2.6  $\ \mu m$ . In order to identify all the families that may exist a mixed Gaussian model was used with Python. This allowed to identify the particle size families presented in Table 4.3.

Here the standard deviation gives an idea of the precision of the parameters that are the amplitude, the mean value and the standard deviation of the Gaussian model. It should be noted that the standard deviation of the parameters can be quite large. However, what we are particularly interested in here is the mean value obtained for each Gaussian. If we look at them carefully, we can see that 4 families of particle size appear. The first is centred on 0.5  $\mu m$ , the second on 1.1  $\mu m$ , the third on 4.2  $\mu m$  and the last is centred on 13.7  $\mu m$ . These values will be used later to study the sedimentation of particles. The SEM picture Figure 4.7 illustrates the particle size variation

Let's now look at the sedimentation of particles. Figure 4.8a shows the evolution of the height of the two experimentally observed sedimentation fronts as a function of time. The particle

| "Family"       | Amplitude      | Average value $(\mu m)$ | Standard deviation $(\mu m)$ |
|----------------|----------------|-------------------------|------------------------------|
| Heavy number 1 | $7.5 \pm 1.5$  | $0.5 \pm 0.1$           | $0.3 \pm 0.1$                |
| Heavy number 2 | $3.3 \pm 1.7$  | $1.4 \pm 0.5$           | $0.8 \pm 0.4$                |
| Heavy number 3 | $1.9 \pm 4.4$  | $12.3 \pm 10.7$         | $4.0 \pm 11.5$               |
| Heavy volume 1 | $0.4 \pm 0.4$  | $1.3 \pm 0.4$           | $0.5 {\pm} 0.4$              |
| Heavy volume 2 | $1.1 \pm 0.6$  | $3.3 \pm 0.5$           | $0.7 \pm 0.2$                |
| Heavy volume 3 | $96.6 \pm 1.8$ | $15.2 \pm 0.1$          | $3.9 \pm 0.1$                |
| Light number 1 | $2.7 \pm 1.3$  | $0.5 {\pm} 0.1$         | $0.2 \pm 0.1$                |
| Light number 2 | $6.8 \pm 1.4$  | $1.1 \pm 0.1$           | $0.2{\pm}0.1$                |
| Light number 3 | $2.9 \pm 1.9$  | $4.4 \pm 1.2$           | $1.5 \pm 1.1$                |
| Light volume 1 | $0.6{\pm}0.1$  | $1.0 \pm 0.1$           | $0.2 \pm 0.1$                |
| Light volume 2 | $64.6 \pm 5.5$ | $4.9 \pm 1.1$           | $1.4 \pm 10.3$               |

Table 4.3: Particle familly. "Heavy" or "light" are linked to the phase study, "number" or "volume" are linked to the analyse of population.



Figure 4.7: Starch particles of different sizes. Photo obtain by SEM.

density is  $1500kg \cdot m^{-3}$ . We can see that one front, called 'Heavy particles', sedimented much faster until 19000 s, then tended more slowly towards a plateau. The front called "Lightweight particles" settles much more slowly. Figure 4.8b shows the sedimentation rates as a function of time.

It can be seen that for the "Heavy particles", the sedimentation speed is divided by 10 in 1h45 min (6330 s). Indeed, these "heavy" particles become compacted at the bottom of the beaker and its height eventually tends towards a plateau. Consequently, the sedimentation speed associated with this front tends towards 0  $mm \cdot s^{-1}$ . It is possible to compare the experimental sedimentation values with the different sedimentation models proposed in the literature review (equation 2.2 and equation 2.4). It is assumed that Brownian motion is negligible in this case. By fixing the volume fraction at 14.28% (calculated from the mass fraction), the Richardson-Zaki (R-Z) law [46] is applied to the 4 particle size diameters (0.5  $\mu m$ , 1.1  $\mu m$ , 4.2  $\mu m$  and 13.7  $\mu m$ ) to determine sedimentation velocities (starch grains density is 1.5). The value of S is fixed at 4.65 using LSM methode with GRG algorithm. Table 4.4 presents the results of the



Figure 4.8: Evolution of the height of the sedimentation front and of the sedimentation rate over time.

| Diameter $(\mu m)$ | Stokes speed $(mm.s^{-1})$ | $V_{Richardson-Zaki} \ (mm.s^{-1})$ |
|--------------------|----------------------------|-------------------------------------|
| 0.5                | $6.85 \cdot 10^{-5}$       | $3.35\cdot10^{-5}$                  |
| 1.1                | $3.27 \cdot 10^{-4}$       | $1.60 \cdot 10^{-4}$                |
| 4.2                | $5.06 \cdot 10^{-3}$       | $2.47 \cdot 10^{-3}$                |
| 13.7               | $5.39 \cdot 10^{-2}$       | $2.64 \cdot 10^{-2}$                |

Table 4.4: Particle speed results from the 2 different models.

modelling obtained and also includes the velocity of the particles according to Stokes' law.

According to the literature [47], it is expected that the velocity according to the R-Z model is higher than that of the Stokes model. Indeed, the interactions between particles slow down the falling motion. This point is verified in the models. Now it is possible to compare the model and experimental values. The experimental maximum sedimentation velocities are between  $10^{-3}mm \cdot s^{-1}$  and  $4.3 \cdot 10^{-2}mm \cdot s^{-1}$ . Only the particles with diameters of 4.2  $\mu m$  and  $13.7\mu m$ are exactly in the experimental range. As for the particles with diameters of 0.5  $\mu m$  and 1.1  $\mu m$ , their velocities modelled by the Richardson-Zaki law are outside the experimentally obtained velocity range. This could be explained by a possible Brownian behaviour (which contradicts our first hypothesis) of the smallest particles, which could remain suspended in the water, above the sedimented layer. Consequently, it is possible to associate the 4.2  $\mu m$  particles with the front of the "Heavy particles".

The final point of this section to be discussed is the practical use of this information. The storage tank for the coating color is a trapezoidal shape as shown in Figure 4.9. The maximum depth is therefore 35 mm. As the storage container is never full for ease of handling, the maximum depth will be taken to be 30 mm. Considering the maximum sedimentation speed measured experimentally equal to  $4.3 \cdot 10^{-2} mm \cdot s^{-1}$ , it takes the associated sedimentation front ("heavy particles") 11 min 37s to sediment in the water and cover the 30 mm of the storage tank. This is a calculation made for a quiet environment with no agitation or coating process



Figure 4.9: Dimension of the coating tank used on the coating pilot.

taking place. This means that :

- $\rightarrow$  Sedimentation on the slopes of the tank occurs rapidly and will therefore not be negligible. In addition, it has been found experimentally that once sedimented, the starch particles form a thick paste, which is difficult to agitate.
- $\rightarrow$  The bubbling roller of the coating process is located in the centre of the tank. It creates little movement in the coating color because it only "licks" the surface of the fluid. It therefore does not allow sufficient agitation to avoid sedimentation of the starch particles in the water.

However, in this case, the suspending medium is not water but starch. Therefore the viscosity of the fluid is different. Furthermore, starch gel is a shear thinning fluid unlike water which is a Newtonian fluid. So, it is necessary to take into account the characteristic shear gradient which is  $0.3 \ s^{-1}$ . The temperature of the starch gel is fixed at 35°C. The value of  $n_{odw}$  is fixed at 0.09 and  $k_o dw$  is fixed at 104  $Pa \cdot s^{n_{odw}}$  at 35°C for a mass fraction of 20%. The viscosity obtained is therefore 836.51  $Pa \cdot s$ . Thus the sedimentation speed obtained with equation 2.5 is equal to  $6.05 \cdot 10^{-9} mm \cdot s^{-1}$ . This speed is 10,000 times lower than the sedimentation speeds in water. This also means that a particle settling in starch gel would take several days to settle. This does not take into account possible interactions between the suspending fluid and the settling particles.

These results, although derived from modelling, suggest that no sedimentation problems are to be expected when using a starch gel. However, the experiments carried out proved the contrary. Indeed, sedimentation, although slower and less important than in water, appeared in the starch gel. This can be due to three things: the dispersion of the starch particles was not done correctly in the starch gel (which was also observed). Agglomerates formed and settled faster than expected. The other possibility is the presence of physico-chemical interactions neglected here. Finally, a third possibility is that the particles could have settled on the sloping walls and then slid to the bottom of the coating color storage tank.

## 4.2 Study of the wettability and water absorption by papers

In the context of liquid absorption in porous media, the Lucas-Whasburn model is regularly quoted and used as a basis for work. Equation 4.2 expresses the liquid intake (height or mass) of a porous material as a function of time
$$h = \left(\frac{\gamma_{lg} \cdot r_{cap} \cdot \cos(\theta_c)}{2\eta}\right)^{0.5} \cdot t^{0.5}$$
(4.2)

- . As a reminder, it integrates different characteristics of the material and the fluid:
- $\rightarrow$  The surface tension of the liquid  $\gamma_{lq}$
- $\rightarrow$  The radius of the pore(s) of the material  $r_{cap}$
- $\rightarrow$  The contact angle between the fluid and the material  $\theta_c$
- $\rightarrow\,$  The viscosity of the fluid  $\eta$

If the fluid studied is the starch gel studied previously, then only its viscosity as a function of temperature is known. Finally, no information about the paper used is known. In this section, the missing characteristics of the paper and the starch gel will be determined in order to see to what extent the Lucas-Washburn model applies in this case. The modelling will be set alongside experimental results, which will be used to confirm or refute the relevance of the models used. The final objective is to obtain a relationship between the mass of liquid (water or starch gel) absorbed by the paper as a function of time.

# 4.2.1 Study of the papers wettability

This sub-section is concerned with the wettability of the papers used and the surface phenomena taking place between the paper and the water or starch gel. This will allow us to know the contact angle  $\theta_c$  existing between the paper and the water or the starch gel. Furthermore, by using other liquids the SFE of the paper will be determined. The surface tension of the starch gel will also be determined.

#### 4.2.1.1 Contact angle between paper and liquids

The static contact angle between the paper used and different liquids was measured by the sessile drop method. The aim of these measurements is to be able to trace the SFE of the paper and also to know the behaviour with water. As a reminder, the different liquids used are : Hexadecane (Hxdc), 1-Bromonaphthalene (1-Br-Napht), Glycerol (Gl-ol), Ethanol, Ethylene Glycol (Et-G) and lab-made distilled water.

The results of the contact angle measurements are shown in Figure 4.10 for the coated side of the GHDS 35 paper.

Between 10.00 and 60.00 s, the contact angles are all lower than 90°, whatever the test liquid used. The material is therefore hydrophilic. A decrease in the contact angle over time is observed which is more or less important. This can be explained by a spreading of the drop or its absorption. The signals are also noisy due to the safety ventilation and lead to high standard deviations values (represented by a light area around the main curve) especially for water, glycerol and ethylene glycol. This can be explained by the different surface roughness of the paper from one point to another and the chemical heterogeneity that the paper surface can offer.



Figure 4.10: Evolution of the contact angle between different liquids and GHDS 35 paper coated side.

The results for the uncoated side are shown in Figure 4.11.

The hexadecane curve is missing because on the uncoated side the product was wetting the paper directly and spreading. Consequently, it was not possible to obtain a measurement of the contact angle. On the other hand, it was found that the contact angle values for water are above 90°, meaning that the uncoated side of the paper is hydrophobic. This is relatively surprising. However, the supplier told us that the paper was treated to resist the wet state. This could explain the high contact angle value, as the paper fibres have been made hydrophobic (impact of SBR latex or AKD treatment).

With this techniques and the studied paper, no information are available before 3 s (at best), due to the measurement protocol. However, this is an area where it is necessary to have results. In order to have access to this information, the behaviour at very short time (< 3 s) was modelled according to models proposed by Stehr et al [138](cf. equation 4.3) and f Sarma and Vest [139](cf. equation 4.4).

$$\theta_{c} = \frac{\theta_{c,i} \cdot \theta_{c,eq}}{\theta_{c,i} + (\theta_{c,eq} - \theta_{c,i}) \cdot exp} K_{c} \cdot t \cdot \left(\frac{\theta_{c,eq}}{\theta_{c,eq} - \theta_{c,i}}\right)}$$
(4.3)

The physical meaning of  $K_c$  represents how fast the liquid spreads and penetrates into the porous structure of wood. In the present case the unknowns are  $\theta_{c,i}$  and  $K_c$ .

$$\cos(\theta_c) = \left[ 1 - \left( 1 - \frac{\cos(\theta_{c,i})}{\cos(\theta_{c,eq})} \right) \cdot exp^{-\frac{k_s \cdot \gamma_{lg}}{\eta} \cdot t} \right] \cdot \cos(\theta_{c,eq})$$
(4.4)



Figure 4.11: Evolution of the contact angle between different liquids and GHDS 35 paper uncoated side.

| $\lambda_{\mathbf{c}}(\mu \mathbf{m})$ | 10   | 50   | 80   | 250  | 400  | 500  | 800  |
|--|------|------|------|------|------|------|------|
| Roughness $(\%)$                       | 0.66 | 4.2  | 4.39 | 4.45 | 4.44 | 4.44 | 4.43 |
| Waviness (%)                           | 0.21 | 0.07 | 0.02 | 0    | 0    | 0    | 0    |

Table 4.5: Sdr (Developed interfacial area ratio) obtained for different cut-off values  $\lambda_c$ , in the case of roughness or waviness. The GHDS 35 coated face is studied here.

The model of Sarma has the advantage of taking into account two parameters of the test liquid: its viscosity and its surface tension. However it is not perfect to predict behaviour at short time contact [27].

A contact angle correction taking into account the roughness of the paper was also considered with the Wenzel equation presented in the literature review. The Sdr's were thus determined. Table 4.5 presents the results. The Sdr measurements were performed for different cut-off filter values  $\lambda_c$ , and at the scales of roughness and waviness. The scale to be taken into account is the roughness. To choose the right cut-off value, the RSM has been measured and is equal to 39.81  $\mu m$ . The Sdr is thus equal to 4.45 % and the  $r_w=1.0445$ . The same method was applied for the uncoated face, and in this case Sdr = 2.44 %.  $r_w=1.0244$  [66].

According to the Wenzel model, the higher the value of Sdr, the more complex the surface under consideration is. In this case, one would expect the coated surface to have less roughness than the uncoated surface. However, this is not the case. In order to understand this result, a cross-sectional view of the GHDS 35 paper was taken with a SEM (see Figure 4.12). It allows us to see that the coated layer has a certain undulation and that the pigments seem to create asperities (at very small scales). This could explain the difference between Sdr value. However, in needs more investigations.

Tables 4.6 and 4.7 present respectively the results of the modelling for the Stehr and Sarma models, with and without the Wenzel correction. The models were performed for the coated



Figure 4.12: View of the GHDS 35 paper section at different magnifications (SEM).

and uncoated sides of the GHDS 35 paper.

The results from the two models model the experimental data more or less well. First of all, in the case of hexadecane coated side, the Wenzel correction leads to consider a complete wetting of the paper because  $cos(\theta_c^*) > 1$ . Moreover, for the uncoated side, the wetting of the paper was experimentally visible and no data could be recovered. Thus, only the behaviour for the coated side, without Wenzel correction, could be modelled. Considering the  $R^2$  and the sum of the squared deviations  $\Sigma r^2$ , the Stehr model best models the behaviour of hexadecane over the experimental range.

In the case of water, the behaviour on the uncoated side could not be modelled. Regarding the coated side, whatever the models (Stehr or Sarma) and the use or not of the Wenzel correction, the  $R^2 = 0.98$ . The discrimination criterion that can be used is the sum of the squared deviations linked to the use of the LSM method. Thus the lowest sum of squared deviations is obtained for the Sarma method, without Wenzel correction.

The behaviour of 1-bromonaphthalene is poorly modelled with or without contact angle correction and whatever the model for the coated side. However, for the uncoated side, the prediction quality of the models is much better. The Stehr model, without Wenzel correction, will be considered.

Finally glycerol and ethylene glycol are correctly modelled. For the coated face, the values obtained with the Stehr model without Wenzel correction will be used. For the uncoated side, the quality of the prediction is lower. Thus, for glycerol, the Sarma model without Wenzel correction will be kept for the uncoated side. For ethylene glycol, the Stehr model without Wenzel correction will be kept.

From this study of the contact angle between the two sides of the GHDS 35 paper and different liquids, two points are to be retained:

- → The models and predictions of the contact angles are not always good (especially for the uncoated side of the paper); the SFE of each side will be calculated from the values at 6.35 s. A value at 0 s will also be calculated from the predicted initial contact angle values, bearing in mind that the quality of the model predictions is not always perfect.
- $\rightarrow\,$  The contact angle between the water and the coated side will be taken as 74.52  $\pm 5.8$  ° at

| Coated side | Sdr | Parameters     | Water                | Hxdc                 | Gl-ol                | Et-G                 | 1-Br-Napht           |
|-------------|-----|----------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Yes         | No  | $K_c$          | $1.01 \cdot 10^{-2}$ | $5.17 \cdot 10^{-3}$ | $1.69 \cdot 10^{-2}$ | $2.34 \cdot 10^{-2}$ | $1.90 \cdot 10^{-3}$ |
| Yes         | No  | $	heta_{c,i}$  | 78.14                | 11.70                | 88.72                | 57.56                | 26.11                |
| Yes         | No  | $\Sigma r^2$   | 88.71                | 3.92                 | 139.49               | 399.34               | 19.45                |
| Yes         | No  | $\mathbf{R}^2$ | 0.98                 | 0.87                 | 0.99                 | 0.94                 | 0.72                 |
| Yes         | Yes | $K_c$          | $1.08 \cdot 10^{-2}$ | n.a                  | $1.79 \cdot 10^{-2}$ | $2.66 \cdot 10^{-2}$ | $3.31 \cdot 10^{-3}$ |
| Yes         | Yes | $	heta_{c,i}$  | 77.65                | n.a                  | 88.75                | 56.11                | 20.30                |
| Yes         | Yes | $\Sigma r^2$   | 98.42                | n.a                  | 150.92               | 461.84               | 34.32                |
| Yes         | Yes | $\mathbf{R}^2$ | 0.98                 | n.a                  | 0.99                 | 0.94                 | 0.72                 |
| No          | No  | $K_c$          | $9.37 \cdot 10^{-5}$ | n.a                  | $4.72 \cdot 10^{-3}$ | $6.60 \cdot 10^{-3}$ | $1.92 \cdot 10^{-2}$ |
| No          | No  | $	heta_{c,i}$  | 97.22                | n                    | 77.42                | 70.05                | 34.61                |
| No          | No  | $\Sigma r^2$   | 400.86               | n.a                  | 2500.03              | 301.13               | 160.33               |
| No          | No  | $\mathbf{R}^2$ | 0.03                 | n.a                  | 0.71                 | 0.79                 | 0.96                 |
| No          | Yes | $K_c$          | $9.59 \cdot 10^{-5}$ | n.a                  | $4.72 \cdot 10^{-3}$ | $6.85 \cdot 10^{-3}$ | $2.29 \cdot 10^{-2}$ |
| No          | Yes | $	heta_{c,i}$  | 97.40                | n.a                  | 77.42                | 69.54                | 32.59                |
| No          | Yes | $\Sigma r^2$   | 420.98               | n.a                  | 2678.37              | 318.15               | 185.05               |
| No          | Yes | $\mathbf{R}^2$ | 0.03                 | n.a                  | 0.70                 | 0.79                 | 0.96                 |

Table 4.6: Parameters obtained from the modelling using the Stehr model. The first column informs about the GHDS 35 paper side tested (coated or uncoated). The second column indicates if the Wenzel correction is used or not.  $\theta_{c,i}$  is expressed in ° and  $K_c$  in  $s^{-1}$ .

| Coated side | Sdr | Parameters    | Water                | Hxdc                 | Gl-ol                | Et-G                 | 1-Br-Napht           |
|-------------|-----|---------------|----------------------|----------------------|----------------------|----------------------|----------------------|
| Yes         | No  | $k_s$         | $8.99 \cdot 10^{-4}$ | $5.21 \cdot 10^{-3}$ | 1.57                 | $2.68 \cdot 10^{-2}$ | $5.50 \cdot 10^{-3}$ |
| Yes         | No  | $	heta_{c,i}$ | 77.59                | 11.68                | 87.38                | 56.15                | 26.10                |
| Yes         | No  | $\Sigma r^2$  | 85.16                | 4.06                 | 174.70               | 466.98               | 19.67                |
| Yes         | No  | $R^2$         | 0.98                 | 0.86                 | 0.98                 | 0.93                 | 0.72                 |
| Yes         | Yes | $k_s$         | $8.99 \cdot 10^{-4}$ | n.a                  | 1.57                 | $2.67 \cdot 10^{-2}$ | $5.44 \cdot 10^{-3}$ |
| Yes         | Yes | $	heta_{c,i}$ | 77.03                | n.a                  | 87.25                | 54.36                | 20.27                |
| Yes         | Yes | $\Sigma r^2$  | 94.15                | n.a                  | 191.47               | 552.93               | 35.00                |
| Yes         | Yes | $R^2$         | 0.98                 | n                    | 0.98                 | 0.93                 | 0.72                 |
| No          | No  | $k_s$         | $6.18 \cdot 10^{-5}$ | n.a                  | $5.16 \cdot 10^{-1}$ | $2.82 \cdot 10^{-2}$ | $8.68 \cdot 10^{-3}$ |
| No          | No  | $	heta_{c,i}$ | 97.22                | n.a                  | 77.33                | 69.89                | 36.40                |
| No          | No  | $\Sigma r^2$  | 400.86               | n.a                  | 2471.50              | 309.36               | 199.27               |
| No          | No  | $R^2$         | 0.03                 | n                    | 0.71                 | 0.78                 | 0.94                 |
| No          | Yes | $k_s$         | $6.18 \cdot 10^{-5}$ | n                    | $5.62 \cdot 10^{-1}$ | $2.82 \cdot 10^{-2}$ | $8.59 \cdot 10^{-3}$ |
| No          | Yes | $	heta_{c,i}$ | 97.40                | n.a                  | 77.14                | 69.37                | 34.36                |
| No          | Yes | $\Sigma r^2$  | 420.98               | n.a                  | 2647.63              | 327.22               | 244.28               |
| No          | Yes | $R^2$         | 0.03                 | n.a                  | 0.71                 | 0.78                 | 0.94                 |

Table 4.7: Parameters obtained from the modelling using the Sarma model. The first column informs about the GHDS 35 paper side tested (coated or uncoated). The second column indicates if the Wenzel correction is used or not.  $\theta_{c,i}$  is expressed n ° and  $k_s$  in  $m^{-1}$ 

6.35 s and  $77.59^{\circ}$  at 0 s. For the uncoated face, the contact angle will be taken to be 98.22  $\pm 3.71$  at 6.35 s. 6.35s is choose because there is at least one contact angle value for all faces and liquids at that given time.

#### 4.2.1.2 Surface free energy of paper

In order to calculate the SFEs for each side of the paper, the contact angles had to be known. This is now the case. Thus, for each side of the paper, two SFE will be calculated. The first will be calculated using the contact angle at 0 s predicted by the models. The second will be calculated at 6.35 s using the experimental values. Figure 4.13 presents the results obtained using the OWRK method.



Figure 4.13:  $\Omega$  versus  $\Pi$  for the coated and uncoated side of GHDS 35, at different time.

where  $\Omega = \frac{\gamma_{lg} \cdot [1 + \cos(\theta_c)]}{2\sqrt{\gamma_{lg}^d}}$  and  $\Pi = \sqrt{\frac{\gamma_{lg}^p}{\gamma_{lg}^d}}$ . Table 4.8 sum up the results. First of all, it is

possible to note the very variable R<sup>2</sup> values on Figure 4.13, some regressions being very correct, others very poor. This is quite common for paper, which is a very homogeneous material. Furthermore, the impact of the CD or MD directions was not taken into account. This leads to differences in the contact angle depending on the position of the observer during the measurement

| Component                      | Coated - 0s | Coated - 6.35s | Uncoated - 0s | Uncoated - 6.35s |
|--------------------------------|-------------|----------------|---------------|------------------|
| <b>Polar</b> $mJ \cdot m^{-2}$ | 7.73        | 8.41           | 0.16          | 1.37             |
| Dispersive $mJ \cdot m^{-2}$   | 25          | 23.04          | 36.6          | 30.25            |
| <b>SFE</b> $mJ \cdot m^{-2}$   | 32.73       | 31.45          | 36.76         | 31.62            |

Table 4.8: Surface Free Energy (SFE) results of GHDS 35 paper for the 2 faces, at two different time.



Figure 4.14: FTIR spectrum of the GHDS 35 paper sides and bleached cellulose (for reference).

[37]. The SFEs of the coated and uncoated sides are between 31.45 (6.35 s) and 36.76  $mJ \cdot m^{-2}$  (0 s). The SFE of cellulose is about 60  $mJ \cdot m^{-2}$  [140].

The values of the typical latex, calcium carbonate and kaolin coatings are between 30 and  $35 \ mJ \cdot m^{-2}$  [141] The values measured on the coated side are therefore those for coating. For the uncoated side, values closer to those of cellulose were expected. Two hypotheses can be formulated to explain these SFE values: a migration of the coating color from one side to the other but it could be seen with SEM: it is not the case. The other possibility is that fibers were treated, making them more hydrophobic, by increasing the dispersive component on their surface. To see if this second hypothesis could be true, FTIR measurement were done on the two sides of the GHDS 35 paper (Figure 4.14).

The orange and grey cruves are those of the GHDS 35 paper. It can be seen that they overlap almost perfectly (small variations in intensity). This could suggest that, despite the coating applied by the manufacturer, the two sides have more similarities than we think. Although further investigations are required, this superposition of the spectra could indirectly explain the similarity of the SFE of the two sides of the GHDS 35 paper trough a fiber treatment.

In any case, the SFE on the coated and uncoated sides are mostly dispersive and not very polar. In the case of water, this could mean that a drop of water does not spread on the paper faces. This was observed in particular for the uncoated side, and to a lesser extent for the coated side.

# 4.2.1.3 Surface tension of starch gel

The starch gel could not be tested by the sessile drop method. Indeed, the system present in the laboratory does not allow to heat the syringe in which the liquid to be tested is located. At room temperature, after cooking, the starch gel has retrograded and is very viscous. It is therefore very difficult or impossible to make a drop with this fluid without heating. So, the results from another method are presented here as a solution to determine the contact angle between the paper and the starch gel. The surface tension of a starch gel at 20% and 40°C was measured and illustrated with Figure 4.15.



Figure 4.15: Evolution of the starch gel (20%wt) surface tension over time at 40°C. A, B, C and D are different tests made in same conditions.

A great disparity can be seen in the results obtained over time and between the tests themselves. First of all, for test C, the increase in the surface tension value measured is explained by the formation of a skin on the gel during the measurement. Although the gel was heated to  $40^{\circ}$ C, it was not possible to stir it (this would have disturbed the measurement). As a result, the retrogradation of the starch took place on the surface (air colder than the gel), thus creating a skin on the surface which disturbed the measurement. The same phenomenon is found, to a lesser extent, in tests B and D. In fact, only the first test A does not have this phenomenon. Indeed, from a temporal point of view, it was the first one, and the effects of the retrogradation were still minimal. The surface tension value is not stable but over the duration of the test it was calculated at  $\gamma_{lq} = 59 \pm 1.33 \ mN \cdot m^{-1}$ .

In order to know the properties of the starch with the coated and uncoated sides of the paper, the Dynamic Contact Angle (DCA) technique was used. In this case, only the first value of advancing contact angle and receding contact angle are of interest. The measurement results are presented Table 4.9/

There is a statistical difference between the advancing angle and receding angle for both sides. During the first contact, the starch gel at 20% and 40°C does not wet the paper, whatever

| Face     | ACA    | std  | RCA   | SD   |
|----------|--------|------|-------|------|
| Uncoated | 106.37 | 0.87 | 48.10 | 3.78 |
| Coated   | 94.89  | 5.44 | 36.37 | 2.94 |

Table 4.9: Advancing and receding contact angle between starch gel and GHDS 35 paper, obtained with DCA. ACA is Advancing Contact Angle, RCA is Receding Contact Angle and SD is the Standard Deviation.



Figure 4.16: Differential intrusion of mercury as a of the GHDS 35 paper pores diameter.

the side. When the sample is removed from the starch gel, wetting occurs.

## 4.2.2 Papers water absorption analysis

The contact angle between the water (or starch gel) and the paper faces is now known; so is the surface tension of the starch gel. The missing data of the problem is the pore size of the paper. In this sub-section, this will be measured, and subsequently, 3 experimental methods will be presented to measure the water absorption by the paper.

## 4.2.2.1 Paper pore sizes

The pore size of the paper was measured by mercury porosimeter. The results of the two trials carried out are shown in Figure 4.16.

It is possible to identify 3 main pore size families: 0.05  $\mu m$ , 0.78  $\mu m$  and 4.40  $\mu m$ . In addition, the porosity was measured and for "sample 1" it is 35.15% and for "sample 2" 31.58%. This method does not allow to differentiate the porosity of the kaolin, calcium carbonate layer and the fibrous structure. Furthermore, the pressure applied during the measurement (up to 200 MPa) can crush the paper and modify its original structure. These are points to keep in



Figure 4.17: Absorptiveness of paper over time obtained trough the Cobb method.Water is in contact with the coated side of GHDS 35 paper.

mind for the rest of this document.

# 4.2.2.2 First approach: Cobb method (ISO 532-5)

The first method used to determine the amount of water that can be absorbed into a paper is the Cobb method (according to ISO 535-5). The experimental results are shown in Figure 4.17, representing the absorptiveness of paper as a function of time and the modelled results. It is first possible to notice a rapid increase in the absorptiveness of the paper before it tends towards a plateau. This behaviour strongly resembles the index response of a first or second order system in the aperiodic or critical aperiodic regime (damping factor greater than or equal to 1). Thus, the two models tested on the experimental values shown in Figure 4.17 are a first order model (equation 4.5) and a second order model (equation 4.6).

$$A_s(t) = A_{s,eq} \left( 1 - exp^{\frac{-t}{\tau_2}} \right)$$
(4.5)

$$A_s(t) = A_{s,eq} \cdot \left[ 1 - \frac{1}{\tau_1 - \tau_2} \cdot \left( \tau_1 \cdot exp \frac{-t}{\tau_1} - \tau_2 \cdot exp \frac{-t}{\tau_2} \right) \right]$$
(4.6)

where  $A_{s,eq}$  is the plateau value of the aborptiveness,  $\tau_2$  a time constant and  $\tau_1$  is another time constant.

In order to visualise the quality of the modelling a parity diagram is shown in Figure 4.18. The modelling was performed with the LSM method and a solver using the GRG algorithm. The variables of the model as well as the  $R^2$  are summarised in Table 4.10.

The first remarkable point is the similar value of the plateau K whatever the model. The second remarkable point is the proximity of the time constant  $\tau_2$  in the case of the two models.



Figure 4.18: Parity plot comparing the modelled and experimental values obtained with the Cobb method. Water is in contact with the coated side of GHDS 35 paper.

| Model        | $A_{s,eq}(g_{water} \cdot m_{paper}^2)$ | $	au_1$ (s) | $	au_2$ (s) | $\mathbb{R}^2$ |
|--------------|---|-------------|-------------|----------------|
| First order  | 21.69                                   | -           | 18.90       | 0.98           |
| Second order | 21.02                                   | < 0.01      | 17.58       | 0.97           |

Table 4.10: Parameters obtained after the modelling of the paper absorptiveness over time, during Cobb test. Water is in contact with the coated side of GHDS 35 paper.

Finally the third remarkable point is the very low value of  $\tau_1$  compared to  $\tau_2$ . The problem is that no Cobb value can be measured for a time less than 10 s, otherwise it will be very inaccurate. Finally the Cobb values will be modelled by a first order model with  $A_{s,eq} = 21.69$  $(g_{water} \cdot m_{paper}^2)$  and  $\tau_2 = 18.90$  s.

The Lucas - Washburn model is convenient for modelling absorption at short times or for infinitely long media with an unlimited amount of liquid. However, in the case of the Cobb test, as mentioned later, the lack of information below 10 s would make the quality of the LW model poor. It is therefore necessary to have access to very short time information.

#### 4.2.2.3 Second approach: DPM

The second method used is the DPM method. As a reminder, this method measures the evolution of the intensity of an ultrasound signal, passing through a paper in water, over time. Figure 4.19 shows the results with the GHDS 35 paper, for the coated or uncoated side facing the water, and for the flat or grooved surface. A zoom on the area of the first two seconds is proposed each time to better visualise the behaviour at very short times.

For all curves, a rise in signal intensity is observed before the long decrease in signal intensity. According to Waldner and Hirn [75], a signal decrease is caused by entrapped, resonating air bubbles. However, paper where capillary penetration is not possible because they are heavily sized ( $\theta_c > 90$ ) can still exhibit a decrease in signal transmission. Air bubbles cannot be the



Figure 4.19: Signal intensity overs time curves obtained from DPM measurement.Coated and uncoated refereed to the GHDS 35 paper side facing water. Grooved and flat refereed to the sample holder surface.

| Parameters    | Coated - flat | Uncoated - flat | Coated - grooved | Uncoated - grooved |
|---------------|---------------|-----------------|------------------|--------------------|
| $t_{95}$ (s)  | 1.00          | 0.76            | 1.44             | 1.12               |
| slop (%/s)    | -4.87         | -6.60           | -4.44            | -4.87              |
| $t_{max}$ (s) | 0.16          | 0.16            | 0.04             | 0.28               |

Table 4.11: Characteristics parameters measured with DPM method. Coated and uncoated refereed to the GHDS 35 paper side facing water. Grooved and flat refereed to the sample holder surface.

reason for the decrease in this case, as there is no liquid entering the substrate pores. To verify this point, it is sufficient to compare the results for a flat and grooved substrate. In the case of the flat holder, air cannot escape. In the case of the grooved holder, air can escape thanks to the grooves. If air was the reason for this decrease in signal strength, then the curves would be different depending on the sample holder. However, this is not the case: in both cases, an increase and then a decrease in signal strength is observed.

To quote Waldner and Hirn's excellent explanation, "air bubbles cannot be the reason for a signal decrease if capillary penetration is not possible, since there is no liquid front advancing through the sample. However, as mentioned earlier, water can still enter the sample via vapor and surface diffusion, as well as penetration within the paper fibers (which are porous). In that way, water will diffuse into the fibers, filling voids within the fibers, causing them to swell. The filling of the voids should lead to an increase in the speed of sound in the fibers. That would lead consequently to an increased reflection coefficient for air-fiber boundaries. As the fibers are still surrounded by air, this would explain the slowly decreasing ultrasound signal. [75].

This would confirm the hypothesis formulated earlier concerning the treatment of the fibres/paper, explaining also the contact angle value between water and the uncoated side of the paper. Furthermore, it is still possible to measure some parameters with these measurements like the  $t_{max}$ , the  $t_{95}$  and the slope of the signal intensity decay. These results are summarised in Table 4.11.

The standard deviations are significant and not negligible due to the heterogeneity of GHDS 35 paper. Therefore, when the  $t_{max}$  and  $t_{95}$  times are determined by reading the bound intensity value, the latter is subject to statistical error. Consequently, the characteristic times are also subject to statistical error. Therefore, it is difficult to tell the difference between the different  $t_{max}$ . The same is true for the  $t_{95}$  and the slopes, although for this last parameter, the uncoated flat samples seem to show a much faster decrease than the samples.

A statistical difference appears at a time greater than 15 s between the coated and uncoated faces, independently of the geometry of the sample holder (flat or grooved). Indeed, when the uncoated side is exposed to water (coated side stuck to the sample holder), we notice that, for a given time greater than 15 s, the decrease in signal is less.

This method is very interesting for comparing the water behaviour of different papers. However, it does not give any information about the amount of water a paper can absorb per unit of volume, surface or mass. A third method is therefore necessary to know the water absorption at short time in a quantitative way.



Figure 4.20: GHDS 35 paper water absorption versus time. 50 stacks of paper are used, the coated side facing the water.



Figure 4.21: GHDS 35 paper water absorption versus  $\sqrt{t}$ . 50 stacks of paper are used, the coated side facing the water.

# 4.2.2.4 Third approach: Paper discs stack

The last method presented to measure the amount of water absorbed by a paper over time is new. Figure 4.20 shows the average of the experimental results obtained for 50 stacks of paper, coated face down. Further tests were carried out and are presented in Appendix B. The other results in the appendix raise many questions, especially about the repeatability of the measurement, which may be related to the construction of the paper column.

In this case, the standard deviation obtained is not negligible. It is also possible to notice a semblance of linear behaviour between 0 and 2 s. Another way of representing this curve is to plot the mass as a function of  $\sqrt{t}$  according to the LW model. The evolution of the mass is linear as a function of  $\sqrt{t}$  and the slope is related to different characteristic of the fluid and the paper (cf. Figure 4.21).

In Figure 4.21, a regression line has also been drawn. The coefficient of determination is 0.968. However, it should be noted that the regression line greatly overestimates the experimental data

| Name of the model | Equation of the model  |  |  |  |
|-------------------|--|--|--|--|
| L-W               | $m_{wa}(t) = \left(\frac{c \cdot \gamma_{lg} \cdot r_{cap} \cdot cos(\theta_c)}{2\eta}\right)^{0.5} \cdot t^{0.5}$ |  |  |  |
| First order model | $m_{wa}(t) = m_{wa,eq} \left( 1 - exp^{\frac{-t}{\tau_a}} \right)$   |  |  |  |
| Power law model   | $m_{wa}(t) = \lambda_a t^{n_a}$  |  |  |  |

Table 4.12: The 3 different models used to modelled experimental data obtained with the paper disc stacking method.

for  $\sqrt{t} < 1.200 \ s^{0.5}$ . This non-linear relationship at the beginning of the absorption is also cited in the literature [142]. Moreover, at the beginning of the absorption a linear relation between the absorbed mass and time would be observed, as evoked by Quéré [74], for whom this would be due to a variable contact angle [74]; this linear relation was noticed in Figure 4.20 and also cited in the literature review. Experimental values have been modelled via three different models presented in Table 4.12.

The modelling was carried out between 0 and 10 s. The results of the modelling are presented in Table 4.13

| L-W  | First order               | Power law              |
|--|---------------------------|------------------------|
| c $(m^5) = 7.40 \ 10^{-12}$                    | $m_{wa,eq} = 0.029$       | $\lambda_a = 0.0063$   |
| $\rho~(kg\cdot m^3)=1000$                      | $\tau_a = 4.900$          | $n_a = 0.6376$         |
| $\gamma_{lg} \ [0.001 N \cdot m^{-1}] = 0.072$ | $\Sigma r^2 = 0.00000438$ | $\Sigma r^2 = 0.00007$ |
| $\theta_c = 75^{\circ}$                        | $R^2 = 0.999$             | $R^2 = 0.988$          |
| $\eta \ Pa \cdot s^{-1} = 0.001$               | -                         | -                      |
| $\Sigma r^2 = 1.64 \ 10^{-4}$                  | -                         | -                      |
| $R^2 = 0.993$                                  | -                         | -                      |

Table 4.13: The modelled parameters obtained from the 3 different models used.  $\rho$ ,  $\gamma_{lg}$ ,  $\theta_c$ ,  $\eta$  are input values.

The models are generally very good if we look at the  $R^2$ . However, Figure 4.22 showing the parity diagrams and comparing the experimental and modelled values provides additional information. Indeed, it is possible to observe the global overestimation of the models for the low experimental values (i.e. values at short time). However, this overestimation does not have the same intensity and the first order model is the one that most closely matches the x = y curve. This model gives two pieces of information: a characteristic time  $\tau$  and a mass related to the plateau K.  $\tau$  corresponds to the time to reach 63% of the maximum value and  $3 \cdot \tau$  corresponds to the time necessary to reach 95% of the maximum value.

The same method and models were used for the uncoated side of the paper. Figure 4.23 shows the average of the experimental results obtained for 50 stacks of paper, uncoated side down. Note the linear behaviour between 0 and 1 of the mass as a function of time.

Figure 4.24 is the same as Figure 4.23 but as a function of  $\sqrt{t}$ . The linear behaviour for  $t^{0.5} > 1s^{0.5}$  for the mass as a function of the square root of the time can be seen.

The experimental results were compared with the same 3 models as the recumbent face (LW,



Figure 4.22: Parity plot comparing the modelled and experimental values obtained with the paper discs stacking method for the GHDS 35 coated side down.



Figure 4.23: GHDS 35 paper water absorption versus time. 50 stacks of paper are used, the uncoated side facing the water.



Figure 4.24: GHDS 35 paper water absorption versus  $\sqrt{t}$ . 50 stacks of paper are used, the coated side facing the water.



Figure 4.25: Parity plot comparing the modelled and experimental values obtained with the paper discs stacking method for the uncoated face.

| L-W  | First order               | Power law              |
|--|---------------------------|------------------------|
| c $(m^5) = 7.40 \ 10^{-12}$                    | $m_{wa,eq} = 0.014$       | $\lambda_a = 0.0070$   |
| $\rho \ (kg \cdot m^3) = 1000$                 | $	au_{a} = 1.717$         | $n_a = 0.3526$         |
| $\gamma_{lv} \ (0.001 N \cdot m^{-1}) = 0.072$ | $\Sigma r^2 = 0.00003718$ | $\Sigma r^2 = 0.00007$ |
| $\theta_c = 75$                                | $R^2 = 0.970$             | $R^2 = 0.962$          |
| $\eta \ Pa \cdot s^{-1} = 0.001$               |                           |                        |
| $\Sigma r^2 = 3.97 \ 10^2$                     |                           |                        |
| $R^2 = 0.926$                                  |                           |                        |

first order and power law) (cf Figure 4.25. The results are presented in Table 4.14.

Table 4.14: The modelled parameters obtained from the 3 different models used  $\rho$ ,  $\gamma_{lg}$ ,  $\theta_c$ ,  $\eta$ are input values

Overall the quality of the models is less good. The most convincing model remains the first order model with a lower  $\tau$  and K than before. It is not impossible that the absorption of water by the uncoated face is slower in this direction: lower contact angle of the surface, creating a brake on wettability, and the latex layer slowing down the progression in this direction.

The last point to be discussed concerns the linear part of the curve. The question is: up to what time, the evolution of the mass can be considered linear as a function of time. For this purpose, the experimental results for the face (coated and uncoated) were modelled as linear function, for different durations between 0 and 10 s. For each range of duration, the  $R^2$  was calculated. Figure 4.26a shows this for the coated side, and Figure 4.26b for the uncoated side.

However, this method, although very interesting, raises questions about the repeatability of the measurements. A major point for improvement would be the construction of the paper column. Short-cut phenomena and privileged passages could be at the origin of these important standard deviations. Moreover, the very small size of the discs (15 mm) poses a problem for handling. Finally, the cylinder-piston pair is not designed for this type of handling and is not perfectly sealed.



Figure 4.26: Evolution of the mass of water absorbed by the paper over time; and the coefficient of determination for a linear model applied to the mass, as a function of time. The GHDS 35 paper is used with the coated and uncoated sides facing the water.

# 4.3 Conclusion

In the study of the coating color it was shown that the cooking of the starch is an important point in the process, as this impacts on the rheology of the sauce. It has been proved that the starch gel has a shear thinning behaviour (Ostwald-de-Waele law) and that its behaviour also depends on the temperature at which it is used (Eyring law), which is in line with the literature. The sedimentation of starch particles has also been studied in water and quickly observed in starch gel. The particles have a significant sedimentation speed in water when considering the dimensions of the sauce storage tank on the pilot: it needs 12 minutes for the heaviest particles to sediment in the storage tank. For the coating sauce, the models calculated a sedimentation rate 10,000 times lower than in water. However, experimentally, sedimentation and aggregation of the starch particles in the starch gel was observed. A recirculation of the coating sauce should be installed to avoid this kind of sedimentation phenomenon.

In the a second time, the wettability and water absorption of GHDS 35 have been discussed. The SFEs of the paper showed larger dispersive components than the polar components on both sides. This possibly means that the fibres were treated with wet strength, thus explaining the high contact angles between water and paper on all sides. The study of water absorption by the paper was carried out using three methods: the COBB method, the DPM method, and the paper discs stacking method. The Cobb method showed a first order water absorption behaviour of the paper. The paper disc stacking method is a new method proposed to follow water absorption in paper at short times. A first order model seems to be the one that best models the observed behaviour. However, very large standard deviation of the experimental data should be considered. Then comes the need to optimize the protocol and the measurement apparatus. Finally, the DPM technique has shown a particular behaviour of the coated papers looking at an AKD treated paper. This confirms the hypothesis put forward following the determination of the SFE.

# Chapter

# The wrinkling phenomena of paper

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Before being able to make the wrinkles disappear, it is necessary to be able to make them appear and to understand the underlying mechanical phenomena. This chapter will therefore focus on the appearance of wrinkles on a web paper. This has been described in the literature review and two central equations have been isolated. The first one puts forward a misalignment angle of a roll (equation 5.1). The second allows us to determine a critical strip tension above which wrinkles can appear (equation 5.2).

$$\theta_{cr} = \frac{6\tau_{cr}a^2}{E_x b^2} \tag{5.1}$$

$$T_{cr} = \frac{2t_f^2}{\mu b} \sqrt{\frac{E_x \cdot E_z}{3\left(1 - \nu_{xz}\nu_{zx}\right)}}$$
(5.2)



Figure 5.1: 3D topographic view of speckled GHDS 35 paper obtained with the AIF set up.

Before using equation 5.1 and equation 5.2 it is necessary to observe the wrinkling phenomenon and to collect experimental data. It will be performed trough a multi scale approach, using in-situ and ex-situ experiments. The observations will be made during the pilot and tensile tests: this is the first observation time (in-situ), where the formation of wrinkles will be observed. The second observation phase will be carried out on wrinkles that have already formed (ex-situ) on a macroscopic and microscopic scales. This will be the subject of the first part of this chapter. The second part will allow the modelling of the wrinkle phenomenon and the comparison of the modelling with the experimental values. In order to carry out, it is necessary to know the paper properties. These will also be presented and discussed in the second part of this chapter, separating the "dry" and "wet" properties of the papers.

# 5.1 Observation of the wrinkles phenomena

As explained, this first section will focus on the observation of wrinkles and the recovery of experimental data to feed the different models in the literature.

#### 5.1.1 In-situ observations

## 5.1.1.1 Tensile test and tensile buckling

The purpose of the tensile tests presented here is to see to what extent the wrinkling phenomenon can be described on a microscopic scale and whether it can be reproduced outside of the coating pilot. The measurements were carried out according following MD and CD, on GHDS 35 paper. To follow the paper displacement over time with the D.I.C, it was necessary to speckle the paper samples. A surface reconstruction of the speckle is shown in Figure 5.1, obtained with the AIF (Alicona Infinite Focus). In Appendix C, an example of speckle pattern is presented.

It can be seen from the height scale that the printed ink has a height of up to 4  $\mu m$ . The GHDS 35 paper has a thickness of 33  $\pm 1 \ \mu m$ . The printed ink is therefore up to 12% of the original height of the paper. This is significant. In addition, this printing can cause mechanical



Figure 5.2: Evolution of the stress versus time during a tensile test in MD. The associated pictures correspond to the out of plane displacement of the sample at a given time (speed: 5  $mm \cdot min^{-1}$ ).

discontinuity and variation in local mechanical properties. However, this is the best technique found for using D.I.C. on paper samples. This point should be kept in mind for the rest of this chapter.

The results obtained during the tests are shown in Figure 5.2 for MD and Figure 5.3 for CD. As a reminder, the dimensions of the samples are 15 mm wide by 100 mm long. The ratio  $\beta = \frac{width}{lenath}$  is therefore 0.15. Other results are presented in Appendix D.

Figure 5.2 shows the evolution of the tensile stress over time on a MD sample. The first few seconds of the test show zero stress: the sample was relaxed. Once the specimen is under tension, the stress evolves until the specimen breaks at 76 MPa. A linear zone can be distinguished, comparable to the elastic zone of the material between 1.5 and 5 s. Beyond that, the behaviour of the material can be considered as plastic. For 4 pairs of values (time; stress), it was possible to reconstruct, with the 7D and Matlab software, the evolution of the out-of-plane displacements w(x, z) over time. The more red an area is, the greater the out-of-plane deformation. At 5 s, the out-of-plane deformation is very small, and may be related to measurement/reconstruction artefacts. At 10 s, it starts to appear more clearly in the centre of the sample. At 15 s, a narrow yellow band appears and the out-of-plane deformation is about 0.10 mm. At 20 s, just before breakage, an orange and yellow band appears clearly on the reconstruction. The out-of-plane deformation is close to 0.15 mm.

It is possible to describe the same phenomenon on CD specimens (cf. Figure 5.3). In order to gain more information on the buckling phenomenon, the test presented Figure 5.3 was performed at  $2m \cdot min^{-1}$ . The first few seconds of the test allow the sample to be stretched, which is why no stresses appear. At 30 s of testing, a central area begins to appears. At 90 s, the central zone



Figure 5.3: Evolution of the stress versus time during a tensile test in CD. The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $2 mm \cdot min^{-1}$ ).

buckles more strongly and the out-of-plane strain is close to 0.10 mm. At 160 s, the central area that was buckling showed 2 orange stripes. During the test, it was possible to distinguish not one but two sharp edges. Finally, just before breakage, at 190 s, the two bands are separately identifiable, with one having an out-of-plane deformation greater than 0.15 mm.

Thus, it is indeed possible to detect out-of-plane deformations, related to buckling, during a tensile test. As buckling is an instability phenomenon, it is "all or nothing". Using Figures 5.2 and 5.3 it is possible to link out-of-plane deformation and tensile stress. The only point to be determined is: "at what value of out-of-plane displacement is it possible to consider buckling ?" It is considered that there is buckling if the out-of-plane displacements w(x, z) respect the inequality equation 5.3.

$$w(x,z) > 2 \cdot t_f \tag{5.3}$$

In the present case, if the out-of-plane displacements are greater than 0.06 mm, buckling is considered. Using the results presented in Figure 5.2 and Figure 5.3, as well as those presented in Appendix D, it is possible to present Figure 5.4, linking out-of-plane test displacement, tensile stress and number of strips. 3 clusters are clearly identifiable: "MD", "CD (1 strip)" and "CD (2 strips)".

Zhu et al [97] found the same phenomenon but much more pronounced on very orthotropic polypropylene films. However, buckling does occur in the tensile tests, regardless of the direction tested (CD or MD). In the present case, it is found that the stress to form a strip following MD is very close to the stress at break. This suggests that in order to generate two strips, the stress



Figure 5.4: Tensile stress linked to out of plane displacement obtained during tensile tests of speckle GHDS 35 paper.



Figure 5.5: The evolution of the wrinkles formation with GHDS 35 paper, on the coating pilot in function of the paper state, the misalignment angle and the web tension.

value at break would have to be exceeded. It can also be seen that the magnitude of the out-ofplane displacement increases with the number of strips for the samples following CD. Moreover, to have a second strip, an increase in tensile stress of 80% is required. It is now time to see if this phenomenon appears in the same way on the coating pilot.

## 5.1.1.2 Pilot scale wrinkles formation

The appearance of wrinkles when using the coating pilot is not trivial. As pointed out in the literature review and at the beginning of this chapter, the misalignment angle  $\theta_{cr}$  and the critical web tension  $T_{cr}$  are important process parameters. Then, by controlling these two parameters, wrinkles were deliberately generated. Figure 5.5 shows the appearance of wrinkles for different misalignment angle - web tension combinations on GHDS 35 paper.

Once the wrinkles and troughs have been generated, various points need to be highlighted. First of all, one to many troughs (Figure 5.5a) are formed at the downstream roll with lengths of approximately 30 to 40 mm. The lengths of the troughs vary until they become wrinkles. As



Figure 5.6: Experimental highlighting the appearance of wrinkles as a function of the pair: web tension - angle of misalignment (GHDS 35 paper, uncoated side touching the rollers).

a matter of fact, the troughs gradually grow and reach lengths of approximately 150 mm under certain conditions in favour of wrinkles formations. Finally, when the mechanical limit between no-wrinkle/wrinkle is reached, the troughs have a length between 580 and 590 mm (diagonal on the web span). The next step is the formation of wrinkle. Concerning the appearance of the wrinkles (Figure 5.5b), they are never parallel to the machine direction of the paper but tilted. Before the non-reversible wrinkle formation, a trough from the upstream roll to the downstream roll is coming out. This trough starts at the upstream roll, widens to half of the web span before tapering and converging to the downstream roll. As soon as the trough passes the downstream roll, and is still there, it becomes a wrinkle and irreversibly marks the paper.

The last point to look at is the formation of wrinkles on wet paper (Figure 5.5c). Preliminary tests were performed by wetting the paper just before the web span on which the study is focused. It was found that for a web tension and misalignment angle for which no wrinkles were observed on dry paper (despite the presence of troughs), it was not necessarily the case for wet paper. Wrinkles starts to appear much more easily due to the presence of water.

From the observations made, as well as the measurements of the misalignment angle - web tension pairs, Figure 5.6 and Figure 5.8 could be plotted for the GHDS 35 paper. Figure 5.6 was plotted for the uncoated side of the GHDS 35 against the roll. Figure 5.8 was plotted for the coated side against the roll. These two figures represent the presence of wrinkles or troughs for different misalignment angle - web tension combinations (M - T combinations).

First, region I (with the squares) corresponds to the  $\theta$  - T combinations for which no wrinkles are detected. The orange diamonds correspond to the  $\theta$  - T combinations for which out-of-plane deformations (troughs) are detected. No wrinkles or creases were detected. The same is true for the orange triangles. Finally, the yellow circles correspond to  $\theta$  - T combinations for which wrinkles appear. It is therefore possible to isolate three zones from this graph: Region I where the web is flat, Region II where the web has troughs and Region III where wrinkles appear on the



**MISALIGNMENT ANGLE** 

Figure 5.7: Web tension versus misalignment angle proposed by David Roisum [54]. 3 Regions are highlighted: planar web, slack edge web and wrinkled web.



Figure 5.8: Experimental highlighting the appearance of wrinkles as a function of the pair: web tension - angle of misalignment (GHDS 35 paper, coated side touching the rollers).

web. These 3 regions are also found in the literature. Region I is for a flat and unwrinkled web which occurs when misalignment is sufficiently small. Region II is for a web with a "slack edge" but no wrinkling which occurs when tension is sufficiently small (Figure 5.7). However, an out of plane displacement appear. Region III is where the "shear wrinkles" crosses the downstream roll [54].

The same observation can be made for Figure 5.8. However, no wrinkle could be detected in this configuration.

Furthermore, the results between the coated and uncoated side of the paper are compared to study the influence of the friction coefficient. It has been seeing that differences exist between the areas of regions I and II of each face, especially when the angle of misalignment is greater than 1.5°. Region III didn't appear because no wrinkles could be formed on the uncoated face. This could be explained by the difference in the friction coefficient of the 2 faces of the paper. A friction test has been made on the two GHDS 35 paper sides in MD. It was found that there



(a) Troughs after the applicator roller



(b) Troughs after the Mayer rod



(c) Oriented troughs and futures wrinkles after IR drying

Figure 5.9: Troughs and wrinkles appearing on CPRAW paper during "coating" with water, while using the coating pilot.

was more friction on the coating side. Other wrinkles are observed in tests with other papers. Figure 5.9 shows the appearance of wrinkles on CPRAW paper. Figure 5.9a, is of the paper just after the applicator roller. There is no coating color, only water in the coating tank. You can see the beginnings of wrinkles appearing. In Figure 5.9b, the paper passes the Mayer rod of the coating system and troughs are seen. Finally, Figure 5.9c is the paper after the IR dryer. The roll visible in the picture was deliberately and roughly misaligned (the misalignment angle is unknown). Before the roller, troughs are visible and are tilted. If one zooms on the roller, it is possible to see wrinkles forming and becoming creases. The number of troughs is also significant: the paper is still a little wet, which seems to be favourable to the appearance of troughs. The roller is also hot (at least 80° C or more) as it is close to the dryers. Moreover, this paper, with a lower grammage than GHDS 35, seems to be a perfect candidate for wrinkles to appear.

Wrinkles therefore appear more or less easily on the coating pilot depending on the web tension and the angle of misalignment of the rollers with respect to each other. This phenomenon is paper dependent: some papers seem to be affected more strongly than others : refining, fibre lengths and fibre composition can be related to wrinkle appearance.

# 5.1.2 Ex-situ observations

The in-situ observations (i.e. during the formation of the wrinkles) provided a lot of information. However, not everything could be characterised. It is therefore necessary to characterise the wrinkles formed. The following observations were made on wrinkles formed on the coating pilot.



Figure 5.10: CPRAW, CPBS, GHDS 35 papers appearence after "coating" with water, using the coating pilot.

# 5.1.2.1 Macro-scale observation

Firstly, macroscopic observations are made with the "naked eye" and with the help of the Alicona Infinite Focus (AIF) on CPRAW, CPBS and GHDS 35 paper on Figure 5.10. Each picture of the different papers corresponds to a representative sample of the paper after "coating" with water (for CPRAW AND CPBS) and with starch gel (for GHDS 35). For each picture, an overall view and a focus on a wrinkle is presented. For GHDS 35, a second focus is proposed on a phenomenon frequently found and very visible on GHDS which is a pinch of the wrinkle. On each paper, an asymmetric wrinkle is visible. In addition, the surfaces of the papers have an "orange peel" effect, like small scale cockling. CPRAW has a "silk paper" or "crepe paper" feel/touch. The wrinkle on CPRAW paper is crushed on one side and the asymmetry is therefore more pronounced. GHDS 35 has a sticky feel/touch due to starch gel coating. As shown in Figure 5.10c, the wrinkle is oriented and very pronounced. In addition, there is the aforementioned pinch. And this is repeated more or less regularly along the wrinkle:  $23 \pm 2$  pinches over 300 mm (values taken from 3 wrinkles), about 0.08  $pinch \cdot mm^{-1}$ . AIF allows access to more information about wrinkles, at an intermediate scale. Thanks to the surface reconstructions, it is possible to see the elevation profiles of wrinkles as well as the possible periodicity of wrinkles. First of all, an analysis has been made Figure 5.11 on the wrinkled GHDS 35.

The first analysis is carried out on a 1.39 mm depth analysis zone. Figures 5.11a and Figure 5.11b represent 5 elevation profiles of a wrinkle measured at different depths in 3D view and in front view. The first thing that stands out is the asymmetry of the wrinkle. The wrinkle height, whatever the chosen depth, increases drastically to reach its maximum value between 620 and 630  $\mu$ m. The wrinkle height decreases slowly between 0.700 and 2.400 mm. The other remarkable point is the strong overlap of the different elevation profiles. This suggests that over the 1.39 mm considered, wrinkle does not change its orientation. This impression is also supported by Figure 5.12, which is a wrinkle height map. It shows the variation in wrinkle height as a function of wrinkle height and depth.

The rapid decrease of the wrinkle height for a width between 0.300 and 0.500 mm also poses



Figure 5.11: 3D and 2D reconstructions of a wrinkled GHDS 35 paper.



Figure 5.12: Wrinkle height map for a GHDS 35 paper (1.39 mm deep)

a problem with regard to the low number of data. Indeed, it is difficult for the AIF device to reconstruct surface variations for which part of the surface is almost vertical. This leads to a large standard deviation when calculating an average wrinkle representing the studied area. This average wrinkle is used as a basis for modelling the wrinkle shape. In the literature, a polynomial curve model of degree 3 is used [143]. However, the wrinkle asymmetry is not negligible. Therefore, the Weibull model is proposed in this study to model the wrinkle height as a function of its width. This model is normally used to model failure laws (failure time of an electronic component or the failure time for car tyres). This law is presented in equation 5.4.

$$H_{Wr}(l_{Wr}, k_{Wr}, \lambda_{Wr}, \theta_{Wr}, A_{Wr}) = A_{Wr} \cdot \frac{k_{Wr}}{\lambda_{Wr}} \cdot \left(\frac{l_{Wr} - \theta_{Wr}}{\lambda_{Wr}}\right)^{k_{Wr} - 1} \cdot e^{-\left(\frac{l_{Wr} - \theta_{Wr}}{\lambda_{Wr}}\right)^{k_{Wr}}}$$
(5.4)

It normally incorporates 2 or 3 parameters:  $k_{Wr} > 0$  the shape parameter;  $\lambda_{Wr} > 0$  the scale parameter (directs the dispersion of the distribution) and  $\theta_{Wr}$  the position parameter (determines the position of the origin). In this case, the Weibull distribution must integrate a fourth parameter: the amplitude  $A_{Wr}$  (the Weibull distribution is a probability distribution,



Figure 5.13: Wrinkle height as a function of its width. Comparison between experimental and modelled values obtained with the Weibull law on a wrinkled GHDS 35 paper. The experimental values are the average of a wrinkle with a depth of 1.39 mm.

| Parameters                | Model (3 parameters) | Model (4 parameters) |
|---------------------------|----------------------|----------------------|
| $k_{Wr}$                  | 2.7                  | 1.6                  |
| $\lambda_{Wr} \ [\mu m]$  | 905.8                | 638.2                |
| $\theta_{Wr}$ [ $\mu m$ ] | 0.00                 | 300.00               |
| $A_{Wr} \ [\mu m^2]$      | 509723               | 517676               |
| $\Sigma r^2 \ [\mu m^2]$  | 4940828              | 635923               |
| $R^2$                     | 0.92                 | 0.99                 |

Table 5.1: Parameters obtained from the 3 and 4 parameters Weibull models ( $\Sigma r^2$  is the sum of the squares of the deviations used is the LSM methode). The experimental values are the average of a wrinkle with a depth of 1.39 mm. The paper is the GHDS 35.

the obtained values are generally between 0 and 1, which is not the case here). Note that for the Weibull law  $l_{Wr} \ge \theta_{Wr}$  and  $H_{Wr}(l_{Wr}, k_{Wr}, \lambda_{Wr}, \theta_{Wr}, A_{Wr}) = 0, \forall x < \theta_{Wr}$ . To determine the model parameters the LSM method combined with the GRG algorithm is used. Figure 5.13 shows the shape of an average wrinkle as well as two modelled curves. The black diamonds are the Weibull model with  $\theta_{Wr} = 0$  (model with only 3 parameters) and the yellow triangles are the Weibull model with  $\theta_{Wr}$  variable. The light orange band represents the standard deviation of the experimental values.

With this model, it is possible to model the wrinkles more or less correctly. The results of the modelling are presented in Table 5.1 .

The 3-parameter model gives  $R^2 = 0.92$  while the 4-parameter model gives  $R^2 = 0.99$ . Moreover,  $\lambda_{Wr}$  of the 4-parameters model is closer to the experimental data than the 3-parameters model. The abrupt height decay is also better represented with the 4-parameters model. The same analyses were performed on another wrinkle but at a greater depth (25 mm). The elevation profiles are shown in Figure 5.14a and the level map is shown in Figure 5.14b.

The difference with the previous dataset is the lack of overlap between the different elevation profiles of the wrinkle at different depths. Differences in width are also observed, suggesting the pinches mentioned earlier. The abrupt variation in height is also observed but is less important.



Figure 5.14: Elevation profiles of a 25 mm deep wrinkle (GHDS 35 paper) and its height map.



Figure 5.15: Wrinkle height as a function of its width. Comparison between experimental and modelled values obtained with the Weibull law on a wrinkled GHDS 35 paper. The experimental values are the average of a wrinkle with a depth of 25 mm.

The Weibull model with 3 or 4 parameters is also used. The results are shown in Figure 5.15 and the modelling parameters are summarised in Table 5.2.

The  $R^2$  of the models are 0.96 and 0.98, which is very correct. The 4-parameters model seems to model the wrinkle shape better for widths greater than 700  $\mu m$ , notably thanks to the value of  $\lambda_{Wr}$  which is very close to the experimental value. However, for widths less than 700 $\mu m$ , the wrinkle shape is not perfectly represented by the 4-parameters model.

On the 2 data sets studied, the Weibull model allows to model the wrinkles very correctly. It is however recommended to use the 4-parameters model. These first ex-situ observations have already provided a lot of information on the wrinkles: asymmetric shape, widths, heights and pinches. It is now necessary to decrease the scale of observation to complete the information already acquired.

| Parameters                | Model (3 parameters) | Model (4 parameters) |  |
|---------------------------|----------------------|----------------------|--|
| $k_{Wr}$                  | 3.44                 | 2.23                 |  |
| $\lambda_{Wr} \ [\mu m]$  | 1170.85              | 773.24               |  |
| $\theta_{Wr}$ [ $\mu m$ ] | 0.00                 | 409.98               |  |
| $A_{Wr} \ [\mu m^2]$      | 542668.90            | 535711.73            |  |
| $\Sigma r^2 \ [\mu m^2]$  | 2415756.72           | 884593.99            |  |
| $R^2$                     | 0.96                 | 0.98                 |  |

Table 5.2: Parameters obtained from the 3 and 4 parameters Weibull models ( $\Sigma r^2$  is the sum of the squares of the deviations used is the LSM methode). The experimental values are the average of a wrinkle with a depth of 25 mm. The paper is the GHDS 35.







(b) GHDS 35 uncoated side (x200)

Figure 5.16: The 2 sides of GHDS 35 paper observed using SEM (Low vaccum mode, secondary electrons).

# 5.1.2.2 Micro-scale observation

Microscopic observations were carried out with 2 techniques: S.E.M and X-Ray tomography. Information about the techniques is given in the chapter materials and methods. The S.E.M. images of the both sides of GHDS 35 are shown in Figure 5.16 for reference.

It is easy to identify the two faces du to the fact that fibers are not visible on the coated side. The wrinkled GHDS 35 is taken in a S.E.M. photo (Figure 5.17). The target area is a pinch zone as previously shown in Figure 5.17. Thanks to the S.E.M. image, it is possible to see the delamination of the pinched area. For further information, a wrinkled GHDS 35 chip was subjected to X-Ray tomography. Figure 5.18 shows the results of the 3D reconstruction, with a focus on a "damaged" area (Figure 5.18b).

Two cracks can be seen: one at the beginning of the wrinkle and the other at the top of the wrinkle. Furthermore, on the "damaged" area, a delamination of the pigment coating layer is seen. Images of two cross-sections of the 3D reconstruction are taken to gain more information about this delamination. These slice planes are shown in Figure 5.19 for a non-damaged wrinkle area and Figure 5.20 for a damage wrinkle area (with a focus on the damaged wrinkle).



Figure 5.17: Delamination phenomenon observed by SEM on a wrinkled and pinched area of GHDS 35 paper.



(a) GHDS 35 paper sample reconstruction using X-Ray tomography

(b) Focus on a damaged area of a GHDS 35 paper sample)  $\,$ 

Figure 5.18: X-Ray tomography of a GHDS 35 paper sample.



Figure 5.19: Cross-section of a wrinkled GHDS 35 sample observed by X-ray tomography.



Figure 5.20: Damaged cross-section of a wrinkled GHDS 35 sample observed by X-ray tomography. The observed area is delaminated.

For an undamaged wrinkle (cf. Figure 5.19) asymmetry observed previously is found. The second section is an area of the "damaged" wrinkle (Figure 5.20). It can be seen that a non-negligible area of the wrinkle is delaminated and that some of the fibres appear to be out of contact on this section. The study of the causes of the delamination will not be presented in this manuscript. The CPRAW and CPBS papers have not been studied by SEM and tomography. However, the SEM images of these unwrinkled papers are presented in the Appendix F to allow these two papers to be viewed at different scales.

It was possible to reuse Weibull model for the sectional plane of the undamaged wrinkle in Figure 5.19. Figure 5.21 presents the result of the modelling with a 4-parameters model. Table 5.3 summarises the modelling parameters.

The  $R^2$  is 0.99. The modelling is very correct as soon as the width in abscissa is higher than the value of  $\theta_{Wr}$ .  $\theta_{Wr}$  can be considered as the abscissa from which the wrinkle starts. The

| $k_{Wr}$                   | 2.64      |  |  |
|----------------------------|-----------|--|--|
| $\lambda_{Wr}$ ( $\mu m$ ) | 740.75    |  |  |
| $	heta_{Wr}$ ( $\mu m$ )   | 549.32    |  |  |
| $A_{Wr}~(\mu m^2)$         | 380396.88 |  |  |
| $\Sigma r^2$ ( $\mu m^2$ ) | 23471.59  |  |  |
| $R^2$                      | 0.99      |  |  |

Table 5.3: Parameters obtained from the 4 parameters Weibull models ( $\Sigma r^2$  is the sum of the squares of the deviations used is the LSM methode). The experimental values (height as a function of width) are obtained from Figure 5.19.



Figure 5.21: Modelisation of X-ray tomography wrinkle using 4 -parameters Weibull law.

Weibull model still allows the wrinkle shape to be modelled properly.

# 5.1.3 Conclusion

In this section we have seen the formation of buckling and wrinkles through different tools and scales. The in-situ observation has allowed to acquire mechanical data which will be compared with the models used in the following section. It has already been possible to observe a different behaviour between the tensile tests and the pilot case. On the wrinkles formed with the pilot, whatever the paper used, more or less oriented wrinkles are observed. The ex-situ observations, at different scales, allowed to highlight the wrinkle asymmetry, as modelled by the Weibull model, on 3 different data sets. The modelling had very good results. In addition, pinching phenomena, also linked to a decohesion/delamination of the industrial pigment coated layer, are observed for the GHDS 35 paper.

# 5.2 Modelling of the wrinkling phenomenon

In this section, the models presented in the literature review will be used and compared to the experimental values. Before that, the results concerning the mechanical characterisation of the papers in dry and wet conditions will be discussed.

# 5.2.1 Paper mechanical characteristics

# 5.2.1.1 Dry state

Table 5.4 below summarises the properties of the paper used, speckled or not. The difference in grammage and thickness between the papers is clear. It is also important to note that the printing of speckles on the papers has an impact on their weight and thickness: around  $2 g \cdot m^{-2}$ 



Figure 5.22: Typical stress - strain curves of the 4 different papers in CD and MD.

and 2  $\mu m$  with speckle. However, regarding the thickness of the speckled papers, it should be noted that despite the different initial thickness, the two speckled papers have the same final thickness (37 ±1  $\mu m$ ). As for the mechanical properties, the GHDS 35 and GHDS 40 have equivalent Young's MD and CD moduli. The CPRAW and CPBS have lower Young's moduli compared to the GHDS 35 and GHDS 40.

| Name             | $\mathbf{G}~(g\cdot m^{-2})$ | $t_f$ ( $\mu m$ ) | $E_{MD}$ (GPa)  | $E_{CD}$ (GPa)  |
|------------------|------------------------------|-------------------|-----------------|-----------------|
| GHDS 35          | $36.2 \pm 0.2$               | $33 \pm 1$        | $8.92 \pm 0.88$ | $4.15 \pm 1.17$ |
| GHDS 40          | $40.6 \pm 0.2$               | $35 \pm 1$        | $9.20 \pm 0.17$ | $3.93 \pm 0.35$ |
| GHDS 35 speckled | $38.2 \pm 0.4$               | $37 \pm 1$        | $8.46 \pm 0.34$ | $4.27 \pm 0.23$ |
| GHDS 40 speckled | $42.4 \pm 0.2$               | $37 \pm 1$        | $9.88 \pm 0.33$ | $4.08 \pm 0.36$ |
| CPRAW            | $14.1 \pm 0.2$               | $24 \pm 1$        | $7.21 \pm 0.33$ | $2.81 \pm 0.36$ |
| CPBS             | $23.7 \pm 0.4$               | $37 \pm 1$        | $4.47 \pm 0.74$ | $2.06 \pm 0.10$ |

Table 5.4: Mechanical characteristics of tested papers.

When it comes to the impact of the speckle, it seems that the speckle increases the MD Young's modulus for GHDS 40 reference and has no statistically significant impact on the GHDS 35. Figure 5.22 represents the stress - strain curves of the 4 papers in CD and MD.

Table 5.5 gives access to the bending stiffness of GHDS 35 and GHDS 40 in both directions.

Although there is a difference between the bending stiffness following MD and CD for each reference or speckled paper, it is not possible to make a statistically significant difference between the papers themselves. The bending stiffness of CPRAW and CPBS papers were not measured because these papers are too flexible. Using the Baum method, the calculated values of the shear modulus  $G_{xz,Baum}$  are between 2.32 and 2.45 GPa (Table 5.6). As for the values of the Poisson's ratio  $\nu_{xz,Baum}$  and  $\nu_{zx,Baum}$ , the values are between 0.18 and 0.20 or 0.41 and 0.47.  $G_{xz,Baum}$  and  $\nu_{xz,Baum}$  can be compared with the results obtained with the method derived from the constitutive equations of mechanics for orthotropic materials.
| Name             | Bending stiffness MD (mN.m) | Bending stiffness CD (mN.m) |
|------------------|-----------------------------|-----------------------------|
| GHDS 35          | $0.030 \pm 0.014$           | $0.014 \pm 0.002$           |
| GHDS 40          | $0.034 \pm 0.013$           | $0.016 \pm 0.002$           |
| GHDS 35 speckled | $0.032 \pm 0.013$           | $0.015 \pm 0.002$           |
| GHDS 40 speckled | $0.035 \pm 0.014$           | $0.017 \pm 0.002$           |

Table 5.5: Bending stiffness in CD and MD of GHDS 35 and GHDS 40 papers with and without speckle.

| Name             | $G_{xz,Baum}(\mathbf{MPa})$ | $\nu_{xz,Baum}$ | $\nu_{zx,Baum}$ |
|------------------|-----------------------------|-----------------|-----------------|
| GHDS 35          | 2.35                        | 0.19            | 0.42            |
| GHDS 40          | 2.32                        | 0.19            | 0.44            |
| GHDS 35 speckled | 2.32                        | 0.20            | 0.41            |
| GHDS 40 speckled | 2.45                        | 0.18            | 0.45            |
| CPRAW            | 1.74                        | 0.18            | 0.47            |
| CPBS             | 1.17                        | 0.20            | 0.43            |

Table 5.6: Poisson's coefficient  $\nu_{xz,Baum}$ ,  $\nu_{zx,Baum}$  and shear modulus  $G_{xz,Baum}$  of tested papers calculated following Baum's method.

Determination of Poisson's ratio and shear modulus using constitutive equations of mechanics for GHDS 35 and GHDS 40: To determine the Poisson's ratio  $\nu_{xz}$  and the shear modulus  $G_{xz,Baum}$ , the tangent elastic modulus  $E_{tan}$  is plotted as a function of the angle  $\Phi$  (Figure 5.23).  $\Phi$  is the angle between the direction of the tensile test and MD. Thus, when  $\Phi = 0^{\circ}$ , the samples are tested along MD and when  $\Phi$  is equal to 90°, the samples are tested in the CD. Once the curve plotted, the LSM is applied to compare experimental and model values (cf. equation 3.5. In order to highlight the correspondence of the values, parity diagrams are plotted Figure 5.23. In this case, y = 0.99x for GHDS 40 paper ( $R^2 = 0.98$ ) and y = 0.96xfor GHDS 35 paper ( $R^2 = 0.99$ ). Therefore, there is a good match between theoretical and experimental values (cf. Table 5.7). Note that the values predicted by the Baum model for the Poisson's ratio match the experimental values perfectly. However, this is not the case for the shear moduli where absolute relative errors of 26.79% and 16.24% are calculated.

As mechanical properties in the dry state are now known, let's have a look at the properties of papers when they are wet and contain a large amount of water. In this way it will be possible to approach the conditions close to the coating process.

| Name    | $G_{xz}$ (MPa) | Relative error on $G_{xz}$ | $\nu_{xz}$ | Relative error on $\nu_{xz}$ |
|---------|----------------|----------------------------|------------|------------------------------|
| GHDS 35 | 3.21           | -26.79%                    | 0.19       | 0%                           |
| GHDS 40 | 2.77           | -16.24%                    | 0.19       | 0%                           |

Table 5.7: Poisson's coefficient  $\nu_{xz}$  and shear modulus  $G_{xz}$  of tested papers calculated following mechanical constitutive equation and error compare to Baum's method.



Figure 5.23: Evolution of tangent elastic modulus  $E_{tan}$  versus the angle between MD and test direction  $\Phi$  and parity plot comparing experimental and modelled for GHDS 35 and GHDS 40 papers.

# 5.2.1.2 Wet state

The mechanical properties for wet papers will be discussed through 3 aspects: the Young's moduli of papers with different water contents, the elongation of paper under constant stress when one side is in contact with water (WSD) and the wet tensile strength (Finch test). This is intended to approximate the evolution of the mechanical properties of the papers studied during the coating process. It should be noted that in this subsection only GHDS 35 and GHDS 40 papers are tested.

Young's moduli of papers at different water contents: The first point is the Young's moduli/ It is well known that paper and water do not mix well. Thus, it is easy to understand that the water brought by the coating color during the coating process on the pilot will have an unfavourable impact on the mechanical properties of the paper. The drying kinetics of a tensile specimen after immersion and saturation in water had to be determined. Figure 5.24 shows the evolution of the mass of a specimen after water saturation. Two specimens are blotted to remove excess water before air drying.



Figure 5.24: Drying dynamic of tensile test sample (GHDS 35 paper) in conditionned room.

The first striking point is the decrease of the mass with time which seems exponential. It is also noticeable that the signals are noisy. The balance used is a precision balance. This balance has doors to isolate the weight measurement. In this case, to be sure to be as faithful as possible to the drying phenomenon taking place in room where the tensile tests are carried out, the doors of the balance were left open. This explains the noisy signal. It can also be seen that when the excess water is removed with blotters, the mass value at t = 0 s is lower than when the excess water is not removed. Blotters save drying time in one direction. For the rest of the study, the values with blotters will be retained and modelled. The drying behaviour of the tensile specimen



Figure 5.25: Parity plot comparing modelled and experimental values from the drying of a tensile test sample (GHDS 35 paper) in a conditioned room.

was modelled with a decreasing exponential law as presented equation 5.5.

$$m(t) = K_d \cdot e^{\frac{t}{\tau_d}} + m_f \tag{5.5}$$

with  $K_d = m_0 - m_f$  in grams where  $m_0$  is the initial mass of the sample,  $\tau_d$  is a time constant (s) corresponding to the loss of 63% of the initial mass ( $3\tau_d$  corresponds to the loss of 95% of the initial mass and  $m_f$  is the final mass of the sample). The parity plot comparing experimental and model values is shown in Figure 5.25. The experimental data are globally well represented ( $R^2 = 0.97$ ).

The modelled parameters are  $\tau_d = 306.66$  s,  $m_f = 0.142$  g and  $K_d = 0.088$  g. The values  $m_f$  and  $K_d$  correspond to the experimental values. This model will therefore be retained for the rest of the study. However, it should be kept in mind that this model is valid for the drying of paper and not for the absorption of water: a hysteresis certainly exists but is not taken into account in this study [144][26].

It is now possible to measure the Young's moduli of different samples, following MD and CD, at different amounts of water (thanks to equation 5.5 when dividing the calculate mass by the sample surface). Thus, Figure 5.26 presents the evolution of the Young's modulus for GHDS 35 as a function of the absorptiveness  $A_s$ , following MD and CD.

Whatever the direction (MD or CD), two plateaus can be seen on the two curves in Figure 5.26. Between these two plateaus, a more or less important decrease of the Young's moduli is visible. It should also be noted that the maximum values of the Young's moduli are different from those presented previously for the GHDS 35. The drying of the specimens is carried out without stress contrary to what happens on a paper machine as well as on the coating pilot where the paper is under tension. Without this pre-stress imposed on the paper, the Young's



Figure 5.26: Evolution of Young's modulus in MD and CD versus absorptiveness  $A_s$  for GHDS 35 paper.

modulus value is lower than with pre-stress :

- $\rightarrow$  8.92 GPa for  $E_{MD}$  under constrained drying and 5.74 GPa under free drying;
- $\rightarrow$  4.15 GPa for  $E_{CD}$  under constrained drying and 2.20 GPa under free drying;

The shape of the curves is reminiscent of the behaviour found in rheology for shear thinning fluids with two Newtonian plateaus. These fluids are modelled by Cross's law (presented in the literature review of this document). The form of this law will be used to model the evolution of the Young's modulus (CD or MD) as a function of absorptiveness. The following law equation 5.6 is therefore proposed for the Young's modulus following MD ( $E_{MD}$ ) :

$$E_{MD} = \frac{E_{MD,min} \cdot (\lambda_s \cdot A_s)^{n_e} + E_{MD,max}}{1 + (\lambda_s \cdot A_s)^{n_e}}$$
(5.6)

where  $E_{MD,min}$  is the minimum value of Young's modulus following MD (value of the high absorptiveness plateau) in GPa and  $E_{MD,max}$  is the maximum value of Young's modulus following MD (value of the low absorptiveness plateau) in GPa.  $\lambda_s^{-1}$  (in  $g_{water} \cdot m_{paper}^{-2}$ ) is the absorptiveness value for which the Young's modulus is  $\frac{E_{MD,min} + E_{MD,max}}{2}$ . Finally  $n_e$  is a factor of severity of the Young's modulus decay, it is dimensionless.

A similar reasoning is made for the Young's modulus following CD  $E_{CD}$  equation 5.7. The meaning of the coefficients is the same as the equation 5.6 but following CD.

$$E_{CD} = \frac{E_{CD,min} \cdot (\lambda_s A_s)^{n_e} + E_{CD,max}}{1 + (\lambda_s A_s)^{n_e}}$$
(5.7)

Using the method of least squares and the non-linear GRG algorithm, this model was fitted to the experimental data. The results of the modelling are presented in Table 5.8.

The models have a  $R^2 > 0.98$ . There are nevertheless areas of under- and over-estimation. It is also worth noting the equality of the  $\lambda_s$  values between CD and MD (0.13  $m_{paper}^2 \cdot g_{water}^{-1}$ ). Furthermore, the value of  $n_e$  for  $E_{CD}$  is larger than that for  $E_{MD}$ , indicating a more severe

| Parameters   | CD    | MD    |
|--------------|-------|-------|
| $\lambda_s$  | 0.14  | 0.13  |
| $n_e$        | 38.43 | 16.66 |
| $\Sigma r^2$ | 0.13  | 0.15  |
| $R^2$        | 0.986 | 0.995 |

Table 5.8: Results of modelling Young's modulus versus absorptiveness using a Cross like model for GHDS 35 paper.



Figure 5.27: Impact of the absorptiveness at half height  $\lambda_s$  value on the evolution of the CD Young's modulus  $E_{CD}$  as a function of the GHDS 35 paper absorptiveness  $A_s$ , for  $n_e = 38.43$ .

decay of  $E_{CD}$ . To confirm the significance of  $\lambda_s$  and  $n_e$ , a sensitivity study is carried out on these two parameters. Thus, Figure 5.27 represents the evolution of  $E_{CD}$  as a function of  $A_s$ , for different values of  $\lambda_s$  ( $n_e$  being fixed at 38.43).

The black dots correspond to the experimental values. As the value of  $\lambda_s$  increases, the fall in Young's modulus occurs at low  $A_s$ . This validates the hypothesis of the significance of  $\lambda_s$ . Similarly, Figure 5.28 corresponds to the study of the sensitivity of the parameter  $n_e$  on the model,  $\lambda_s$  being fixed at 0.13.

Here again, the black dots are the experimental values. When  $n_e$  increases, the decrease of  $E_{CD}$  occurs for a larger value of  $A_s$ , but it is more abrupt. After verification, this value is found to be  $\lambda_s^{-1}$ . In any case, our hypothesis posing  $n_e$  as a factor of severity of the growth of  $E_{CD}$  is validated.

The Cross like model is therefore presented to model the evolution of the Young's moduli of a paper as a function of the absorptivenes. This model differs from one proposed in the literature [145]. It concerned the evolution of the tensile stiffness  $(kN \cdot m^{-1})$ . It is presented as equation 5.8.

$$\Theta_t = \Theta_{t,0} \cdot e^{-f \cdot mc(\%)} \tag{5.8}$$

However, this model is used in an experiment where the paper sample under test was moistened by water vapour, and no drying preceded the test. Furthermore, it does not consider an upper plateau. Salmen also proposed a figure (cf. Figure 5.29) where the relative modulus of paper is drawn as a function of moisture content [146]. If we just look at the curve shape, it can



Figure 5.28: Impact of the factor of severity  $n_e$  value on the evolution of the CD Young's modulus  $E_{CD}$  as a function of the GHDS 35 paper absorptiveness  $A_s$ , for  $\lambda_s = 0.14$ .



Figure 5.29: The relative modulus, where  $E_0$  is the modulus at 0 % moisture content, as a function of moisture content. Solid line is the laminate model and the black dots the measured value. The paper sheet used was isotropic [146].

be seen a similarity with our models. The question is still the values of  $\lambda_s^{-1}$ . For  $\lambda_s^{-1} = 7.69$ , we estimated the moisture content to 18%. When compared to Salmen results, the equivalent to  $\lambda_s^{-1}$  is associated to 10% of moisture content. This may suggest that our moisture content value (18%) is high, but the order of magnitude is not totally inconsistent.

However, some points remain unresolved: the value of  $\lambda_s^{-1}$  is large and one would expect Young's moduli to fall for lower values of  $A_s$ . Furthermore, this model is based on the drying of the paper and not on the absorption of water. As mentioned before, a hysteresis certainly exists and it is not impossible that this leads to a more abrupt drop in Young's modulus for much lower values of  $A_s$ . Finally, the control of the drying can gain in precision and the tests could give different values if the excess of water were not removed with the blotters.

Wet Stretch Dynamics analyses: This paragraph focuses on the results obtained using the WSD technique presented earlier. In this case only GHDS 35 paper is tested using this technique. Both sides of the paper are tested, following CD and MD, for 4 different forces. Figure 5.30 shows the 5 experimental curves for the coated side of GHDS 35 against water, in



Figure 5.30: Example of experimental values and average value obtained during WSD test. The sample here are in CD, tested 5 times with a force of 2 N. The average curve is also represented. The GHDS 35 paper is used, with the coated face in contact with water.

CD (coloured markers), with a 2 N tensile strength of 2 N applied on the paper. The average curve is also shown (black markers - 2N \_ Average).

The high reproducibility of the measurements can already be noted. The standard deviation is difficult to see, its maximum value is 0.14% (for an associated dispersion coefficient of 0.03%). Thus, for the GHDS 35 having two different faces, two directions (CD and MD) and for 4 different test forces, the mean curves are plotted and modelled by a second order law according to equation 5.9.

$$\varepsilon_W(t) = K_p \left[ 1 - \frac{1}{\tau_1 - \tau_2} \cdot \left( \frac{-t}{\tau_1} - \frac{-t}{\tau_2} \right) \right]$$
(5.9)

where  $\varepsilon_W(t)$  is the deformation of the sample over time,  $K_w$  is the gain (%) and its value corresponds to the maximum value of deformation.  $tau_1$  and  $tau_2$  are two time constants specific to each system. The model curves are shown in Figure 5.31.

First of all, if the models between MD and CD are compared (Figure 5.31, a difference in behaviour and maximum values can be observed. Indeed, the maximum elongation is much higher in CD than in MD (identical behaviour to a tensile test). Furthermore, the behaviour during the first 2 seconds is different. A horizontal slope is visible on the CD models and then an inflection and growth of the slope value. This could indicate a second order behaviour for the CD samples. It should also be noted that for times greater than 20 s for the CD models and for times greater than 5 s for the MD models, the curves are always ordered in the same way: for a given time, the greater the force, the greater the elongation. However, there is no regularity of spacing between the curves. The other experimental curves can be found in Appendix G.

In addition, the parameters of the 16 models are presented in through histograms for a



(c) MD - coated side in contact with water

(d) MD - uncoated side in contact with water

Figure 5.31: Model curves obtained from WSD tests on GHDS 35 paper. The tests were performed according to CD and MD (row), with the coated or uncoated side of the paper in contact with water (column). The tests were carried out for 4 different strength: 1, 1.5, 2 and 2.5 N.



Figure 5.32: Parameters of the second order models obtained from the WSD curves, at different forces, according to CD or MD, with the coated or uncoated side of the GHDS 35 paper in contact with water.

better reading Figure 5.32. First of all, for the tests following MD, the values of  $\tau_1$  are equal to 0.00s. This means that the hypothesis made concerning the first order behaviour of the samples following MD is validated. For the CD samples, 0.20 s  $\leq \tau_1 \leq 1.70$  s. No logical order appears in these values according to the force applied during the test. The second-order behaviour of the tests following CD could be explained by a difference in water penetration between CD and MD, which would result in an "ignition delay".

The values of  $\tau_2$  are globally ordered: the greater the force applied during the test, the greater the value of  $\tau_2$ . The values of  $\tau_2$  for the tests following CD are greater, at equivalent force, than the values of  $\tau_2$  following MD. Finally, the values of the coefficient of determination  $R^2$  show that the models are, overall, much better for the CD samples than for the MD samples.

Using the models presented in Figure 5.31, 4 stress [MPa] versus strain [%] graphs could be drawn. They were constructed in the following way: for each of the 4 tests, at a given time, 4 couples (strain, stress) are accessible. Figure 5.33 is one of these graphs (for CD\_ uncoated). For better readability only a selected number of times are shown but the data are available every 0.1 s. For short times, the points are aligned vertically. As time passes, they trace a straight line with slope  $E_{w,tan}$  (WSD tangent modulus) and y-intercepts  $b_{w,tan}$ .  $E_{w,tan}$  and  $b_{w,tan}$  seem



Figure 5.33: Stress versus strain curves, at different time, from WSD. The sample are in CD, with the GHDS 35 paper uncoated side facing water. Each markers represent a given time in second.



Figure 5.34: Evolution of WSD tangent modulus  $E_{w,tan}$  over time. The values are for GHDS 35 paper in CD and MD direction, with the coated side or uncoated side facing water.

to tend towards a constant value.

Figure 5.34 is plotted adding the other 3 tests (MD\_ coated, MD\_ uncoated and CD\_ coated). The slopes  $E_{w,tan}$  and orders at the origin  $b_{w,tan}$  were determined for each curve and plotted Figure 5.34 for  $E_{w,tan}$  and Figure 5.35 for  $b_{w,tan}$ . For these two figures, the triangle shape corresponds to the CD direction and the circles to the MD direction. Similarly, black is related to the uncoated side facing the water and orange to the coated side facing the water.

Concerning the Figure 5.34 presenting the evolution of  $E_{w,tan}$  versus time, different points are to be noticed. First of all, the values for the CD tests are lower than those for the MD tests. The tested face has little or no impact. The values of  $E_{w,tan}$  at time 0.07 s are 8000.00 MPa (coated side) and 8150.00 MPa (uncoated side) for MD and 3925.00 MPa (coated side) and 3827.24 MPa (uncoated side) for CD. These values are very close to the values of the Young's moduli  $E_{MD}$  and  $E_{CD}$  of the tested paper (GHDS 35). Thus, the following hypothesis can be



Figure 5.35: Evolution of WSD vertical intercept  $b_{w,tan}$  over time. The values are for GHDS 35 paper in CD and MD direction, with the coated side or uncoated side facing water.

made (cf. equations 5.10 and 5.11).

$$\lim_{t \to 0} E_{w,tan,MD} = E_{MD} \tag{5.10}$$

$$\lim_{t \to 0} E_{w,tan,CD} = E_{CD} \tag{5.11}$$

Thus the parameter  $E_{w,tan}$  could be a characteristic parameter of the evolution of the properties of a paper during a WSD test, and of processes approaching this test, such as one-sided coating for example.

With regard to Figure 5.35, which shows the evolution of  $b_{w,tan}$  as a function of time, things are different. The physical meaning of  $b_{w,tan}$  is still difficult to approach. However, there is a convergence of  $b_{w,tan}$  at long times, the values are different between CD and MD. The behaviour for times below 10 s is more difficult to explain. There is just one more difference between the behaviour of the CD and MD samples. Moreover the curves "coated" or "uncoated" in CDs are overlaid. As for the curves following MD, they are parallel for a time greater than 20 s, with a difference of less than 1 MPa.

The WSD is not found much in the literature. However, the measurement principle is very similar to what can happen on the coating pilot. The measurements carried out have shown a difference in the behaviour of the different directions of the paper and a new parameter  $E_{w,tan}$  has been developed to characterise the evolution of the mechanical properties of the paper as a function of time (and consequently the quantity of water) during the WSD.

Finch test and wet tensile strength: The last paragraph of this sub-section will briefly present the results of the Finch test for determining the wet tensile strength of a paper. Figure 5.36 illustrates the results obtained.

The GHDS 35 and GHDS 40 papers were tested according to MD and CD. The average values according to MD are higher than those according to CD. However, this value is very interesting for controlling the web tension in the coating process. Indeed, we now know that for the GHDS 35, the process must be conducted in such a way as not to exceed a web tension



Figure 5.36: Wet tensile strength, obtained with the Finch's test, for GHDS 35 and GHDS 40 in CD and MD.

of 85.27 ±15.25  $N \cdot m^{-1}$  with a wet paper, so ideally avoid exceeding 70  $N \cdot m^{-1}$  in the areas where the paper still has a very high water content (typically between the coating zone and the IR dryer).

# 5.2.2 Is it possible to forecast wrinkles with models?

The dry and wet properties of different papers are now known. It is therefore possible to model the different behaviours that can occur during a tensile test or on the coating pilot. The results of the models will be compared with the experimental values obtained in the first part of this chapter.

#### 5.2.2.1 Tensile test case

As described previously, the buckling coefficient  $k_c$  (equation 2.43) is used in literature dealing with plates stability under compressive or shear loading. Knowing the aspect ratio  $\beta$ , it is possible to calculate  $k_c$  and then to know the critical compression value  $\sigma_{z,cr}$  for which a plate buckles. In the case of buckling due to constrained edges, a similar formulation can be obtained for tensile loading  $\sigma_{x,cr}$ . Figure 5.37 presents the results obtained for the modelling of the buckling coefficient  $k_c$  versus plate aspect ratio  $\beta$  for GHDS 35 paper.

Based on the work of Zhu et al. [97] and the experimentally determined data, the  $k_c$  criterion was determined for different  $\beta$  and i (number of strip on the sample). The graph shows that for a large aspect  $\beta > 1$  ratio it is easier to buckle the plate than for an aspect ratio  $\beta < 1$ . Also, for a given aspect ratio,  $k_c$  increases with the number of wrinkles on the plate. This means that it will take more stress to form more wrinkles. In this case, the web tension is increasing and then the secondary compressive stress too.

For the tensile test of this study, the plate aspect ratio  $\beta = 0.15$ . The results are summarized Table 5.9. First of all, it is possible to notice that it is easier to form wrinkles (or waves in this case) when the sample is tested following CD than following MD. Moreover, the logical order of things is respected: it takes more stress to form 2 waves than to form 1 wave.



Figure 5.37: Buckling coefficient  $k_c$  versus aspect ratio  $\beta$  for GHDS 35 for tensile test in CD direction (left) and MD (right). *i* is the number of strip on the sample.

| Direction | i | $k_c$   | Critical tensile stress [MPa] |
|-----------|---|---------|-------------------------------|
| CD        | 1 | 190.75  | 5.78                          |
| CD        | 2 | 1332.68 | 40.36                         |
| MD        | 1 | 881.3   | 26.7                          |
| MD        | 2 | 6156.87 | 186.57                        |

Table 5.9: Buckling coefficient and critical tension stress to have buckling determined with Zhu model, for the GHDS 35 paper following CD and MD.

Figure 5.38 shows the experimental results and compares them with the results presented in Table 5.9. The lines represent the critical tensile stress to go from i waves to i +1, depending on the orientation of the fibres in the sample (MD or CD), on a dry paper.

Concerning the threshold values following CD, it can be seen that the values chosen experimentally to go from 0 to 1 wave are very high compared to the models. The same observation is made for the samples following MD. This suggests that the limit criterion for considering experimental buckling of a specimen is possibly overestimated. As for the threshold value between 1 and 2 waves, following CD, it is close to the values considered experimentally. The difference is on the out-of-plane displacement value considered. Concerning MD, the threshold value between 1 and 2 waves is higher (186.57 MPa) than the value of stress at failure of the samples. Physically, it does not exist and cannot be reached, which agrees with reality.

However, two points should be kept in mind: in the present study  $k_c$  is calculated in the case of a plate in tension where both ends are clamped, and the load is uniformly distributed. However, these two assumptions cannot be applied in the context of the work carried out on the coating pilot (simply supported plate and non-uniform web tension on the width). Nevertheless, this criterion is in line with the reality of the observed facts. It would just be necessary to review the conditions at the limits and to consider the use of a stress function to determine the evolution of the web tension over the width. Finally, such a criterion would be ideal for an industrial production. It would help to dimension roll-to-roll process by knowing the characteristics of the web. It makes possible to choose the good span between rollers in order to avoid wrinkles while



Figure 5.38: Comparison between experimental data and model values of critical tensile buckling limits for GHDS 35 paper of "dry" GHDS 35 paper.

having a sufficiently large web width to allow the production.

# 5.2.2.2 Pilot case

The experimental data are compared with the theoretical model for orthotropic materials proposed by [124] (equation 5.1). Figure 5.39 compares them. In this case, the friction coefficient  $\mu$  between paper and roll is unknown. It is a delicate parameter to determine. Thus, this factor was considered as a variable to match as well as possible with the experimental values and to be able to determine the critical tension  $T_{cr}$  from which wrinkles can appear (equation 5.2). It was set at  $\mu = 0.17$  as it seems consistent with the observed phenomena: this value enable to match the experimental boundary between troughs and wrinkles, especially at high misalignment values.

However, the experimental misalignment angle values obtained in this project are high compared to the values that can be found in the literature (Figure 5.40 et Figure 5.41). This point is still under investigation.

Impact of the discretization of the wrinkles number i: During this study, it was found that making the variable representing the number of wrinkles i continuous raise two questions. The first of these issues is to ask what is the physical representation of a non-integer number of wrinkles. The second issue is the impact of the discretization of the variable i on the model linking misalignment angle and web tension. In order to answer these questions, two figures have been drawn: one for a paper considered dry (Figure 5.42a), one for a paper saturated with water (Figure 5.42b). They represent the evolution of the misalignment angle as a function of the web tension (equation 5.1) as well as the evolution of the number of wrinkles i versus the web tension. They are plotted twice: once considering i continuous, once considering i as a integer. In the case of dry paper, the maximum number of wrinkles in the considered web tension



Figure 5.39: Comparison of experimental and model values for the evolution of misalignment angle versus web tension for dry paper ( $\mu = 0.17$ ). The paper studied is the GHDS 35, uncoated side touching the rollers.



Figure 5.40: Highlighting the web width (L here) (row) and web speed (columns) on the areas of wrinkle appearance by Hashimoto [124].



Figure 5.41: Demonstration of the impact of the friction coefficient on the critical band voltage value by Martz [126]. The critical band tension is inversely proportional to the friction coefficient (all other things being equal).

range is 4 (integer i) and less than 4 (continuous i). In the case of water-saturated paper, the maximum value is 6 (integer i) and is slightly lower than 6 in the continuous case. Comparing the model curves linking misalignment angle and web tension, it appears that the misalignment angle values are alternately overestimated and underestimated when i is continuous.

The model curves for discontinuous i also show a sharp drop in the permissible angle value. These drops correspond to the appearance of a new wrinkle according to the variation of discontinuous i. Thus, these sudden variations can be interpreted as a zone of instability: they are i wrinkles and the system tends towards a zone of unstable equilibrium before having i+1 wrinkle. This would also lead to the following interpretation: having a non-integer number of wrinkles would be a transition phase between two different equilibria. It should also be noted that as the number of wrinkles i increases, the range of web tension allowing i wrinkles increases.

It is also observed that the curves representing the number of continuous and discrete wrinkles as a function of the web tension intersect at several points. When there is a break with a horizontal plateau, the value of the associated web tension corresponds to a value for which the boundary criterion (equation 2.57) is no longer verified for a discontinuous number of wrinkles. When there is a break with a vertical zone, the boundary criterion is true again. Thus, to the right of a cut with a vertical zone and to the left of a cut with a horizontal plateau, the boundary equation is true. To the right of a cut with a horizontal plateau and to the left of a cut with a vertical zone, the boundary criterion.



Figure 5.42: Evolution of misalignment angle and number of wrinkles versus web tension for a considered dry or wet GHDS 35 paper, with discrete and continuous i. The uncoated side is touching the rollers.

# 5.3 Conclusion

In this chapter different points concerning the wrinkling mechanics have been put forward. The buckling phenomenon has been highlighted in two different ways. The first one is to show buckling in a tensile test. During these tests, 1 (MD) or 2 (CD) buckling waves appeared. The values were compared with the values that could be obtained with the Zhu model [97]. The experimental criterion chosen over estimated the stress values for which buckling could occur. However, the orders of magnitude are respected. The other way to generate buckling and by extension wrinkles is to use the coating driver by choosing the values of misalignment angle and web tension. Wrinkling phenomena have been observed on different papers and at different scales. The wrinkle shapes could be modelled with a 4-parameter Weibull law. Knowing the wrinkle shape and their location on the web width makes it possible to choose the type of correction to be made (roll shape, orientation, etc.) and can be a measure of sensitivity / a criterion of discrimination to the wrinkle for different papers. At the microscopic scale, delamination was observed, where pinching was observed at the macroscopic scale. In order to model the wrinkling phenomenon on the pilot, laws proposed in the literature by Gehlbach or Hashimoto were used [124][122]. In order to use these laws, it was first necessary to know the dry and wet properties of the papers used. This study has enabled the development of a new parameter called "WSD tangent modulus" and noted  $E_{w,tan}$ . This parameter makes it possible to quantify the evolution of the mechanical properties of the paper over time, during a WSD test. In addition, thanks to tensile tests on wet paper specimens, it was possible to model the evolution of Young's moduli, as a function of absorptiveness  $A_s$ , using a Cross-like model. Finally, the comparison between the experimental values obtained on the pilot and the models showed that the experimental values were very far from those found in the literature. The hypothesis made to explain this difference is that in our study, the web speed was much lower than in Hashimoto's work. This impacts the air film that may exist between the roll and the paper. This affects the

friction coefficient  $\mu$  between paper and roller and therefore the critical misalignment angle  $\theta_{cr}$ . However the model isolated properly the wrinkled and unwrinkled areas.

# Chapter 6

# Study of the coating process on the laboratory pilot

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In this last chapter results, the process aspects of this project will be discussed. First, the temperature measurement during the process on the laboratory coating pilot will be presented. A study of the factors impacting the non-contact temperature measurement of the paper web by IR measurement will first be carried out; before looking at the temperature profile on the web during the process. Finally, it will be shown to what extent temperature monitoring on the coating pilot is useful in the context of laboratory coating. This section only focussed on the GHDS 35 paper.

In a second step, an optimisation of the process will be presented. This will use the previous chapters in order to create a control map that will allow the process to be carried out under the best conditions while controlling the web speed, the web tension and the misalignment angle. Following this optimisation, the papers obtained will be presented and a perspective will be proposed for the use of CPRAW and CPBS papers.



Figure 6.1: Measured temperature by the IR sensor (°C) versus the heating temperature (°C) and measuring height  $h_s$  (mm) (standard deviation: ±1 °C).

# 6.1 Control of the temperature during the process

# 6.1.1 Factors influencing a non contact IR temperature measurement

First of all, the impact on the temperature measurement of the measuring height  $h_s$  (mm), the measuring angle  $\kappa_s$  (°) as well as the emissivity set on the sensor  $\varepsilon_s$  have been studied. In Figure 6.1, the temperature measured by the sensor  $T_{measured}$  is compared with the heating temperature  $T_{heating}$ , which the paper sample is supposed to reach, for different measuring heights. It should also be noted that the measurements are made for a measurement angle  $\kappa_s = 0^\circ$  and an emissivity  $\varepsilon_s = 0.95$  [147].

Thus, Figure 6.1 shows that for temperatures between 20 °C and 60 °C, no major difference is found between the heating temperature and the measured temperature. However, from a heating temperature greater than 60 °C, the measuring height starts to impact more and more the temperature measured by the sensor. Indeed, a difference of 20 °C can be observed between the heating temperature and the measured one for a measuring height  $h_s = 300$  mm. This continues to increase up to 190 °C where a difference of 40 °C can be observed between the measured and heating temperature for  $h_s = 250$ mm. The origin of this variation seems to be twofold: the further the sensor moves away from the measuring sample, the more the measuring surface grows and thus if the heating of the sample is heterogeneous, the measured temperature (which is an average over the measuring surface) will be affected. The other important point is the increasing impact of the environment, whose temperature can change the measured temperature, as well as a draught that will be more easily noticed if the sensor moves away from the sample.

Figure 6.2 shows the volution of the measured temperatud versus the heating temperature at different measure angle  $\kappa_s$  which varies from 0 ° to 60 ° ( $h_s = 150$  mm and  $\varepsilon_s = 0.95$ ). Small



Figure 6.2: Measured temperature by the IR (°C) sensor versus the heating temperature (°C) and measuring angle  $\kappa_s$  (°) (standard deviation: ±1 °C).



Figure 6.3: Schematic views of the impact of the measurement angle on measuring area shape (h = 150 mm).

differences are observed between the heating temperature and the measured temperature up to 60 °C. However, as for Figure 6.1, above 60 °C significant and not negligible differences between  $T_{heating}$  and  $T_{measured}$  are observed. Indeed, differences of 50 °C are observed for  $T_{heating} = 190$  °C with a measurement angle  $\kappa_s = 60$  °. In addition, it is also possible to note that the curve corresponding to the equality between  $T_{heating}$  and  $T_{measured}$  is close, or merge with the curve for a measurement angle of 0 °.

The origin of these variations seems to be the variation in size and shape of the measuring area. Figure 6.3 may help to understand this phenomenon. Using the sensor manufacturer's data [3], it is possible to obtain the size and shape of the measuring area as a function of  $h_s$  (mm) and  $\kappa_s$  (°). Two measuring angles  $\kappa_s$  were tested in order to show the evolution of the measured surface.

For  $\kappa_s = 0$  ° (Figure 6.3 (a)), the measurement surface is a disc with a center of coordinates



Figure 6.4: Highlighting of the evolution of the surface of (a) the measurement area and (b) the evolution of the ellipse-centre distance of the sample (OM distance).

(0.0), whose radius increases as the measuring height  $h_s$  increases. However, when  $\kappa_s$  increases, the measuring disc becomes a measuring ellipse whose center is no longer (0,0) but M(x,0)where  $x \in \mathbb{R}^*_+$  and such as  $x = f(\kappa_s)$  (Figure 6.3 (b)). This symbolizes the translation of the center of the ellipse M along the horizontal axis x. The variation of the large radius of the ellipse remains minimal for  $\kappa_s = 30$  ° compared to the radius of the circle for a given  $h_s$ . However, at  $\kappa_s = 60$  °, the elliptic shape is quite recognizable and the variation of the large radius of the ellipse is very important.

It is also illustrated with Figure 6.4. In fact, with this figure, it is easy to show the impact of  $h_s$  and  $\kappa_s$  on the measuring area and the *M*-point shift. One will even notice that for  $h_s = 300$  mm, the measuring ellipse is outside the sample area therefore unheated areas could be seen by the sensor. It is also necessary to consider the possible variations of out-of-plane heights which could cause other problems.

The last point of attention is the emissivity set on the sensor  $\varepsilon_s$ . In Figure 6.5, the measured temperature is again compared to the heating temperature but this time by varying the emissivity  $\varepsilon_s$  between 0.1 and 1.In this case  $h_s = 150$  mm and  $\kappa_s = 0$ °. As a reminder, the emissivity  $\varepsilon_s$  corresponds to the radiative flux of the thermal radiation emitted by a surface element at a given temperature, compared to the reference value which is the flux emitted by a black body at this same temperature.

As soon as the temperature exceeds 25°C, the emissivity impacts more and more the temperature measurement when  $\varepsilon_s < 0.80$ . Indeed, when  $T_{heating} = 190$ °C, a difference of 610°C is noted between the heating and the measured temperature for  $\varepsilon_s = 0.1$ . This gap decreases with the increase of  $\varepsilon_s$  until it reaches the limit represented by the heating temperature (curve *Measured temperature = Heating temperature* on Figure 6.5).

In order to understand this phenomenon, it seems interesting to refer to Stefan-Boltzmann's law (equation 6.1 [148] considering the emissivity  $\varepsilon_s$ :

$$M = \varepsilon_s \cdot \sigma \cdot T^4 \tag{6.1}$$

where  $T_{measured}$  is the absolute temperature (K), M is the energy emittance  $(W \cdot m^{-2})$  and  $\sigma$  the Stephan-Boltzmann constant (5.6697.10<sup>-8</sup> $W \cdot m^{-2} \cdot K^{-4})$ . It is therefore realized that a



Figure 6.5: Measured temperature by the IR sensor (°C) versus the heating temperature (°C) and sensor emissivity  $\varepsilon_s$  (standard deviation:  $\pm 1$  °C).

| <br>               |            |      |      |      |      |      |      |      |      |      |      |      |
|--------------------|------------|------|------|------|------|------|------|------|------|------|------|------|
|                    | Emissivity |      |      |      |      |      |      |      |      |      |      |      |
| $T_{heating}$ (°C) | 0.10       | 0.20 | 0.30 | 0.40 | 0.50 | 0.60 | 0.70 | 0.80 | 0.85 | 0.90 | 0.95 | 1.00 |
| 21.3               | 0.1        | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.1  | 0.0  | 0.0  | 0.0  | 0.0  | 0.0  |
| 57.5               | 50.4       | 26.7 | 17.0 | 11.4 | 7.7  | 5.2  | 3.2  | 1.7  | 1.1  | 0.5  | 0.0  | 0.5  |
| 100.0              | 78.2       | 42.0 | 26.5 | 17.6 | 12.0 | 7.8  | 4.9  | 2.6  | 1.7  | 0.8  | 0.0  | 0.9  |
| 120.0              | 92.4       | 48.7 | 31.0 | 20.9 | 14.1 | 9.4  | 5.9  | 3.1  | 1.8  | 0.7  | 0.0  | 1.1  |
| 150.0              | 108.9      | 57.0 | 35.8 | 24.9 | 16.6 | 11.5 | 7.4  | 3.6  | 2.6  | 1.4  | 0.0  | 0.7  |
| 190.0              | 130.1      | 69.1 | 43.6 | 29.4 | 20.2 | 13.6 | 8.6  | 4.6  | 2.9  | 1.4  | 0.0  | 1.3  |

Table 6.1: Relative error (%) on the measured temperature compared to a reference  $(\varepsilon_s = 0.95).$ 

change in emissivity will impact the temperature read by the sensor and thus generate an error [149]. The relative error  $\delta_{\alpha_r}$  (%) was calculated as follows (equation 6.2) and reported in Table 6.1

$$\delta_{\alpha_r} = \frac{T_{measured,\varepsilon_s} - T_{heating,\varepsilon_s=0.95}}{T_{heating,\varepsilon_s=0.95}} \times 100$$
(6.2)

Table 6.1 shows that the relative error on the measured temperature related to the emissivity  $\varepsilon_s$  setting has a non-negligible impact. Indeed, relative errors of 5% or more are common. Moreover, this is mostly the case for temperatures greater than or equal to 100 °C. For example, when  $\varepsilon_s = 0.1$ ,  $\delta_{\alpha_r} = 78.2\%$  for  $T_{heating} = 100$ °C, which can have a considerable impact on the process and the product.

# 6.1.2 Inhomogeneous temperature and sensor position on the web width

This part deals with the positioning of the temperature sensor on the paper width. Preliminary tests had highlighted a temperature heterogeneity at the exit of the IR dryer. The hypothesis is that the positioning of the sensor on the web width would impact the measurement and thus mislead an operator in a paper-mill. Figure 6.6 represents the position of the isotherm curves on a web coming out of an IR dryer, for web speed ranging from 5  $m \cdot min^{-1}$  to 10  $m \cdot min^{-1}$ .

As can be seen, the area under a given isotherm decreases as the web speed increases. In fact, the dryer's power is constant, it delivers the same energy in a given time. However, as the speed increases, the time available for the paper to recover this energy and to dry is reduced. Thus, at a higher speed, paper will heat less and will exit the dryer colder.

About the shape of the temperature profiles, it can be seen that the different isotherms are not straight vertical lines. This could be related to the difference in energy that the paper web receives at its centre and at its edges. Figure 6.8 propose an explanation to this phenomenon.

By considering the problem symmetrical (OO' axis symmetry), it is noted that the reception areas 1 and 1' are very brightly illuminated by the IR lamp: they receive energy from the emission points O, A, A', B and B'. As for the reception zones 3 and 3' only receive energy from the emission points B, B', C and C'. Moreover, the emission zone of these last 2 points is only 50% useful. Please note that, as the IR dryer manufacturer does not give all the characteristics of their equipment, Figure 6.8 is a schematic figure to illustrate the above hypothesis. However, one side (0 mm) seems hotter than the other (300 mm). Asymmetric heating of the IR lamps or an off-centred web could be the reason.

If the attention is now focused on the positioning of the sensor on the web, considering the information given in Figure 6.6, it is legitimate to wonder where and how exactly to put the sensor. Depending on the position on the web width and the temperature profiles, the measurement would not be the same everywhere on the web width. Figure 6.9 shows an IR image of the paper web after the IR dryer. Using processing software, grey levels (corresponding to temperatures) were measured in 3 different surfaces to see the impact of the shape of the measurement area.

It is now possible to see that in a disc-shaped measurement area (sensor perpendicular to the web), an average temperature of  $113 \pm 9$  °C is measured, just like for the horizontal ellipse. For the vertical ellipse, the average temperature measured is  $128 \pm 15$  °C. With the uncertainties, it can be seen that no statistical difference is seen. However, when the temperature is read on the sensor by a machine operator, for example, only the mean value will be visible. This will result in an incomplete interpretation of the measurement. Thus, it will be more suitable to work with a disc-shaped measurement area to avoid any lecture measurement error and to keep a good runnability.

Thus, when using a temperature sensor, care must be taken to ensure that the emissivity  $\varepsilon_s$  is correctly adjusted if possible. An error of 0.2 on the emissivity is acceptable to have an accurate measure (with 2.6% error at 100 °C). The angle of measurement  $\kappa_s$  must be equal to  $0 \pm 2$  °, between the studied support and the sensor. The distance  $h_s$  between the sensor and the substrate depends on what must be measured but the further away you are, the larger the



(c) Speed: 20  $m \cdot min^{-1}$ 

Figure 6.6: Highlighting of the evolution of temperature isotherms on the paper web according to different web speeds (standard deviation:  $\pm 2$  °C). 300 mm correspond to the driver side of the coating pilot.



Figure 6.7: Displacement of the 85°C isotherm at different web speeds (standard deviation:  $\pm 2$  °C). 300 mm correspond to the driver side of the coating pilot.



Figure 6.8: Area illuminated by an IR lamp and overlapping of the illumination areas).



Figure 6.9: Different placement for IR sensors on a web after an IR dryer (web speed: 5  $m \cdot min^{-1}$ ,  $h_s$  and  $\varepsilon_s$  constant,  $\kappa_s = 60^{\circ}$  for the ellipses).

measurement area will be and will consider temperature heterogeneity. In the present case, a measurement angle  $\kappa_s = 0$ , a measurement height  $h_s = 30mm$  and an emissivity of  $\varepsilon_s = 0.95$  are kept and will enable to have good measures.

The study of the temperature profile at the exit of the dryer can be a good element of



Figure 6.10: Temperature monitoring screen installed next to the driver.

decision to choose the exact location on the web width of a temperature sensor with the couple (height h, position on width). Moreover, it can also help to understand problems induced by heterogeneous drying. In our case, the placement at 30 mm from the dryer outlet and in the middle of the web would be relevant.

# 6.1.3 Following the process temperature

This sub-section will look at the practical use of the temperature sensors studied earlier. These are installed on the coating pilot and are connected to a data acquisition card, which is connected to a computer. A home made python code is used for data acquisition and communication between the different elements (cf. Figure 6.10).

It can be seen immediately that the signal is very noisy. This phenomenon will be found on the other figures resulting from the measurements of temperatures during coating on the pilot. No explanation has been found to explain this phenomenon which was not present during the laboratory measurements presented subsection 6.1.1. But, speed could be the reason of this noisy signal. Figure 6.11 shows the temperature data recorded during a run on 22 March 2022. The temperature T0 is measured after the coating station, 200 mm before the entrance to the IR dryer. The temperature T1 is measured 300 mm after the exit of the IR dryer. The temperature T2 is the temperature of the paper web between the two hot air dryers. Finally the temperature T3 is measured 230 mm after the exit of the second hot air dryer.

Between 0 and 2000 s, the two hot air dryers are switched on, so that the set temperatures, 130 and 150 °C respectively for hot air dryers A and B, can be reached, according to an internal temperature control loop. Once the plateaus are stabilised, the IR dryer is switched on. However, for safety reasons, the IR dryer only works if the paper web has a minimum speed of  $3 \ m \cdot min^{-1}$ . Therefore, the paper speed is set to  $5 \ m \cdot min^{-1}$  in order to allow the IR dryer to start. We can now look at the events taking place between 2100 and 3900 s. It can be seen that the temperature T1 (red curve) drops 5 times in the considered time interval. This is due to the contact of the paper with the applicator roller. The starch gel is then deposited on the paper. The energy used to heat the paper before is used to dry the deposited (aqueous) starch gel. The



Figure 6.11: Trial conducted on 22-03-2022 on the GHDS 35 paper with a starch gel coating.

paper therefore comes out cooler. The different peaks can be explained by repeating the tests with different parameters. Shortly before 4000 s, there is a clear drop in the temperatures T1, T2 and T3. This phenomenon is due to a breakage of the paper web. Following this problem, it takes about 30 minutes to clean and replace the web. It is also necessary to wait for the hot air dryers temperature to decrease to avoid any risk of burning. This time is reduced by allowing the hot air to come on. However, this will make it more difficult for the web to pass through the hot air dryers because of the air circulation. At 6000 s, the same process resumes: heating the hot air dryers, heating the IR dryers and resuming the tests.

Figure 6.12 shows the measurements taken on 23 May 2022, on CPRAW paper and GHDS 35, during a water coatin. The paper is just re-wetted with the applicator roller and the excess is removed with a Mayer bar .002 or .012 here.

Between 0 and 400s, the system worked with GHBS 35 paper. At 400s, the IR and hot air drying systems are voluntarily shut down. This can be seen by the stepwise decrease of T1: first the dryer is stopped but the web is still moving to avoid any risk of overheating (first step); then the web is also stopped (second step). In 400 and 1200 s the GHBS 35 is replaced by CPRAW paper. A first heating phase is performed ("Heating n°1"). This is fast (250 s) because the system was not completely cooled down. Then the first test starts with the Mayer bar .002. We start slowly to see the behaviour of the paper by increasing the speed to 20  $m \cdot min^{-1}$ . Once this speed has been reached, we go back up to 15, 10, 7.5 and 5  $m \cdot min^{-1}$  in order to be able to take photos with the D.I.C. system. It is then decided to carry out the same tests with the Mayer .012 bar (which means that the excess of water removed will be more than with the .002). At 20  $m \cdot min^{-1}$ , the web resisted. At 15  $m \cdot min^{-1}$ , it breaks directly after the IR dryer. The test is stopped.



Figure 6.12: Trial conducted on 23-05-2022 on CPRAW paper and GHDS 35 paper with a "water coating".

Finally, Figure 6.13 represents the data acquired during a trial carried out on 24 May 2022. "Trial n°1" was performed on the CPRAW with a .006 Mayer bar. Then the reel is changed to CPBS paper. The latter is very difficult to use and broke several times as it seams very sensitive to water. It was possible to use the CPBS paper only at 30  $m \cdot min^{-1}$ , with a Mayer bar .002.



Figure 6.13: Trial conducted on 24-05-2022 on CPRAW paper and CPBS paper with a "water coating".

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Thus, after observing the 3 previous figures, several conclusion can be drawn. First of all, temperature sensors are very useful in order to better understand the phenomena taking place during the process. They allow the monitoring, indirectly, of certain production events: change of equipment, web breakage, coating, preheating of dryers. They also make it possible to determine, thanks to these same indirect measurements, the time required for a given operation. The most obvious example is web breaking. It takes up to 30 minutes to restart paper production on our pilot. In this case, the temperature sensors really allow us to acquire information on production and their importance is not negligible. Overheating can lead to deformation of the material, and underheating will lead to inadequate moisture content of the material, leading to problems for future use. In an industrial case, the means available and implemented are considerably more important and the use of temperature sensors is one means among others to monitor production.

# 6.2 **Process optimization**

In this part, process optimization will be discussed. In a first step, the results presented in the previous chapters will be used together to present a control map to drive the process in the best way. To do so, the models described and developed previously will be used together. In a second step, the coated papers will be presented and briefly studied.

# 6.2.1 Process regulation: web speed, tension and misalignment angle

On the coating pilot presented previously, different parameters can be controlled: temperature, speed, web tension, misalignment angle, number of IR lamps on,... Within the framework of this project, we have chosen to take into account the speed, web tension and misalignment angle in order to build a process control document.

# 6.2.1.1 Creation of a control map to run the coating process

In order to run the process in the best possible way, the idea came up to create a document that could be used by all people, from operators to engineers. The choice fell on a control map. The "manufacturing" philosophy of the latter is presented in Figure 6.14.

The starting point is the web speed  $V_{web}$ : this is between 5 and 40  $m \cdot min^{-1}$  on the pilot. From this speed, the contact time  $t_c$  between the water and the coating is defined. This contact time is defined as a function of the distance that the paper travels between the coating station and the IR dryer inlet. It is noted  $d_{c-IR}$  and is equal to 0.70 m. Consequently,  $t_c$  is defined by the equation 6.3

$$t_c = \frac{d_{c-IR}}{V_{web}} \tag{6.3}$$

The time  $t_c$  is used in the following equation relating the absorptiveness  $A_s(t)$  and time. The equation 6.4 is thus obtained.



Figure 6.14: Construction diagram of the control maps as a function of the paper absorptiveness or of the web speed.

$$A_s(V_{web}) = A_{eq} \left( 1 - exp^{\frac{d_{c-IR}}{\tau_2 \cdot V_{web}}} \right)$$
(6.4)

Subsequently, the equation 5.6 and the equation 5.7 will allow the link between the Young's moduli  $E_{MD}$  and  $E_{CD}$  and the absorptiveness  $A_s(V_{web})$ . Note that in this scheme a correction of the Poisson's ratio  $\nu_{xz}$  and  $\nu_{zx}$  will be made thanks to Baum's empiric models (equation 3.4). The Poisson's ratio and Young's modulus will be inserted in the equations of the misalignment angle (equation 5.1) and the critical band tension (equation 5.2). With this approach, it was possible to generate control maps as a function of absorptiveness Figure 6.15 and Figure 6.16.

The difference between Figure 6.15 and Figure 6.16 lies in the variation of the  $\beta$  value, which corresponds to the web aspect ratio. Similarly, the control maps Figure 6.17 and Figure 6.18 were generated but this time as a function of the web speed.

What can be seen in Figures 6.15, 6.16, 6.17, 6.18 is that the higher the coefficient of friction, the lower the critical web tension. Moreover, this critical web tension decreases as the absorptiveness increases (and therefore as the web speed decreases). Regarding the impact of  $\beta$ , we note that the greater it is, the less tolerant the system is to de-salting, especially at high absorptiveness (and therefore at low web speed).

The remaining question is: how to use these maps? We invite the reader to proceed as follows using Figure 6.17b. Choose a web speed value and draw a vertical line on the map starting from the chosen speed. Choose a web tension value and draw a horizontal line from that web tension value. The intersection of the horizontal line and the vertical line will give the maximum permissible misalignment angle value to avoid shear wrinkles. If the web tension value is below the critical web tension value, it is even better: you have "the boots and the umbrella". To give an example, if the chosen speed is  $5 m \cdot min-1$  and the chosen web tension is 200  $N \cdot m^{-1}$ , then the intersection of the two lines gives a critical misalignment angle value of 1.20 ° (in Figure 6.17b). If this angle is too high, it is then possible to decrease the speed or increase the web tension. This corresponds to what David Roisum [54] already proposed for the web tension but it is the opposite of what he proposed for the speed. Indeed, for the speed, the graph proposed by David Roisum was not in the framework of a coating process.

However, one point remains sensitive. Experimentally, creases could appear although no roll misalignment could be measured or at very small misalignments, especially on rewetted papers. On these wrinkles, one point was striking: it was parallel to the direction of paper travel and not aligned like the classic shear wrinkle. Earlier in this paper, tension buckling phenomena were discussed, but in the context of tensile testing. It would appear that tension buckling is also a phenomenon present on the pilot but more in the context of rewetted papers. To justify this, the evolution of the buckling coefficient (according to MD)  $k_c$  as a function of  $\beta$  is again presented in the dry state, but also for a paper saturated with water Figure 6.19.

In Figure 6.19, it can be seen that for the same value of  $\beta$  in dry or wet conditions, and for the same number of folds *i*, the buckling coefficient is lower in wet conditions than in dry conditions. The buckling coefficient even collapses. By extension, the lower  $k_c$  is (for a given  $\beta$  and *i*), the lower the associated critical buckling stress will be to make the *i* troughs



Figure 6.15: Control map for GHDS 35, at different paper friction coefficient  $\mu$  and for a web aspect ratio  $\beta = 0.2$ . The green lines at the bottom of each subfigures corresponds to the value of the critical web tension that should not be exceeded in order to avoid shear wrinkling.



Figure 6.16: Control map for GHDS 35, at different paper friction coefficient  $\mu$  and for a web aspect ratio  $\beta = 0.5$ . The green lines at the bottom of each subfigures corresponds to the value of the critical web tension that should not be exceeded in order to avoid shear wrinkling.



Figure 6.17: Control map for GHDS 35 as a function of web speed, at different paper friction coefficient  $\mu$  and for a web aspect ratio  $\beta = 0.2$ . The purple lines at the bottom of each subfigures corresponds to the value of the critical web tension that should not be exceeded in order to avoid shear wrinkling.


Figure 6.18: Control map for GHDS 35 as a function of web speed, at different paper friction coefficient  $\mu$  and for a web aspect ratio  $\beta = 0.5$ . The purple lines at the bottom of each subfigures corresponds to the value of the critical web tension that should not be exceeded in order to avoid shear wrinkling.



Figure 6.19: Buckling coefficient  $k_c$  versus aspect ratio  $\beta$  for GHDS 35 in MD, in dry (left) or fully wet (right) state.

appear. Thus, it is possible to understand that in the case of the pilot, when the paper is wet, a combination of shear buckling and tension buckling effects can exist and lead to the appearance of wrinkles although very little (if any) misalignment has been measured. It also highlight that the Hashimoto model is incomplete : tension buckling without misalignment should be added to the model. In addition, the control charts do not take into account the change in stress at break between dry and wet paper, and the deformation phenomena (as observed on the WSD) that may be present.

The readers must keep in mind that the presented control maps are valid for a given triptych paper, coating color and coating device. Nevertheless, the control map is a very useful tool to help the process control and the concept could be reused in the industrial context. It could even be improved thanks to the experience of the operators on the machine. Indeed, operators with 10, 15, 20 or 30 years of experience in paper mills are a very important resource, allowing to advance the understanding of certain phenomena sometimes difficult to approach from a theoretical point of view.

### 6.2.1.2 Use of D.I.C during the process

As presented earlier in this document, a digital stereo-vision system have been installed on the coating pilot for process monitoring. This adapted system using stereo-vision technology have been designed to enable wrinkles detection and characterisation during processing on the coating pilot. The APS-C (Advanced Photo System type-C) sensors of the two DSLR with the 24 mm focal length of the two lenses give a 49,84 ° horizontal field of view that allows placing the cameras at approximately 35 cm from the characterised paper to visualise the whole width. Considering that configuration and the definition of the DSLR sensors (5184 x 3456  $px^2$ ) the resolution of the digital images is about 63  $\mu m \cdot px^{-1}$ . Such a system is compact and might detect and analyse submillimetric wrinkles. The distance and the tilt between the cameras are approximately, and respectively, 30 cm and 30 °.

The stereo-system is installed on a rigid metallic truss-structure that enables adjustments



Figure 6.20: Stereo-system mounted on the coating pilot (left) and printed paper with wrinkle taken from both cameras (top right). 3D Reconstructions (bottom right) have been performed in order to analyse the wrinkle geometry.

for clear and sharp images acquisition. During the first trials done, it seems that this truss strucutre does not suffer form vibration created by the coating pilot. DSLR cameras are remotely controlled and energetically autonomous for eliminating every noise after calibration. After installation of the image acquisition system, the first step consists on calibrating the cameras using a chess-board that is located and rotated at different positions and angles every time a picture has been taken. The calibration phase is done once, since the system has not been moved or changed, and give the intrinsic parameters of the DSLRs and the positions and rotations of one camera relative to the other one. Knowing these parameters, it is possible to compute the position of a point in the 3D space if that point is observable on both pictures taken from the two DSLRs thanks to triangulation computation.

A hand-crafted code has been developed in order to reconstruct the surface of the characterized paper thanks to stereo-vision. Difficulties in that project consist on correlating both images since the surfaces to characterised are uniformly diffused whether the wrinkles are not big enough, and computing quickly to correct the pilot behaviour fast enough. At the time of writing, the first difficulty has been resolved by projecting a precise and random speckled pattern on the surface of the paper. Considering the other difficulty, the code is being developed in order to increase the computation speed.

A first experiment of the stereo-system coupling to the computation code is shown in Figure 6.20. The characterised wrinkle is large, however that test proves the feasibility of the surface reconstruction. The 3D reconstruction (at the centre bottom) was chosen to be fast to compute with a large stereo-grid and small stereo research areas. Because of that last point, it was impossible to find the stereo-correspondent points at the top of the wrinkle (white areas on Figure 6.20). Another computation was performed in order to test the resolution of the system: the linear reconstruction of a cross-section of the wrinkle (at the right bottom). The linear profile was chosen to be dense (very thin stereo-grid) with large stereo research areas. The linear reconstruction gave a complete profile of the wrinkle and proves that 3D reconstruction with dense stereo-grids and large research areas might characterise wrinkles that appear on the coating pilot. Tests on smaller sizes of wrinkles are currently performed and multi-threading







(b) Right picture of the DIC system.

Figure 6.21: CPRAW paper with wrinkles passing in front of the DIC system and a speckles spotlight (red laser). A contrast issue is seen.

techniques are currently developed on the stereo-correlation part in order to speed up the process.

The DIC system have also been tested on the CPRAW paper as presented Figure 6.21. As seen, the image quality is not good and not enough contrast could be recovered and the exposure is not good. In fact, the photo set-up used were the ones for the GHBS 35. It means that if the paper is changed during the process, the camera set-up should also be changed. This could lead to movement and leads to another calibration.

Figure 6.22 show the GHDS 40 paper used on the pilot. One wrinkled s easily visible on the right photo but much less on the left one. The light used could be the reason of this, while creating a shadow on one side of the wrinkle. The pictures exposure are better even if they are still blur. The shutter speed of the cameras is difficult to adjust because a compromise must be found between a large aperture (f/18), a not too high ISO (=3200 here) value to avoid digital noise linked to the cameras and the shutter speed (1/250 s). It was therefore necessary to invest in industrial cameras more adapted to the phenomena (Figure 6.23).

The set-up with the new cameras is presented Figure 6.23. This new set-up used another code to take the picture. The same code than before is used to reconstruct the surface of the characterized paper thanks to stereo-vision

## 6.2.2 Characteristics of finished products

#### 6.2.2.1 A wrinkle free coated paper

Thanks to the coating process, it has been possible to produce some coated, wrinkle-free GHDS 35 papers. The characteristics of these papers are presented in Table 6.2. Firstly, there is a clear increase in grammage for the coated papers. This increase is significantly greater for the "GHDS 35 coated 1" reference because a Mayer .012 bar was used, unlike the "GHDS 35 coated 2" reference, which was coated with a Mayer .002 bar (less coating color). This impact of the coating color is also visible on the thickness, which increased following the coatings, but to a greater extent for the reference "GHDS 35 coated 1".

Regarding the mechanical properties, the Young's moduli according to MD increased with



(a) Left picture of the DIC system.



(b) Right picture of the DIC system. A wrinkle is present.

Figure 6.22: GHDS 40 paper with wrinkles passing in front of the DIC system and a speckles spotlight (red laser). The wrinkle is easily visible on the right photo but much less on the left one.



Figure 6.23: The new industrial cameras (in red) with the lens, installed on the D.I.C. system mounted on the coating pilot (model cameras: AV ALVIUM 1800U-1620M-CH-C - High resolution monochrome matrix camera).

| Characteristics            | GHDS 35           | GHDS 35 coated 1 | GHDS 35 coated 2 |
|----------------------------|-------------------|------------------|------------------|
| ${f G}~(g\cdot m^{-2})$    | $36.2 \pm 0.2$    | $37.9 \pm 0.3$   | $37.1 \pm 0.2$   |
| $\mathbf{t_f} \; (\mu m)$  | $32 \pm 1$        | $37 \pm 1$       | $35 \pm 1$       |
| $\mathbf{E_{CD}}$ (GPa)    | $4.15 \pm 1.17$   | $4.94 \pm 0.44$  | $5.01 \pm 0.28$  |
| $\mathbf{E_{MD}}$ (GPa)    | $8.92 \pm 0.88$   | $10.24 \pm 0.17$ | $10.62 \pm 0.58$ |
| Strain at break (MD) (%)   | $1.53 \pm 0.38$   | $1.49 \pm 0.21$  | $1.63 \pm 0.28$  |
| Strain at break (CD)(%)    | $5.52 \pm 0.22$   | $4.18 \pm 1.28$  | $4.51 \pm 0.97$  |
| Stress at break (MD) (MPa) | $76.23 \pm 14.85$ | $85.71 \pm 7.13$ | $85.82 \pm 6.36$ |
| Stress at break (CD) (MPa) | $49.89 \pm 1.79$  | $44.07 \pm 3.27$ | $44.38 \pm 1.50$ |

Table 6.2: Characteristics of GHDS 35 uncoated, coated with .006 Mayer bar and 15%wt coating color (GHDS coated 1) and coated with .012 Mayer bar and 15%wt coating color by weight (GHDS coated 2) Both colors contained 1% particles.

the coating. The Young's moduli following CD also seem to have increased but the standard deviation of  $E_{CD}$  of GHDS 35 does not allow for a statistical difference. The strains at break following CD or MD cannot be considered identical due to the overlapping standard deviations. Finally, the stresses at break can be considered identical according to MD but it seems that the coating reduces the stresses at break according to CD after coating.

The coated papers presented were made with a starch gel containing uncooked starch grains. As part of the Roll and Fun project preceding this thesis, a specification was defined with the following constraints:

- $\rightarrow\,$  The height of the starch grains outside the layer must be between 5 and 10  $\mu m.$
- → The density of starch grains on the surface of the deposited layer must be close to 3.2  $10^7$  particles  $\cdot m^{-2}$ .
- $\rightarrow\,$  The surface condition of the paper must be homogeneous.

Point number 1 of the specification is one of the goals of this thesis. Point number 2 has been studied briefly here, as shown in Figure 6.24, representing a coated paper with starch grains on its surface.

The number of grains was determined using thresholding and particle detection with the ImageJ software. Thus, the surface studied here is  $1.70 \ mm^2$  and 637 particles were detected. We therefore obtain a particle density of  $375 \ particles \cdot mm^{-2}$ , or  $3.75 \cdot 10^8 \cdot particles \cdot m^{-2}$ . The result obtained is above the value required by the specifications. We are therefore able to meet this criterion with our coating technique.

## 6.2.2.2 Extension to very lightweight paper grades

As mentioned earlier in this document, an opportunity arose during this project to obtain a roll of CPRAW and a roll of CPBS. These papers could only be roughly characterised, and the studies carried out for the most part on GHDS 35 could not be completed. However, it was possible to use these two papers during a test on the coating pilot. Phenomena already observed on GHDS 35 and GHDS 40 were observed but in a more pronounced way.



Figure 6.24: Starch particles on a GHDS 40 paper after coating with a .002 Mayer rod (picture obtained using SEM).

Figure 6.25a shows the CBPS paper between the two hot air dryers. There are large out-ofplane displacements: the paper undergoes what is called "flutting" in the printing industry. This term has been defined in the literature review. For fluting to occur there must be a combination of web tension, heat and hygroexpansion or water drying. In our case, it can be due to drying heterogeneity on the web as shown in the temperature profiles Figure 6.6. Figure 6.25b shows wrinkles forming on the roll before the first hot air dryer in the pilot. The wrinkles formed are parallel to the direction of the paper flow (the roll not being misaligned). The buckling tension phenomena could therefore be the cause of these folds. It should also be noted that the roller in the photo has a strong tendency to heat up. Consequently, this can cause thermal shock and promote shrinkage when the paper dries. Since wrinkles are a mechanical instability, this kind of thermal disturbance can promote the wrinkling phenomenon or even accentuate it.

In Figure 6.26, it shows the CPRAW paper in use on the pilot. In Figure 6.26a, the paper is fluttering and 8 bands of water are visible, making the paper more translucent. No reason for these bands was found. Figure 6.25b shows numerous wrinkles forming on a slightly misaligned roll (the amount of misalignment is not known).

In view of the large number of wrinkles, thresholding with ImageJ software was carried out in order to be able to discern them as well as possible. The results are presented in Figure 6.27. Each yellow band is linked to a peak where the gray value locally tends towards black. In this way, 18 wrinkles could be identified, without being evenly spaced. These wrinkles appear to be shear wrinkling, but in view of the number of folds, tension buckling phenomena may also be present and thus amplify the wrinkling phenomenon.



(a) Fluting of CBPS paper between the two hot air dryers.



(b) Wrinkling of CPBS paper after the IR dryer.





(a) Fluting of CPRAW paper after the IR dryer. Bands of water are visible and seem regular



(b) Shear wrinkling of CPRAW paper after the IR dryer.

Figure 6.26: Fluting and wrinkling on CPRAW paper during coating with water.



Figure 6.27: Counting the number of wrinkles using image analysis and tresholding.

## 6.3 Conclusion

In this chapter, different points concerning the process have been discussed. Firstly, the temperature of the sheet and its measurement through the use of temperature sensors. It was shown that the temperature sensors should be as perpendicular as possible to the surface of the paper, with an emissivity  $\varepsilon_s = 0.95$ . The distance between the sheet and the sensor depends on what is being measured. The distance between the sheet and the sensor depends on whether one wishes to measure a global temperature (distant sensor) or a local temperature (very close sensor). It was also shown that the temperature profil of the paper at the exit of the IR dryer shows that the sheet edges are cooler than the centre of the web. This heterogeneity during the drying process can be the cause of a heterogeneity of the water content on the web and consequently favour the wrinkling phenomena. It has been shown that, in the context of this study, temperature monitoring provides access to production events and better monitoring of the latter.

In a second step, the optimisation of the process was addressed. Through the creation of a control chart using the models developed in this project and those found in the literature. This map allows to link web speed, web tension and misalignment angle. It can be further improved by taking into account buckling tension phenomena and the limit stress at break of the papers, especially when they are wet. These phenomena have also been observed on CPRAW and CBPS papers, which seem to be much more sensitive to moisture. Finally, the GHDS 35 and GHDS 40 papers were characterised. It was even found that the specifications of the Roll and Fun project could be met to some extent. This process chapter also opens many doors and possibilities. For the time being, only one web tension measurement is on the pilot, but others could be installed. They could also be installed to a control system allowing to vary it and thus avoid wrinkles. The brake should also be changed : a torque-controlled unwind motor should be installed for better web tension control and connected to the web tension measuring roller. Finally, a study on the link between the Mayer bar and its paper coating color supply could be carried out. Empirically, it has been observed that a .002 or .006 mayer bar would limit the appearance of wrinkles because the water supply is lower. The sensor for this system could be the D.I.C system developed during this project. Finally, in order to best meet the specifications of the Roll and Fun project, a recirculation of the coating color could be implemented, with a system as shown in Figure 6.28.



Figure 6.28: Schematic diagram for the recirculation of the coating color on the coating pilot using an Arduino controller and two volume pumps.

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# Chapter

# General conclusion

In the context of this thesis, various points have been put forward. We will go through them in the chronological order of this document. First of all, we were interested in the penetration of water into the paper. Two main aspects were studied: the properties of the coating sauce and the wettability and absorption of water by the paper. In the study of the coating sauce it was shown that the cooking of the starch is an important point in the process, as this impacts on the rheology of the sauce. It was shown that there starch sauces has a rheofluidic behaviour (OdW law) and that its behaviour also depends on the temperature at which it is used (Eyring law), which is in line with the literature. The sedimentation of starch particles was studied in water and quickly observed in starch gel. The particles have a significant speed when considering the dimensions of the sauce storage tank on the pilot: it was estimated that it took less than 12 minutes for the heaviest particles to settle in the storage tank. For the coating sauce, the models calculated a sedimentation rate 10,000 times lower than in water. However, experimentally, sedimentation and aggregation of the starch particles in the starch gel was observed. A recirculation of the coating sauce should be installed to avoid this kind of sedimentation phenomenon.

The wettability and water absorption of GHDS 35 was also discussed. We started from the Lucas-Washburn law, for which we had to retrieve the different parameters allowing us to use it. An interesting point is that the SFEs of the paper showed larger dispersive components than the polar components on both sides. This possibly means that the fibres were treated with wet strength, thus explaining the high contact angles between water and paper on all sides. The study of water absorption by GHDS 35 paper was carried out using three methods: the COBB method, the DPM method, and the Paper discs stacking method. Over long times, the Cobb method showed a first order water absorption behaviour of the paper. The paper disc stacking method is a new method proposed to follow water absorption in paper at short times. Three models were tested on the experimental values: LW, first order and power law. The first order model seems to be the one that best models the observed behaviour. However, it is necessary to take into account the very large standard deviation of the experimental data. Then comes the need to optimise the protocol and the measurement apparatus. Finally, the DPA technique has shown a particular behaviour of the coated papers looking at an AKD treated paper. This confirms the hypothesis put forward following the determination of the SFE (Surface

Free Energy).

The second experimental part of this work was concerned with the properties and mechanical behaviour of wrinkled papers. Based on the literature on the occurrence of wrinkles in web materials, we investigated the impact of a roll misalignment angle and a critical tension at which wrinkles can occur. During in-situ tests, the tension buckling was observed in the following CD and MD. Wrinkles were also observed on the coating pilot by varying the web tension and the misalignment angle of a roll. These observations were made on 4 different light weight papers and the conclusions were the same: wrinkles appeared. The ex-situ observations were made on samples of wrinkled papers when using the coating pilot. Using the Alicona device, it was possible to confirm the asymmetric shape of the wrinkles, as well as a pinching phenomenon observed along the wrinkles. The shape of the wrinkles do not follow the MD: they are oriented due to the misalignment of the rollers. Microscopic observations using SEM and X-Ray tomography have allowed us to highlight the pinching phenomenon. The latter seems to be responsible for a decohesion of the fibrous network as well as a delamination of the industrially deposited layer on the GHDS 35.

Following these observations, modelling was carried out using models from the literature. The mechanical properties of the papers had to be determined. Two challenges were faced: the characterisation of wet paper (saturated in water) and the determination of Poisson's ratio. An elegant method was used to access the Poisson's ratio. Regarding the behaviour of the water-saturated GHDS 35 paper, we were able to quantify its drying in a conditioned room by a decreasing first order law. Following this, it was possible to model the evolution of Young's moduli as a function of the quantity of water absorbed per square meter of paper. The law used is inspired by Cross' law, and is a key element of this project. The measurement method still needs some improvement as a hysteresis in the water absorption of the paper may exist and may impact the evolution of the Young's moduli. Nevertheless, the observed behaviour is close to that of the literature: this is reassuring for the possible continuation of this work. The WSD allowed to highlight the  $2^{nd}$  order behaviour according to the CD and a first order behaviour according to the MD during this test. Thanks to the results obtained, a new parameter was identified: the tangent modulus obtained with WSD measurement. This parameter makes it possible to quantify the evolution of the mechanical properties of the papers as a function of the WSD test time, and consequently as a function of the quantity of water during an absorption phase. To improve the experiment, a measurement of local water content of paper, on the width should be installed.

All this information was used to feed the Hashimoto model for the appearance of wrinkles on the coating pilot. Our experimental values were compared with the model predictions. It was surprising to find that our values, especially the misalignment angle, are very large compared to the literature. Although not inconsistent, the slow speed used during the experiment could explain this difference. To a lesser extent, the discretization of the number of wrinkle in the Hashimoto model has been studied. We were able to show that making the variable representing the number of wrinkles integer led to not respecting the bounding equation allowing to define i



Figure 7.1: Evolution of paper quality. N°0 is a sample prepared during the Roll and Fun project, before this PhD thesis; N°1 is one of the first sample coated during this project; N°2 were made in March 2022 (the one below the arrow is nearly "perfect" but has no uncooked starch particles. Finally N°3 is the last sample coated in May 2022.

and to over or underestimate the misalignment angle from which wrinkles could appear. Nevertheless, the very notion of a non-natural number of wrinkles is difficult to grasp. However, this could be related to equilibrium transition zones. Finally, the analysis of the tensile tests and their comparison with the Zhu model validated our values. This model could also be used to predict the tension buckling that can occur on the pilot when the rolls are well aligned, the paper is wet and wrinkles are formed.

The last experimental chapter deals with the study of the coating process on the pilot itself. Two points were addressed: temperature measurement during the process and process optimisation. Temperature measurement during the process was studied using IR sensors. It was shown that the emissivity set on the sensors should be close to 0.95 and that the sensors should be as perpendicular as possible to the web. The distance between the sensor and the web is dependent on the value sought: local or global. This study also highlighted the non-homogeneity of the temperature isotherms at the outlet of the IR dryer on the paper. This phenomenon could also justify the fluting of the paper, due to heterogeneous drying, although no roll misalignment was observed. The sensors made it possible to follow the coating process during different runs and to illustrate the different events taking place during the process such as web breakage, equipment change or coating at different speeds. The last aspect of this chapter was the optimisation of the process by linking web tension, misalignment angle and web speed. For this, all the tools and models developed earlier have been used. Thus, we linked the web speed to the water absorption, which in turn was linked to the Young moduli by the Cross type law. This model was itself integrated with the laws proposed by Hashimoto, by adding a variation of Poisson coefficients thanks to the empirical model of Baum. This allowed the generation of process control and driving maps that allowed the determination of the misalignment angle not to be exceeded as a function of the pilot speed and the web tension. However, these charts do not take into account the phenomena of buckling tension. For this, it is necessary to use the  $k_c$  coefficient proposed by Zhu as a first approach. This thesis allowed to understand the phenomena related to the

appearance of wrinkles. This work offers a new perspective to the study of this kind of phenomenon. It would be interesting to acquire more data concerning the typical Cross like model of water absorption and Young's modulus of the paper. Being able to acquire more information with the DIC system developed during this thesis when the process is running would also be a plus for understanding the in-situ phenomena and regulating the process through measurement and control of web tension. A measurement of the moisture profile of the paper on the web would be a plus as well as a measure on the web tension along the web width. To conclude, we will answer this last question: was it possible to coat a paper, without wrinkles, with a starch gel containing starch granules? The answer is yes (Figure 7.1, because the process is now controlled through the creation of control maps and the process is waiting to be improved for this particular application.

# Bibliography

- [1] Timothy J Walker. The taxonomy of wrinkles. In *Tenth International Conference on Web Handling (IWEB*, page 15, Stillwater, OK., June 2009. Oklahoma State University.
- [2] FCBA. Mémento FCBA 2020, https://www.fcba.fr/ressources/memento-2020/.
- [3] Erik Orsenna. Sur la route du papier. Petit précis de mondialisation. Stock, Paris, 2012. Publication Title: Sur la route du papier.
- [4] Joël Boulier and Laurent Simon. Atlas des forêts dans le monde. Atlas/Monde. Autement, Paris, 2022.
- [5] Tatjana Stevanovic and Perrin Dominique. *Chimie du bois*. Presses polytechniques et universitaires romandes, Lausanne, 2009.
- [6] E. Renault. Délignification du bois de châtaignier par une approche de chimie verte. Mise en œuvre et impacts sur la structure et le potentiel anti-radicalaire des phytopolysaccharides extraits. Phd dissertation, Université de Limoges, December 2014.
- [7] Marie-Christine Trouy and Pascal Triboulot. Matériau bois structure et caractéristiques. *Techniques de l'ingénieur Les superstructures du bâtiment*, base documentaire : TIP253WEB.(ref. article : c925), 2019. fre.
- [8] Eero Sjöström. Wood Chemistry: fundamentals and applications. Academic Pr, San Diego,2. ed. edition, 1997.
- [9] Harry Phillips Brown, A. J. Panshin, and C. C. Forsaith. *Textbook of wood technology*. American forestry series. McGraw-Hill, New York, 1st edition edition, 1949. Publication Title: Textbook of wood technology.
- [10] D. H. Page. A method for determining the fibrillar angle in wood tracheids. Journal of Microscopy, 90(2):137–143, October 1969.
- [11] Mohamed Naceur Belgacem and Antonio Pizzi. Lignocellulosic Fibers and Wood Handbook: Renewable Materials for Today's Environment. Wiley, 2016.

- [12] Dietrich Fengel and Gerd Wegener, editors. Wood: Chemistry, ultrastructure, reactions. De Gruyter, 2011.
- [13] C. Monot. Contribution à l'étude des complexes lignine-hydrates de carbone (LCC) dans le bois: étude de l'impact des différentes étapes d'un procédé de bioraffinerie sans soufre sur les LCC. Phd dissertation, Université Grenoble Alpes, December 2015.
- [14] Roger M. Rowell, editor. Handbook of wood chemistry and wood composites. Taylor & Francis, Boca Raton, Florida, 2005.
- [15] Monica Ek. *Pulping chemistry and technology*. Number 2 in Pulp and paper chemistry and technology. De Gruyter, Berlin, 2009.
- [16] Herbert Holik. Handbook of paper and board. Wiley-VCH, Weinheim, 2006.
- [17] Valentin I. Popa, editor. Pulp production and processing: from papermaking to high-tech products. Smithers Rapra, Shawbury, 2013.
- [18] Herbert Sixta. Handbook of pulp, volume 1. Wiley-VCH, Weinheim, 2006.
- [19] C.J. Biermann. Handbook of Pulping and Papermaking. Elsevier Science, 1996.
- [20] Jean-Claude Roux. Désintégration et raffinage de la pâte à papier. Techniques de l'ingénieur Bois et papiers, base documentaire : TIP590WEB.(ref. article : j6903), 2008. fre.
- [21] André Lemaître. Procédés papetiers préparation des pâtes. Techniques de l'ingénieur Bois et papiers, base documentaire : TIP590WEB.(ref. article : j6901), 2003. fre.
- [22] E. Tourette. Étude mécanique et physico-chimique du contact rouleau papier lors du calandrage. Phd dissertation, École Nationale Supérieure des Mines de Paris, December 2007.
- [23] Ruben Miranda, Ana Balea, Emilia Sanchez de la Blanca, Isabel Carrillo, and Angeles Blanco. Identification of Recalcitrant Stickies and Their Sources in Newsprint Production. Industrial & Engineering Chemistry Research, 47(16):6239–6250, August 2008.
- [24] COPACEL. COPACEL, https://www.copacel.fr/, 2022-03-06.
- [25] Martin A. Hubbe, Douglas J. Gardner, and Wei Shen. Contact Angles and Wettability of Cellulosic Surfaces: A Review of Proposed Mechanisms and Test Strategies. *BioResources*, 10(4):8657–8749, September 2015.
- [26] Niskanen Kaarlo. Papermaking science and technology / book ed. Kaarlo Niskanen. 16. Paper physics. Papermaking science and technology. Fapet Oy Published in cooperation with the Finnish Paper Engineers' Association and TAPPI, Helsinki (Finlande), cop. 1998.
- [27] M. Bouchon. Etude de l'influence des phénomènes de mouillage sur la pénétration de l'eau dans le papier aux temps courts. PhD dissertation, Grenoble INP, May 2004.

- [28] T. Karppinen. Characterizing physical properties of wetting paper by air coupled ultrasound and light. Phd dissertation, University of Helsinki, September 2008.
- [29] M.J. Moura, P.J. Ferreira, and M.M. Figueiredo. Mercury intrusion porosimetry in pulp and paper technology. *Powder Technology*, 160(2):61–66, December 2005.
- [30] S. Rolland du Roscoat. Contribution à la quantification 3D de réseaux fibreux par microtomographie au rayonnement synchrotron : applications aux papiers. PhD Thesis, Université de Grenoble, 2007.
- [31] E. A. Barclay, J. E. Donahue, D. A. Hughes, R. H. Rogers, J. R. Simpson, and R. N. Thompson. *Preparation of paper coating colors*. TAPPI Press, New York, 1954.
- [32] Robert H. Mosher. The technology of coated and processed papers. Chemical Pub. Co, New York, 1952.
- [33] Lehtinen Esa. Papermaking science and technology / book ed. Esa Lehtinen; book reviewer Charles P. Klass. 11. Pigment coating and surface sizing of paper. Papermaking science and technology. Fapet Oy Published in cooperation with the Finnish Paper Engineers' Association and TAPPI, Helsinki, cop. 2000.
- [34] Jan C. Walter. The coating processes. TAPPI Press, Atlanta, 1993.
- [35] Pierre Valette and Christian De Choudens. Le bois, la pâte, le papier. CTP, Grenoble, second edition, 1989.
- [36] Naceur Belgacem. De la fibre à l'imprimé / Grenoble INP Pagora. Tome III. Procédés de finition et de transformation des papiers et cartons. Agefpi, Saint-Martin-d'Hères, France, 2016. Backup Publisher: École internationale du papier, de la communication imprimée et des biomatériaux Saint-Martin-d'Hères, Isère Publication Title: De la fibre à l'imprimé . Tome III . Procédés de finition et de transformation des papiers et cartons.
- [37] S. Cena. Etude d'un système d'enduction par presse à transfert de film. PhD dissertation, Grenoble INP, December 1997.
- [38] S. Moreau. Structure des couches pigmentaires : étude de leur séchage. PhD dissertation, Grenoble INP, 1994.
- [39] Alain Buléon, Gabrielle Véronèse, and Jean-Luc Putaux. Self-Association and Crystallization of Amylose. Australian Journal of Chemistry, 60(10):706, 2007.
- [40] D. Le Corre. Starch nanocrystals: preparation and application to bio-based flexible packaging. Phd dissertation, Université de Grenoble, October 2011.
- [41] Costas G. Biliaderis. Structural Transitions and Related Physical Properties of Starch. In Starch, pages 293–372. Elsevier, 2009.

- [42] Bernard Boursier. Amidons natifs et amidons modifiés alimentaires. Techniques de l'ingénieur Agroalimentaire, base documentaire : TIP700WEB.(ref. article : f4690), 2005. fre.
- [43] E. Schwach. Etude de systèmes multiphases biodégradables à base d'amidon de blé plastifié : relations structure-propriétés, approches de la compatibilisation. PhD dissertation, Université de Reims - Champagne Ardenne, 2004.
- [44] James N. BeMiller and Kerry C. Huber. Starch. In Wiley-VCH Verlag GmbH & Co. KGaA, editor, Ullmann's Encyclopedia of Industrial Chemistry, page a25\_001.pub4. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, January 2011.
- [45] G Bacquet. La physico-chimie des bains de couchage. Revue A.T.I.P, 50(4):8, July 1996.
- [46] J.F. Richardson and W.N. Zaki. The sedimentation of a suspension of uniform spheres under conditions of viscous flow. *Chemical Engineering Science*, 3(2):65–73, April 1954.
- [47] B. Gueslin. Etude de la sédimentation de particules non-browniennes dans un fluide thixotrope à seuil: la laponite. Phd dissertation, Université de Paris 6, November 2006.
- [48] James Brander and Ian Thorn, editors. Surface Application of Paper Chemicals. Springer Netherlands, Dordrecht, 1997.
- [49] J. Jäder. Consolidation and rheology at high solids content. PhD dissertation, Karlstad University, 2004.
- [50] Reinhard Sangl, Werner Auhorn, Werner Kogler, and Martin Tietz. Surface Sizing and Coating. In Herbert Holik, editor, *Handbook of Paper and Board*, pages 745–784. Wiley, 1 edition, April 2013.
- [51] Stephan F. Kistler, editor. Liquid film coating: scientific principles and their technological implications. Springer, Dordrecht, 1. ed edition, 1997. OCLC: 935042650.
- [52] Savolainen Antti. Papermaking science and technology. Fapet Oy Published in cooperation with the Finnish Paper Engineers' Association and TAPPI, Helsinki (Finlande), cop. 1998.
- [53] Jan C. Walter. Chapter 4: Drying. In *The coating processes*, page 260. Tappi, Atlanta, 1993.
- [54] David R. Roisum. The mechanics of web handling. TAPPI PRESS, Atlanta, 1998.
- [55] David R. Roisum. The mechanics of rollers. TAPPI Press, Atlanta, 1996.
- [56] Roll-2-Roll Technologies LLC. Roll-2-Roll, https://r2r.tech/, 2022-08-09.
- [57] William B. Gilbert. Optimizing web tension control for high productivity: Part 1. Official Publication of the Association of International Metallizers, Coaters and Laminators, (2019 - 2nd quarter):66-71, 2019.

- [58] PFF-online. Web tension control fundamentals, https://www.pffconline.com/ pffcon5/news/15515-web-tension-control-fundamentals, 2022-08-09.
- [59] J J Shelton. Simplified model for lateral behavior of short web spans. In Sixth International Conference on Web Handling (IWEB), page 16, Stillwater, OK., June 2001. Oklahoma State University.
- [60] David R. Roisum. The mechanics of web spreading Part 1. TAPPI Journal, 76(10):8, October 1993.
- [61] D. K. Owens and R. C. Wendt. Estimation of the surface free energy of polymers. Journal of Applied Polymer Science, 13(8):1741–1747, August 1969.
- [62] D. H. Kaelble. Dispersion-Polar Surface Tension Properties of Organic Solids. The Journal of Adhesion, 2(2):66–81, April 1970.
- [63] Naceur Belgacem and Alain Dufresne. Phénomène d'adhésion et le collage. In De la fibre à l'imprimé - tome 1 : Sciences de l'ingénieur pour les industries des fibres, des biomatéraux et de la communication imprimée, volume 1, page 28. Agefpi, Saint Martin d'Hères, 2016.
- [64] Robert N. Wenzel. Resistance of Solid Surfaces to Wetting by Water. Industrial & Engineering Chemistry, 28(8):988–994, August 1936.
- [65] David Quéré. Wetting and Roughness. Annual Review of Materials Research, 38(1):71–99, August 2008.
- [66] Nuria Gómez, Ester Quintana, and Juan Carlos Villar. Effect of Paper Surface Properties on Coated Paper Wettability with Different Fountain Solutions. *BioResources*, 9(3):4226– 4241, May 2014.
- [67] Hedieh Modaressi and Gil Garnier. Mechanism of Wetting and Absorption of Water Droplets on Sized Paper: Effects of Chemical and Physical Heterogeneity. *Langmuir*, 18(3):642–649, February 2002.
- [68] A. B. D. Cassie and S. Baxter. Wettability of porous surfaces. Transactions of the Faraday Society, 40:546, 1944.
- [69] A. Pons. Simulation numérique de la montée capillaire en espace confiné, en vue de l'application à des procédés d'élaboration de matériaux composites par imprégnation nonréactive ou réactive. PhD dissertation, Univesité de Bordeaux, October 2017.
- [70] D. Dallel. Etude expérimentale modèle de l'imbibition capillaire de substrats poreux à volume et structure de pores ajustables. Phd dissertation, Université de Haute-Alsace, December 2012.
- [71] P. Salminen. Studies of Water Transport in Paper during Short Contact Times. Phd dissertation, Abo Akademi, October 1988.

- [72] N. Fries. Capillary transport processes in porous materials experiment and model. PhD dissertation, Universität Bremen, 2010.
- [73] C. H. Bosanquet. On the flow of liquids into capillary tubes. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 45(267):525–531, 1923. Publisher: Taylor & Francis \_\_eprint: https://doi.org/10.1080/14786442308634144.
- [74] D Quéré. Inertial capillarity. Europhysics Letters (EPL), 39(5):533–538, September 1997.
- [75] Carina Waldner and Ulrich Hirn. Ultrasonic Liquid Penetration Measurement in Thin Sheets—Physical Mechanisms and Interpretation. *Materials*, 13(12):2754, June 2020.
- [76] J. Hyväluoma, P. Raiskinmäki, A. Jäsberg, A. Koponen, M. Kataja, and J. Timonen. Simulation of liquid penetration in paper. *Physical Review E*, 73(3):036705, March 2006.
- [77] R. J. Roberts. Liquid penetration into paper. PhD dissertation, Australian National University, September 2004.
- [78] Jianchao Cai, Tingxu Jin, Jisheng Kou, Shuangmei Zou, Junfeng Xiao, and Qingbang Meng. Lucas–Washburn Equation-Based Modeling of Capillary-Driven Flow in Porous Systems. Langmuir, 37(5):1623–1636, February 2021.
- [79] Sarah Krainer and Ulrich Hirn. Short timescale wetting and penetration on porous sheets measured with ultrasound, direct absorption and contact angle. RSC Advances, 8(23):12861–12869, 2018.
- [80] T. Karppinen, I. Kassamakov, J. Aaltonen, H. Pajari, and E. Hæggström. Measuring liquid penetration in the thickness direction of paper. *The European Physical Journal Applied Physics*, 32(1):65–71, October 2005.
- [81] Narpinder Singh, Jaspreet Singh, Lovedeep Kaur, Navdeep Singh Sodhi, and Balmeet Singh Gill. Morphological, thermal and rheological properties of starches from different botanical sources. *Food Chemistry*, 81(2):219–231, May 2003.
- [82] Narpinder Singh, Naoto Isono, Sathaporn Srichuwong, Takahiro Noda, and Katsuyoshi Nishinari. Structural, thermal and viscoelastic properties of potato starches. *Food Hydro*colloids, 22(6):979–988, August 2008.
- [83] Dominique Dupuis and Alain Ponton. Mesure de la viscosité principes généraux. Techniques de l'ingénieur Mesures physiques, base documentaire : TIP672WEB.(ref. article : r2350), 2021. fre.
- [84] Henry Eyring. Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates. The Journal of Chemical Physics, 4(4):283–291, April 1936.
- [85] Malcolm M. Cross. Rheology of non-Newtonian fluids: A new flow equation for pseudoplastic systems. Journal of Colloid Science, 20(5):417–437, June 1965.

- [86] Luiz Claudio F. Andrade, Jamilson A. Petronílio, Calos Edilson de A. Maneschy, and Daniel Onofre de A. Cruz. The carreau-yasuda fluids: a skin friction equation for turbulent flow in pipes and kolmogorov dissipative scales. *Journal of the Brazilian Society of Mechanical Sciences and Engineering*, 29(2):162–167, 2007.
- [87] Mohd I Nurul, B. M. N. Mohd Azemi, and D. M. A. Manan. Rheological behaviour of sago (Metroxylon sagu) starch paste. *Food Chemistry*, 64(4):501–505, 1999.
- [88] Yongfeng Ai and Jay-lin Jane. Gelatinization and rheological properties of starch. Starch Stärke, 67(3-4):213-224, March 2015.
- [89] T. Emilia Abraham. Stabilization of Paste Viscosity of Cassava Starch by Heat Moisture Treatment. Starch - Stärke, 45(4):131–135, 1993.
- [90] J.-L. Doublier. Rheological Studies on Starch Flow Behaviour of Wheat Starch Pastes. Starch - Stärke, 33(12):415–420, 1981.
- [91] R.G.M. van der Sman, Job Ubbink, Marina Dupas-Langlet, Magdalena Kristiawan, and Isabel Siemons. Scaling relations in rheology of concentrated starches and maltodextrins. *Food Hydrocolloids*, 124:107306, March 2022.
- [92] J.-Y Thebaudin, A.-C Lefebvre, and J.-L Doublier. Rheology of Starch Pastes from Starches of Different Origins: Applications to Starch-based Sauces. LWT - Food Science and Technology, 31(4):354–360, April 1998.
- [93] Douglas W Bousfield. Rheology Issues in the paper Industry. The British Society of Rheology, pages 47–70, 2008.
- [94] Dominique Dupuis and Alain Ponton. Mesure de la viscosité viscosimètres et rhéomètres. *Techniques de l'ingénieur Mesures physiques*, base documentaire : TIP672WEB.(ref. article : r2351), 2021. fre.
- [95] El Kissi, S Nigen, and Frédéric Pignon. Glissement en rhéologie. Rhéologie, 10:13–39, November 2006.
- [96] Ting Wang, Yifan Yang, and Fan Xu. Mechanics of tension-induced film wrinkling and restabilization: a review. Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences, 478(2263):20220149, July 2022.
- [97] Juner Zhu, Xiaowei Zhang, and Tomasz Wierzbicki. Stretch-induced wrinkling of highly orthotropic thin films. *International Journal of Solids and Structures*, 139-140:238–249, May 2018.
- [98] N Friedl, F.G Rammerstorfer, and F.D Fischer. Buckling of stretched strips. Computers & Structures, 78(1-3):185–190, November 2000.
- [99] F. G. Rammerstorfer. Buckling of elastic structures under tensile loads. Acta Mechanica, 229(2):881–900, February 2018.

- [100] E. Cerda and L. Mahadevan. Geometry and Physics of Wrinkling. *Physical Review Letters*, 90(7):4, February 2003.
- [101] N. Jacques, A. Elias, M. Potier-Ferry, and H. Zahrouni. Buckling and wrinkling during strip conveying in processing lines. *Journal of Materials Processing Technology*, 190(1-3):33–40, July 2007.
- [102] Nicolas Jacques and Michel Potier-Ferry. On mode localisation in tensile plate buckling. Comptes Rendus Mécanique, 333(11):804–809, November 2005.
- [103] N. G. M. Jacques. Modélisation et étude du plissement des tôles lors de leur transport en continu dans les usines sidérurgiques. Phd dissertation, Université Paul Verlaine, Metz, October 2004.
- [104] Eric Puntel, Luca Deseri, and Eliot Fried. Wrinkling of a Stretched Thin Sheet. Journal of Elasticity, 105(1-2):137–170, November 2011.
- [105] Philippe G. Ciarlet. A justification of the von Kármán equations. Archive for Rational Mechanics and Analysis, 73(4):349–389, December 1980.
- [106] Wei Tang, Jiankui Chen, and Zhouping Yin. Elastic buckling analysis of webs transported through rollers with misalignment. *Thin-Walled Structures*, 121:1–7, December 2017.
- [107] Chung Hwan Kim. Stress distribution and wrinkling of webs under non-uniform and asymmetric edge loading. International Journal of Solids and Structures, 46(3-4):851–859, February 2009.
- [108] C. C. Lin and C. D. Mote. The Wrinkling of Rectangular Webs Under Nonlinearly Distributed Edge Loading. *Journal of Applied Mechanics*, 63(3):655–659, September 1996.
- [109] A. Kulachenko. Mechanics of Paper Webs in Printing Press Applications. PhD dissertation, Mid Sweden University, 2006.
- [110] Artem Kulachenko, Per Gradin, and Tetsu Uesaka. Tension wrinkling and fluting in heatset web offset printing process. Post-buckling analyses. In Advances in Paper Science and Technology, page 29, Cambridge, UK, 2005.
- [111] Artem Kulachenko, Per Gradin, and Tetsu Uesaka. Basic mechanisms of fluting formation and retention in paper. *Mechanics of Materials*, 39(7):643–663, July 2007.
- [112] Cecilia Land. Laboratory method for the study of moisture-induced waviness in paper. Licentiate dissertation, Karlstads universitet, 2004.
- [113] Tetsu Uesaka. Variability, non-uniformity, and complexity: from product to process. In Advances in Pulp and Paper Research, page 38, Cambridge, UK, 2013.
- [114] Artem Kulachenko. Chapter 9: Moisture-induced deformations. In Mechanics of Paper Products, pages 163–180. De Gruyter, Berlin, Boston, 2011.

- [115] Douglas Coffin. A Buckling Analysis Corresponding to the Fluting of Lightweight Coated Webs. In International Paper Physics Conference, page 5, Vancouver, 2003.
- [116] T. Uesaka. General formula for hygroexpansion of paper. Journal of Materials Science, 29(9):2373–2377, May 1994.
- [117] Artem Kulachenko, Per Gradin, and Bo Westerlind. Analysis of Paper Web Tension Profiles. TAGA JOURNAL, 2:72–81, 2005.
- [118] Frédéric Parent, Jean Hamel, and J D McDonald. Web lateral instability caused by nonuniform paper properties. *TAPPI Journal*, 21(1):12, January 2022.
- [119] Tetsu Uesaka. Chapter 6: Web dynamics in paper transport systems. In Mechanics of Paper Products, pages 93–110. De Gruyter, Berlin, Boston, 2011.
- [120] Yannick Martz and Dominique Knittel. Dynamics of an elastic web in roll-to-roll systems using finite element method. In 11th World Congress on Computational Mechanics (WCCM XI), page 12, Barcelon, July 2014.
- [121] D. Knittel. Web dynamics analysis using finite element simulations. In AIMCAL Web Coating and Handling Conference, June 2014.
- [122] L. S. Gehlbach, D M Kedl, and James K. Good. Predicting shear wrinkles in web spans. TAPPI Journal, 72(8):6, August 1989.
- [123] James K Good, Joseph A Beisel, and H Yurtcu. Instability of webs: the prediction of troughs and wrinkles. In Advances in Pulp and Paper Research, pages 517–556, Oxford, 2009.
- [124] H. Hashimoto. Prediction model of paper-web wrinkling and some numerical calculation examples with experimental verifications. *Microsystem Technologies*, 13(8-10):933–941, April 2007.
- [125] J. A. Beisel. Single span web buckling due to roller imperfections in web process machinery. Phd dissertation, Oklahoma State University, December 2006.
- [126] Y. Martz. Modélisation et commande de systèmes d'entraînement de bandes flexibles : nouvelles approches à l'aide des éléments finis. Phd dissertation, Université de Strasbourg, June 2017.
- [127] J K Good, D M Kedl', J J Shelton, and M Company. Shear wrinkling in isolated spans. In Fourth International Conference on Web Handling (IWEB), page 19, Stillwater, Oklahoma, June 1997. Oklahoma State University.
- [128] Stephen P. Timoshenko and James M. Gere. Theory of elastic stability. McGraw-Hill book company Inc, 2nd edition, 1963.
- [129] Pierre Lecomte du Noüy. An interfacial tensiometer for universal use. The Journal of General Physiology, 7(5):8, May 1925.

- [130] M.E Biancolini, C Brutti, Ernesto Mottola, and S Porziani. Numerical evaluation of buckling and post-buckling behaviour of corrugated board containers. In Associazioneitaliana per l'analisi delle sollecitazioni xxxiv convegno nazionale, page 14, Milano, September 2005. Politecnico Di Milano.
- [131] G. A Baum, D. C. Brennan, and C.C Habeger. Orthotropic elastic constants of paper. *TAPPI Journal*, 64(8):5, August 1981.
- [132] G. A Baum and L.R Borhoeft. Estimating Poisson ratios in paper using ultrasonic technique. TAPPI Journal, 62(5):5, May 1979.
- [133] J. Viguié. Comportements mécanique et hygroexpansif des matériaux ligno-cellulosiques pour l'emballage. Phd dissertation, Université de Grenoble, May 2010.
- [134] Christer Fellers and Leif A. Carlsson. Bending stiffness, with special reference to paperboard. In *Handbook of physical testing of paper*, volume 1, pages 233–256. Taylor & Francis Group, New-York, 2nd edition edition, 2002.
- [135] Operating Instructions thermoMETER CT, micro-epsilon, 2019.
- [136] M. Dolz, M. J. Hernández, C. Cabeza, A. Casanovas, and J. Delegido. Analysis of stability of food emulsions by Eyring's theory: Influence of different biopolymers: Stability of Food Emulsions. *Journal of Applied Polymer Science*, 92(4):2653–2657, May 2004.
- [137] GuangZe Han, ZengKe Fang, and MingDong Chen. Modified Eyring viscosity equation and calculation of activation energy based on the liquid quasi-lattice model. *Science China Physics, Mechanics and Astronomy*, 53(10):1853–1860, October 2010.
- [138] Micael Stehr, Douglas J. Gardner, and Magnus E. P. Wålinder. Dynamic Wettability of Different Machined Wood Surfaces. *The Journal of Adhesion*, 76(3):185–200, August 2001.
- [139] D. H. R. Sarma and R. W. Vest. Kinetics of Liquid Spreading and Penetration with Application to RuO2-Glass Thick-Film Resistors. *Journal of the American Ceramic Society*, 68(5):249–253, May 1985.
- [140] Belgacem Naceur. Agefpi, Saint-Martin-d'Hères, France, 2016.
- [141] Ying Li, Jie Zhang, Haishan Li, Wen juan Gu, and Banggui He. Analysis of the Coating surface Properties of Coated Paper. In 2015 International Conference on Materials, Environmental and Biological Engineering, Guilin, China, 2015.
- [142] Joel Songok, Pekka Salminen, and Martti Toivakka. Temperature effects on dynamic water absorption into paper. Journal of Colloid and Interface Science, 418:373–377, March 2014.
- [143] Craig R. Friedrich. Geometry and characterization of wrinkles in paper. Tappi Journal, 73(8):159–163, August 1990.

- [144] Jean-Francis Bloch, Pierre J.J. Dumont, Sabine Rolland du Roscoat, Laurent Orgéas, Christian Geindreau, and Nicolas Bouquet. Quelques aspects du comportement hygromécanique du papier. Mécanique & Industries, 10(1):43–48, January 2009.
- [145] S. T. Lehti, J. A. Ketoja, and Kaarlo Niskanen. Measurement of Paper Rheology at Varied Moisture Contents. In *International Paper Physics Conference*, page 4, Vancouver, 2003.
- [146] Lennart Salmen and Myat Htun. A Treatise on the Elastic and Hygroexpansional Properties of Paper by a Composite Laminate Approach. *Fibre science and technology*, 20:14, 1984.
- [147] Micro-Epsilon. Mesure thermique sans contact: fondements, 2019.
- [148] Patrice Nortier. Chapitre 2: Transferts de chaleur. In De la fibre à l'imprimé, volume 1, page 398. Agefpi, Saint Martin d'Hères, agefpi edition, 2016.
- [149] Jean-Pierre Dory, Françoise Evin, and Michel Piro. Chauffage par rayonnement infrarouge, 1999. fre.

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# Appendix A

# Coating pilot diagram

In this Appendix, a more complete diagram of the coating pilot, provided by the manufacturer, is presented.



Figure A.1: The full standard space frame assembly used for the more complex coating, printing and laminating arrangements. Four hot air impingement drying modules (optional equipment) are shown fitted in typical positions. (1) Pilot structure; (2) Lamination station;
(3) Winding station; (4) Unwinding station; (5) Free roller; (6) Speed measurement roller; (7) Coating station; (8) Drive engine; (9) Command board; (10) Fixing table; (12) Drying system (hot air drying, infra-red drying or ultraviolet drying).

# Appendix **B**

# Paper disc stacking : complementary results

In this Appendix, a complementary Figure is presented concerning the Paper Disc stacking.



Figure B.1: Evolution of the water mass in the paper over time using the "Paper Disc Stacking" method. Concerning the notation  $"Xs_Y"$ : X is the number of stacked discs and Y is the sample number.

# Appendix

# Generation of speckle for tensile test used in D.I.C

In this Appendix, the Python code used to generate speckle and the associated speckle picture. The code have been created by Maxime Teil.

## Speckle picture generated

Here a example of the speckle that has been printed on D.I.C sample.



Figure C.1: Generated speckle with the parameters used in the following code. Parameters :  $400 \ge 400$  k 400 dpi with a noised step equal to 25, for a size of 210  $\ge 297$  mm.

### Python code to generate speckle

Here the code used to generate the speckle printed.

```
# -*- coding: utf-8 -*-
# Import modules
from PIL import Image
from random import randrange
from os.path import join
# — Define properties — #
print_resolution = (400, 400) \# in dpi (left to right, top to
   bottom)
image_size = (210, 297)  # in mm (left to right, top to bottom)
noised step = 25
saving_path = './'
INCH_MM = 25.4
                 \# 1 inch = 2.54 cm
# ------ Generate image ------ #
image definition = []
for m, n in zip(image_size, print_resolution):
    image_definition.append(int(m / INCH_MM * n))
image_definition = tuple(image_definition)
img = Image.new(mode='L', size=image_definition, color=255)
pixels = img.load()
# ------ Generate noise ------ #
for j in range(image_definition[1]):
    for i in range(image_definition[0]):
        gray_value = randrange(start=0,
                               stop=256,
                               step=int(noised_step))
        pixels[i, j] = gray_value
\# — Saving the image — \#
image_name = inoised_step \{:03d\}_\{:04d\}x \{:04d\}dpi_\{:03d\}x \{:03d\}mm.
   jpg'.format(
        int(noised_step), int(print_resolution[0]), int(
           print_resolution[1]) ,
        int(image_size[0]), int(image_size[1]))
img.save(join(saving_path, image_name), 'jpeg')
```

Table C.1: Python code to generate speckle made by Maxime Teil.

# Appendix D

# Out of plane displacement of sample during tensile test

### Tensile test in MD

Here are presented other results for tensile linked to buckling. The sample are in MD.



Figure D.1: Evolution of the stress versus time during a tensile test in MD (sample A). The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $5 \ mm \cdot min^{-1}$ ).

## Tensile test in CD

Here are presented other results for tensile linked to buckling. The sample are in CD.



Figure D.2: Evolution of the stress versus time during a tensile test in MD (sample B). The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $5 \ mm \cdot min^{-1}$ ).



Figure D.3: Evolution of the stress versus time during a tensile test in CD (sample A). The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $5 \ mm \cdot min^{-1}$ ).



Figure D.4: Evolution of the stress versus time during a tensile test in CD (sample B). The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $5 \ mm \cdot min^{-1}$ ).



Figure D.5: Evolution of the stress versus time during a tensile test in CD (sample C). The associated pictures correspond to the out of plane displacement of the sample at a given time (speed:  $5 \ mm \cdot min^{-1}$ ).

# Appendix E

# Mechanical properties of papers

## Young's modulus versus apparent density

Here are presented the Young's modulus of papers used in this project according to MD and CD, versus their apparent density.



Figure E.1: Highlighting the Young's modulus of papers used in this project according to MD and CD, versus their bulk density.

# Appendix F

# S.E.M picture of CPRAW and CPBS paper

This Appendix presents complementary SEM pictures of CPRAW and CPBS papers, for both side.

## **CPRAW** paper



(a) Marked side - x200



(c) Unmarked side - x200



(b) Marked side - x400



(d) Unmarked side - x400



## **CPBS** paper

Here are presented CPBS paper poiture at different magnifications.



Figure F.2: SEM picture of CPBS paper.

# Appendix G

# WSD: complementary data

In this Appendix, experimental data not presented in the main body of this document are available.





(d) MD - uncoated side in contact with water

Figure G.1: Evolution of strain over time during WSD test. The first line correspond to test in CD, the second line test following MD.

# Appendix

# Determination of the elliptical shape of the intersection between a plane and a cone

### Definition of the problem in 2D and 3D

This demonstration is linked to the subsection 6.1.1 focusing of the factors influencing a non contact IR temperature measurement. The evolution of the measuring area is discussed and it has been shown that a parallel could be done between this practical question and the more theoretical problem of the intersection of a cone and a plane. The goal of this demonstration is to find the parameters of the shape created with the intersection of this two objects while knowing the cone shape and the angle between a the two object.

Consider a reference orthonormal frame (xyz), of centre O(0,0,0). A cone of revolution II is defined. Its axis of revolution is (Oz) and its apex is the point C(0,0,c) where  $c \in \mathbb{R}^*_+$ . The shape of the cone is known and its aperture angle is  $\Gamma_a$ . A cutting plane P is defined. It intersects the cone II. The plane makes an angle  $\Psi$  with the plane (Oxy). The angle between the cone axis and the plane P is then  $90 - \Psi$  as illustrated in Figure H.1.

In the present case, the cutting plane P does not pass through the apex C of the cone. Moreover, the inclination angle of the cutting plane to the cone axis  $90 - \Psi$  is greater than  $\Gamma_a$  (the angle formed by the cone axis and a cone generatrix). It is then well known that the intersection will be an ellipse.

To make the solution of this problem easier, it will be studied in 2D as shown in Figure H.2. The plane P is shown as a line here (in cross section). This line passes through O(0,0).  $\Psi$  is the angle formed between P and the vector  $\vec{x}$ . C(0,c) is the apex of the cone  $\Pi$ , shown in cross section here. The points  $A_1(x_{A1}, z_{A1})$  and  $B_1(x_{B1}, z_{B1})$  are known. The unknowns of the problem are the points  $A_2(x_{A2}, z_{A2})$  and  $B_2(x_{B2}, z_{B2})$  and  $M(x_M, z_M)$  which is the centre of the segment  $[A_2B_2]$ . The vector  $\vec{n}$  is the normal of P.



Figure H.1: 3D definition of the cone-plane intersection problem.



Figure H.2: 2D definition of the cone-plane intersection problem.

## Intersection between a plane and a cone

First, let's define the equation H.1 of the line (P) which is z(x):

$$z(x) = tan(\Psi) \cdot x \tag{H.1}$$

We must also define the equations of the line  $(A_1C)$  defined as follows by the equation H.2 with  $z_+(x)$ :

$$z_+(x) = p_+ \cdot x + c \tag{H.2}$$

Where:

$$p_{+} = \frac{z_c - z_{A1}}{x_c - x_{A1}} \tag{H.3}$$

The same way,  $(B_1C)$  is defined by equation H.4 with  $z_-(x)$ :

$$z_{-}(x) = p_{-} \cdot x + c \tag{H.4}$$

Where:

$$p_{-} = \frac{z_c - z_{B1}}{x_c - x_{B1}} \tag{H.5}$$

The intersection between P and  $(A_1C)$  is now of interest. Therefore, the equation H.6 is obtained. Moreover, using Figure H.2 it is easily seen that the lines intersect at  $A_2$ . Then:

$$z(x) = z_+(x) \tag{H.6a}$$

$$\iff tan(\Psi) \cdot x_{A2} = p_+ \cdot x_{A2} + c \tag{H.6b}$$

$$\iff x_{A2} = \frac{c}{\tan(\Psi) - p_+} \tag{H.6c}$$

The intersection between P and  $(B_1C)$  is now studied. The equation H.7 is obtained. Moreover, using FigureH.2 it is easily seen that the lines intersect at  $B_2$ . Then:

$$z(x) = z_{-}(x) \tag{H.7a}$$

$$\iff tan(\Psi) \cdot x_{B2} = p_{-} \cdot x_{B2} + c \tag{H.7b}$$

$$\iff x_{B2} = \frac{c}{\tan(\Psi) - p_{-}} \tag{H.7c}$$

Once the abscissae of  $A_2$  and  $B_2$  are known, the corresponding ordinates can be determined as follow with equations H.8 and H.9. Knowing that  $x_{A2} = \frac{c}{tan(\Psi) - p_+}$ , it leads to:

$$y_{A2} = \frac{\tan(\Psi) \cdot c}{\tan(\Psi) - p_+} \tag{H.8}$$

The same way, knowing that  $x_{B2} = \frac{c}{tan(\Psi) - p_{-}}$ , it leads to:

$$y_{B2} = \frac{\tan(\Psi) \cdot c}{\tan(\Psi) - p_{-}} \tag{H.9}$$

The coordinates of the intersections between the cone  $\Pi$  and the cutting plane P are now known in a plane problem.

#### Determination of the parameters of the ellipse

Knowing the coordinates of points  $A_2$  and  $B_2$ , the parameters of the ellipse formed by the intersection of the cone  $\Pi$  and the cutting plane P will be determined. For this, the previously

calculated data will be used. Indeed, the segment  $[A_2B_2]$  corresponds to the major axis of the ellipse, the point M being the middle of this segment. Thus:

$$||A_2B_2|| = \sqrt{\left[\frac{c}{tan(\Psi) - p_+} - \frac{c}{tan(\Psi) - p_-}\right]^2 + \left[\frac{tan(\Psi) \cdot c}{tan(\Psi) - p_+} - \frac{tan(\Psi) \cdot c}{tan(\Psi) - p_-}\right]^2}$$
(H.10)

Finally, the coordinates of M are obtained with equation H.11 and equation H.12:

$$x_M = \frac{1}{2} \cdot \left[ \frac{c}{tan(\Psi) - p_+} + \frac{c}{tan(\Psi) - p_-} \right]$$
(H.11)

$$z_M = \frac{1}{2} \cdot \left[ \frac{\tan(\Psi) \cdot c}{\tan(\Psi) - p_+} + \frac{\tan(\Psi) \cdot c}{\tan(\Psi) - p_-} \right]$$
(H.12)

Appendix

## French extended abstract

### Contexte

Depuis sa création, le papier en tant que matériau n'a cessé d'évoluer pour répondre aux besoins de la société. Actuellement, la recherche se concentre sur la réduction des grammages à caractéristiques mécaniques constantes et la fonctionnalisation des papiers afin d'obtenir des propriétés de surface spécifiques (rugosité, barrière à l'huile et à l'humidité, perméabilité à l'oxygène et à l'eau, etc.) pour la réduction de l'empreinte environnementale de l'industrie papetière. Ces caractéristiques peuvent être obtenues en enduisant la surface du papier avec une sauce de couchage aqueuse appropriée. La qualité du couchage obtenu dépend du triplet : papier/sauce de couchage/procédé de couchage. Une fois le papier couché, des propriétés importantes doivent être contrôlées : absorption d'eau, grammage déposé, surface et hydro-expansion. Pour la sauce de couchage, les propriétés rhéologiques, la teneur en matière sèche et la composition chimique doivent être prises en compte. Quant au procédé, les principaux paramètres sont la quantité de sauce de couchage transférée, le temps de parcours entre le couchage et le séchage, les conditions de séchage, la tension de la bande et l'alignement des rouleaux.

Lors du couchage de papiers de très faibles grammages, des plis peuvent apparaître à la sortie de la zone de couchage (Figure I.1) qui, après séchage et selon la nature de la sauce de couchage, peuvent être irréversibles et entraîner des non-conformités et des déclassements des produits.



Figure I.1: Papier conforme (gauche) et non conforme (droite).

Il s'agit ici d'étudier un couplage entre l'absorption d'eau, qui réduit les propriétés mécaniques du papier, et les phénomènes de flambage, éventuellement dus au cisaillement, au désalignement et à la tension de bande. Premièrement, l'eau provenant de la sauce de couchage affaiblit les propriétés mécaniques du réseau de fibres.

Deuxièmement, la charge imposée par la tension de bande (utilisée pour tendre le papier pendant le processus) peut être non uniforme sur la laize du papier. Cela peut être dû à un mauvais alignement des rouleaux. Cette répartition non uniforme de la charge pourrait générer des contraintes de compression secondaires perpendiculaires à la direction de transport du papier et conduire à une déformation hors plan : c'est le flambement. En passant d'un brin libre à un autre, il se tuile (sur le rouleau). Si le papier tuilé passe sur le rouleau, il créera des plis. Le flambement pourrait aussi n'être qu'un "flambement par tension" si le critère de flambement est faible.

Une question vient alors immédiatement à l'esprit : "qu'est-ce qu'un pli ?" Le pli est un défaut du papier le plus courant et le plus coûteux que l'on rencontre dans la fabrication et la transformation des papiers de faible grammage, de film et de textile. La Figure I.2 représente l'évolution d'un pli : du papier tuilé au pli définitif.



Figure I.2: Du papier tuilé au pli définitif sur le pilote de couchage RK du laboratoire LGP2.

Ce projet se déroule au sein des équipes MatBio et BioChip, du laboratoire LGP2, à Grenoble (France). Il s'inscrit également dans la continuité d'une collaboration avec l'INSA Lyon, soutenue par le LGP2 (projet Roll and Fun, 2018) dans le cadre du développement d'un isolant thermique à base de papier. L'objectif de cet ancien projet était de produire un isolant thermique à base de papier en process continu. Cependant, la problématique du plissement du papier après couchage et séchage demeurait. Il faut également noter que cette thématique des variations dimensionnelles liées à l'hydro-expansion des supports fibreux et à la déformation hors plan est un problème récurrent pour fabriquer des produits fibreux.

### Objectifs de ce doctorat

Ainsi, l'objectif principal de cette thèse de doctorat est de bien comprendre les mécanismes sous-jacents à l'apparition des plis lors du processus de couchage bobine-bobine. L'objectif final est de limiter ou d'éviter totalement l'apparition de plis lors du dépôt d'une couche fonctionnelle à la surface de papiers de très faibles grammages. Ce projet est également basé sur une étude multi-échelle des phénomènes physiques impliqués et de leur compréhension/approche fondamentale. La compréhension et la résolution technologique de ce défi peuvent ensuite conduire au développement de nouvelles fonctionnalités pour la technologie bobine-bobine. Pour atteindre le but du projet, trois objectifs majeurs devront être atteints, chacun constituant un chapitre de résultats, listés ci-dessous et illustrés par la figure I.3.



Figure I.3: Résumé visuel présentant l'organisation du manuscrit.

- → Chapitre 4 connaissance du comportement du papier lorsqu'il est couché : Ce premier chapitre de résultats s'attachera à comprendre les phénomènes d'absorption d'eau du papier GHDS 35. La mouillabilité du papier sera étudiée en tenant compte de sa rugosité. Ensuite, l'absorption d'eau sera analysée à l'aide de 3 techniques : Cobb, DPM et "empilement de disques de papier". Ce chapitre traitera également de la sauce de couchage, en se concentrant sur la cuisson de l'amidon, la rhéologie et les phénomènes de sédimentation qui peuvent se produire avec les particules d'amidon.
- → Chapitre 5 compréhension de la mécanique de la formation des plis à travers une approche multi-échelle: Le deuxième chapitre de résultats s'intéressera fortement de la mécanique des plis. A travers l'observation statique et dynamique du phénomène de pli, des observations seront faites lors d'essais de traction par corrélation d'images numériques (D.I.C) et d'essais sur un pilote de couchage. Les plis produits sur ce dernier seront caractérisés a posteriori aux échelles macroscopique et microscopique. Des modèles issus de la littérature seront utilisés pour mieux comprendre les phénomènes.
- $\rightarrow$  Chapitre 6 instrumentation du pilote de couchage et développement d'un

outil d'aide à la conduite : Le dernier chapitre de résultats présentera en premier lieu l'instrumentation du pilote de couchage. L'étude d'un capteur de température et de son suivi au cours du processus fera l'objet de la première partie de ce chapitre. La seconde partie sera consacrée à la réalisation d'une carte de contrôle, afin de mieux maîtriser le procédé. Les papiers couchés dans le laboratoire seront également présentés, ainsi que leurs caractéristiques.

Ces 3 objectifs (et chapitres) seront précédés d'une revue de la littérature (**Chapitre 2**) et d'une présentation des matériaux et méthodes utilisés dans ce projet (**Chapitre 3**).

### Résultats principaux

#### Absorption de la sauce de couchage

Dans le cadre de cette thèse, différents points ont été mis en avant. Nous allons les parcourir dans l'ordre chronologique de ce document. Tout d'abord, nous nous sommes intéressés à la pénétration de l'eau dans le papier. Deux aspects principaux ont été étudiés : les propriétés de la sauce de couchage et la mouillabilité et l'absorption de l'eau par le papier. Dans l'étude de la sauce de couchage, il a été démontré que la cuisson de l'amidon est un point important du processus, car elle a un impact sur la rhéologie de la sauce. Il a été montré que la sauce d'amidon a un comportement rhéofluidique (loi d'Ostwald-de-Waele) et que son comportement dépend également de la température à laquelle elle est utilisée (loi d'Eyring), ce qui est en accord avec la littérature.

La sédimentation des particules d'amidon a été étudiée dans l'eau et rapidement observée dans le gel d'amidon. La vitesse de sédimentation des particules est importante compte tenu des dimensions de la cuve de stockage de la sauce sur le pilote : il a été estimé qu'il fallait moins de 12 minutes pour que les particules les plus lourdes se déposent dans la cuve de stockage. Pour la sauce de couchage, une vitesse de sédimentation 10 000 fois plus faible que dans l'eau a été calculé grâce aux modèles. Cependant, expérimentalement, une sédimentation et une agrégation des particules d'amidon dans le gel d'amidon ont été observées. Une recirculation de la sauce de couchage devrait être installée pour éviter ce type de phénomène de sédimentation.

La mouillabilité et l'absorption d'eau du GHDS 35 ont également été discutées. Nous sommes partis de la loi de Lucas-Washburn, pour laquelle nous avons dû récupérer les différents paramètres nous permettant de l'utiliser. Un point intéressant est que les énergies de surface du papier ont montré des composantes dispersives plus importantes que les composantes polaires des deux côtés. Cela signifie probablement que les fibres ont été traitées pour la résistance à l'état humide, ce qui explique les angles de contact élevés entre l'eau et le papier sur toutes les faces. L'étude de l'absorption d'eau par le papier GHDS 35 a été réalisée à l'aide de trois méthodes : la méthode COBB, la méthode DPM et la méthode d'empilement des disques de papier. Sur de longues périodes, la méthode Cobb a montré un comportement d'absorption d'eau de premier ordre du papier. La méthode d'empilement des disques de papier est une nouvelle méthode proposée pour suivre l'absorption d'eau dans le papier sur de courtes périodes. Trois modèles ont été testés sur les valeurs expérimentales : Lucas-Washburn, premier ordre et

| L-W  | Premier ordre             | Loi puissance          |
|--|---------------------------|------------------------|
| c $(m^5) = 7.40 \ 10^{-12}$                    | $m_{wa,eq} = 0.029$       | $\lambda_a = 0.0063$   |
| $\rho \ (kg \cdot m^3) = 1000$                 | $\tau_a = 4.900$          | $n_a = 0.6376$         |
| $\gamma_{lg} \ [0.001 N \cdot m^{-1}] = 0.072$ | $\Sigma r^2 = 0.00000438$ | $\Sigma r^2 = 0.00007$ |
| $\theta_c = 75^{\circ}$                        | $R^2 = 0.999$             | $R^2 = 0.988$          |
| $\eta \ Pa \cdot s^{-1} = 0.001$               | -                         | -                      |
| $\Sigma r^2 = 1.64 \ 10^{-4}$                  | -                         | -                      |
| $R^2 = 0.993$                                  | -                         | -                      |

loi de puissance (Table I.1). Le modèle du premier ordre semble être celui qui modélise le mieux le comportement observé.

Table I.1: Les paramètres modélisés obtenus à partir des 3 différents modèles utilisés.  $\rho$ ,  $\gamma_{lg}$ ,  $\theta_c$ ,  $\eta$  sont des valeurs d'entrée.

Cependant, il est nécessaire de tenir compte de l'écart-type très important des données expérimentales. Il est donc nécessaire d'optimiser le protocole et l'appareil de mesure. Enfin, la technique DPM a montré un comportement particulier des papiers couchés pouvant rappeler un papier traité AKD (Figure I.4). Ceci confirme l'hypothèse émise suite à la détermination de l'énergie de surface.

#### Phénomènes de plis sur le papier

La deuxième partie expérimentale de ce travail portait sur les propriétés et le comportement mécanique des papiers pliés. En nous basant sur la littérature relative à l'apparition de plis dans les matériaux sous forme de bande, nous avons étudié l'impact d'un angle de désalignement d'un rouleau et d'une tension critique à laquelle les plis peuvent apparaître. Lors des essais in-situ, le plissement sous tension a été observé dans les CD et MD suivants.

Des plis ont également été observés sur le pilote de couchage en faisant varier la tension de bande et l'angle de désalignement d'un rouleau. Ces observations ont été faites sur 4 papiers différents et les conclusions ont été les mêmes : des plis sont apparus. Les observations ex-situ ont été faites sur des échantillons de papiers pliés lors de l'utilisation du pilote de couchage. En utilisant le dispositif Alicona, il a été possible de confirmer la forme asymétrique des plis (Figure I.5), ainsi qu'un phénomène de pincement observé le long des plis. La forme des plis a pu être modélisée par une loi de Weibull à 4 paramètres I.1.

$$H_{Wr}(l_{Wr}, k_{Wr}, \lambda_{Wr}, \theta_{Wr}, A_{Wr}) = A_{Wr} \cdot \frac{k_{Wr}}{\lambda_{Wr}} \cdot \left(\frac{l_{Wr} - \theta_{Wr}}{\lambda_{Wr}}\right)^{k_{Wr} - 1} \cdot e^{-\left(\frac{l_{Wr} - \theta_{Wr}}{\lambda_{Wr}}\right)^{k_{Wr}}}$$
(I.1)

De plus, il a été constaté que les plis ne suivent pas le MD : ils sont orientées en raison du désalignement des rouleaux. Les observations microscopiques par MEB et tomographie à rayons X nous ont permis de mettre en évidence le phénomène de pincement (Figure I.6). Ce dernier semble être responsable d'une décohésion du réseau fibreux ainsi que d'une délamination de la couche déposée industriellement sur le GHDS 35.

Suite à ces observations, une modélisation a été réalisée à l'aide de modèles issus de la



Figure I.4: Courbes d'intensité du signal en fonction du temps obtenues à partir de la mesure DPM. Couché et non-couché renvoient à la face du papier GHDS 35 tournée vers l'eau. Rainuré et plat renvoient à la surface du porte-échantillon.



Figure I.5: Hauteur du pli en fonction de sa largeur. Comparaison entre les valeurs expérimentales et modélisées obtenues avec la loi de Weibull sur un papier GHDS 35 plié. Les valeurs expérimentales sont la moyenne d'un pli d'une profondeur de 1,39 mm.



Figure I.6: Phénomène de délamination observé par MEB sur une zone pliée et pincée du papier GHDS 35.

littérature. Les propriétés mécaniques des papiers ont dû être déterminées. Deux défis ont été relevés : la caractérisation du papier humide (saturé en eau) et la détermination du coefficient de Poisson. Une méthode élégante a été utilisée pour accéder au coefficient de Poisson, présentée équation I.2).

$$\frac{1}{E_{tan}} = \frac{1}{E_x} \cdot \cos^4 \phi_f + \left(2 \cdot \frac{-\nu_{xz}}{E_x} + \frac{1}{G_{xz}}\right) \cdot \sin^2 \phi_f \cdot \cos^2 \phi_f + \frac{1}{E_z} \cdot \sin^4 \phi_f \tag{I.2}$$

En ce qui concerne le comportement du papier GHDS 35 saturé en eau, nous avons pu quantifier son séchage dans une pièce conditionnée par une loi du premier ordre décroissante. En suivant cette loi, il a été possible de modéliser l'évolution des modules d'Young en fonction de la quantité d'eau absorbée par mètre carré de papier. La loi utilisée est inspirée de la loi de Cross, et constitue un élément clé de ce projet (équation I.3).

$$E_{MD} = \frac{E_{MD,min} \cdot (\lambda_s \cdot A_s)^{n_e} + E_{MD,max}}{1 + (\lambda_s \cdot A_s)^{n_e}}$$
(I.3)

La méthode de mesure doit encore être améliorée car une hystérésis dans l'absorption d'eau par le papier peut exister et avoir un impact sur l'évolution des modules d'Young. Néanmoins, le comportement observé est proche de celui de la littérature : ceci est rassurant pour la poursuite éventuelle de ce travail. Le test WSD a permis de mettre en évidence un comportement d'ordre  $2^{nd}$  selon la CD et un comportement de premier ordre selon la MD lors de cet essai. Grâce aux résultats obtenus, un nouveau paramètre a été identifié : le module tangent obtenu avec la mesure WSD. Ce paramètre permet de quantifier l'évolution des propriétés mécaniques des papiers en fonction du temps de test WSD, et par conséquent en fonction de la quantité d'eau pendant une phase d'absorption. Pour améliorer l'expérience, une mesure de la teneur en eau locale du papier, sur la largeur, devrait être installée.

Toutes ces informations ont été utilisées pour alimenter le modèle de Hashimoto (équation I.4 et équation I.5) pour l'apparition des plis sur le pilote de couchage. Nos valeurs expérimentales ont été comparées aux prédictions du modèle.

$$\theta_{cr} = \frac{6\tau_{cr}a^2}{E_x b^2} \tag{I.4}$$

$$T_{cr} = \frac{2t_f^2}{\mu b} \sqrt{\frac{E_x \cdot E_z}{3\left(1 - \nu_{xz}\nu_{zx}\right)}} \tag{I.5}$$

Il a été surprenant de constater que nos valeurs, en particulier l'angle de désalignement, sont très grandes par rapport à la littérature. Sans être incohérente, la vitesse lente utilisée lors de l'expérience pourrait expliquer cette différence. Dans une moindre mesure, la discrétisation du nombre de plis dans le modèle de Hashimoto a été étudiée. Nous avons pu montrer que rendre la variable représentant le nombre de plis entière conduisait à ne pas respecter l'équation limite permettant de définir *i* et à surestimer ou sous-estimer l'angle de désalignement à partir duquel les plis pouvaient apparaître. Néanmoins, la notion même d'un nombre de plis non entier est difficile à appréhender. Cependant, cela pourrait être lié à des zones de transition d'équilibre. Enfin, l'analyse des essais de traction et leur comparaison avec le modèle de Zhu (équation I.6) ont validé nos valeurs. Ce modèle pourrait également être utilisé pour prédire le flambage en traction qui peut se produire sur le pilote lorsque les rouleaux sont bien alignés, que le papier est humide et que des rides se forment.

$$k_{c} = \left\{ \frac{3\xi_{1} - 1 + 2\xi_{1}^{2}\nu_{xz}}{\xi_{1} + 1 + 2\xi_{1}\nu_{xz}}\beta^{2} + \xi_{1} \left[ \beta^{-2}n^{2}\left(n+2\right)^{2} + n^{2} + \left(n+2\right)^{2} \right] \right\}$$
(I.6)

#### Étude du processus de couchage sur le pilote de laboratoire

Le dernier chapitre expérimental porte sur l'étude du procédé de couchage sur le pilote lui-même. Deux points ont été abordés : la mesure de la température pendant le procédé et l'optimisation du procédé. La mesure de la température au cours du procédé a été étudiée à l'aide de capteurs IR. Il a été montré que l'émissivité réglée sur les capteurs devait être proche de 0,95 et que les capteurs devaient être aussi perpendiculaires que possible à la bande. La distance entre le capteur et la bande dépend de la valeur recherchée : locale ou globale. Cette étude a également mis en évidence la non-homogénéité des isothermes de température à la sortie du sécheur IR sur le papier. Ce phénomène pourrait également justifier le tuilage du papier, due à un séchage hétérogène, bien qu'aucun désalignement des rouleaux n'ait été observé. Les capteurs ont permis de suivre le processus de couchage au cours de différents passages et d'illustrer les différents événements se produisant au cours du processus tels que la rupture de la feuille de papier, le changement d'équipement ou le couchage à différentes vitesses.

Le dernier aspect de ce chapitre était l'optimisation du processus en reliant la tension de la bande, l'angle de désalignement et la vitesse de la bande. Pour cela, tous les outils et modèles développés précédemment ont été utilisés. Ainsi, nous avons lié la vitesse de la bande de papier à l'absorption d'eau, qui à son tour était liée aux modules d'Young par la loi de type Cross. Ce modèle a lui-même été intégré aux lois proposées par Hashimoto, en ajoutant une variation des coefficients de Poisson grâce au modèle empirique de Baum. La Figure I.7 résume la philosophie de création des cartes de contrôle utilisant les différents modèles

Ceci a permis de générer des cartes de contrôle et de conduite du processus permettant de déterminer l'angle de désalignement à ne pas dépasser en fonction de la vitesse du papier sur le pilote et de la tension de bande. Cependant, ces cartes ne prennent pas en compte les phénomènes de tension de flambage. Pour cela, il est nécessaire d'utiliser en première approche le coefficient  $k_c$  proposé par Zhu.

#### Conclusion finale

Cette thèse a permis de comprendre les phénomènes liés à l'apparition des plis. Ce travail offre une nouvelle perspective à l'étude de ce type de phénomène. Il serait intéressant d'acquérir plus de données concernant pour nourrir le modèle de Cross liant absorption d'eau et module d'Young du papier. Pouvoir acquérir plus d'informations avec le système DIC, lorsque le processus est en cours, serait un plus pour comprendre les phénomènes in-situ et réguler le processus par la mesure et le contrôle de la tension de bande. Une mesure du profil d'humidité du papier sur la laize du papier serait un plus. Pour conclure, nous répondrons à cette dernière question : a-t-il été possible de coucher un papier, sans plis, avec un gel d'amidon contenant des granulés d'amidon ? La réponse est oui car le procédé est maintenant maîtrisé grâce à la création des cartes de contrôle.



Figure I.7: Schéma de construction des cartes de contrôle en fonction de l'absorption d'eau par le papier ou de la vitesse du papier.


## **RESUME EN FRANÇAIS :**

Depuis sa création, le papier en tant que matériau n'a cessé d'évoluer pour répondre aux besoins de la société. Actuellement, la recherche se concentre sur la réduction des grammages avec des caractéristiques mécaniques constantes et la fonctionnalisation des papiers afin d'obtenir des propriétés de surface spécifiques et pour réduire l'empreinte environnementale des papeteries. Ces caractéristiques peuvent être obtenues en enduisant la surface du papier avec une couche de revêtement aqueuse appropriée. La qualité du couchage obtenu dépend du triplet : papier/couche déposée/procédé d'enduction. Lors du couchage de papiers très légers, des plis peuvent apparaître à la sortie de la zone de couchage. Après séchage et selon la nature de la couche, les plis peuvent être irréversibles et entraîner des non-conformités. Le but de ce projet est donc de comprendre comment et pourquoi ses plis peuvent apparaitre. Dans un premier lieu, l'étude de l'absorption de l'eau par le papier a été menée. Cette dernière a permis de déterminer une loi du premier ordre reliant la quantité d'eau absorbé par le papier en fonction du temps. Dans un second temps, le phénomène de plis est étudié, à différentes échelles, du point de la mécanique. Cela à permis de mettre en avant l'impact des modules d'Young sur l'apparition des plis, notamment en présence d'eau. De plus, à une échelle microscopique, une décohésion du réseau fibreux est constatée. Les plis ont donc un impact macroscopique et microscopique. Le dernier point abordé lors de ce projet est l'optimisation du procédé de couchage. Trois paramètres de process ont été mis en relation : la vitesse de défilement du papier, l'angle de désalignement des rouleaux les uns par au rapport aux autres et la tension de bande. Cela a permis l'élaboration d'une carte de contrôle permettant de conduire le couchage dans les meilleures conditions. Enfin un papier de faible grammage a pu être couché sans pli.

## ABSTRACT IN ENGLISH :

Since its creation, paper as a material has constantly evolved to meet society's needs. Currently, research focus in the reduction of grammages with constant mechanical characteristics and the functionalization of papers in order to obtain specific surface properties for the reduction of the environmental foot printing of the paper mills. These characteristics can be obtained by coating paper surface with suitable aqueous coating color. The quality of the coating obtained depends on the triplet: paper/coating color/coating process. When coating very light papers, wrinkles may appear at the exit of the coating area. After drying and depending on the nature of the coating, wrinkles can be irreversible and lead to non-conformities. The aim of this project is therefore to understand how and why these wrinkles can appear. Firstly, the study of water absorption by paper was carried out. This allowed to determine a first order law relating the quantity of water absorbed by the paper as a function of time. In a second step, the wrinkle phenomenon is studied, at different scales, from the point of view of mechanics. This allowed to highlight the impact of Young's modulus on the appearance of wrinkles, particularly in the presence of water. Moreover, on a microscopic scale, a decohesion of the fibrous network was observed. Therefore, wrinkles have a macroscopic and microscopic impact. The last point addressed in this project is the optimisation of the coating process. Three process parameters were related to each other: the web speed, the angle of misalignment of the rolls with respect to each other and the web tension. This has enabled the development of a control map that allows the coating to be carried out under the best possible conditions. Finally, a low-weight paper could be coated without wrinkle.

