HABILITATION A DIRIGER DES RECHERCHES
Heterogeneities in polymer matrix materials: consequences on the mechanical properties

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Heterogeneities in polymer matrix materials: consequences on the mechanical properties

Présentée devant l'Institut National des Sciences Appliquées de Lyon et l'Université Claude Bernard

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I CURRICULUM VITAE

Before getting a position at CNRS, I obtained my Ph-D diploma in "Material science" in the Centre de Recherche sur les Macromolécules Végétales (CNRS Grenoble) for the study of « nanocomposites with cellulose whiskers fillers and a Poly-Vinyl Chloride matrix: processing, structural study, mechanical behaviour » ; then I did a postdoc at the « Center for Composite Materials and Structures » (Rensselaer Polytechnic Institute, NY, USA) studying « the study of the non linear viscoelastic behaviour of filled elastomers at small strain level ».

Cf. CV detailed at the end of the report with the résumé of my activities and an exhaustive list of my publications and communications.

II WORKS AND OBJECTIVES

1. Introduction

As soon as people wanted to model the mechanical properties of materials, they had to simplify it. The first simplification was to consider them as homogeneous. In fact, except few cases, all the materials are heterogeneous, and even the purest steel contains, if one looks to it closer, inclusions, grains, all things that, at a moment or another in the thermomechanical history of the material, will have consequences on the macroscopic mechanical behaviour of the material. In the same manner, a polymer material, amorphous, even said homogenous or pure, presents a mechanical response that is the result of localised processes, therefore heterogeneous at the molecular scale. To these heterogeneities, one must add, in the large majority of the polymer materials, those introduced voluntarily by the formulation, for instance fillers, or ingredients used to improve their properties.

In fact, though these heterogeneities, it is always possible for a modelling, to consider *a priori* the behaviour of the material as homogenous at the macroscopic scale, and this is often the route employed in calculation code. The problem is that such an approach, if it is useful for the simulation, rapidly shows its limitations since it neglects the phenomena at the lower scale. Therefore, the question is to know for all the person interested in these problems, what is the pertinent scale to consider, under which the role of the heterogeneities will be included implicitly and not explicitly in a homogeneous description of the material.

Complex question, that one might solve following two manners:
- Either in a pragmatic way, like the calculation code developers do, i.e. by improving step by step a macroscopic (and at the beginning a phenomenological description) to account more an more properly for the behaviours
- Either in a more fundamental way – but less immediate – by studying first the physical mechanisms involved at the different scales, with the risk of losing the objective of a practical description of the behaviour.
Researcher in Material Science in the field of polymer, and hired originally on a pluridisciplinary position on two department of the CNRS, « science for engineering » and « chemical science ». My work has as objective to link both approaches. Thus, as this will be shown in this manuscript, my work devoted to polymer matrices materials consist in - by combining both experimental study and modelling - integrating as much as possible, the physical mechanisms in the description of the mechanical behaviour they originate.

To do so, none scale must be a priori neglected in the analysis of the studied materials. To convince on that, let stop a moment on filled elastomers, materials that I peculiarly studied. The fillers used in these composites generally carbon blacks or silica, are made of primary

particles, with a nanoscopic size, forming by their association aggregates unbreakable of few tenth of nanometers. These aggregates form, with the help of weak bonds, agglomerates of a hundred of nanometers up to several hundreds of microns, and sometimes a percolating structure at the scale of the material. It is therefore obvious, as illustrated in figure 1, that the description of the microstructure of such a nanocomposite, if one is interested in its consequences on the mechanical behaviour, involves several scales, from those of the aggregates, that we will qualify in the manuscript as the mesoscopic scale, up to the macroscopic scale of the percolating structure. It is also necessary to consider the molecular scale of the polymer chains of the matrix, scale at which modifications of polymer mobility are possible, induced by the important quantity of interface created by the nanoscopic size of the primary particles…
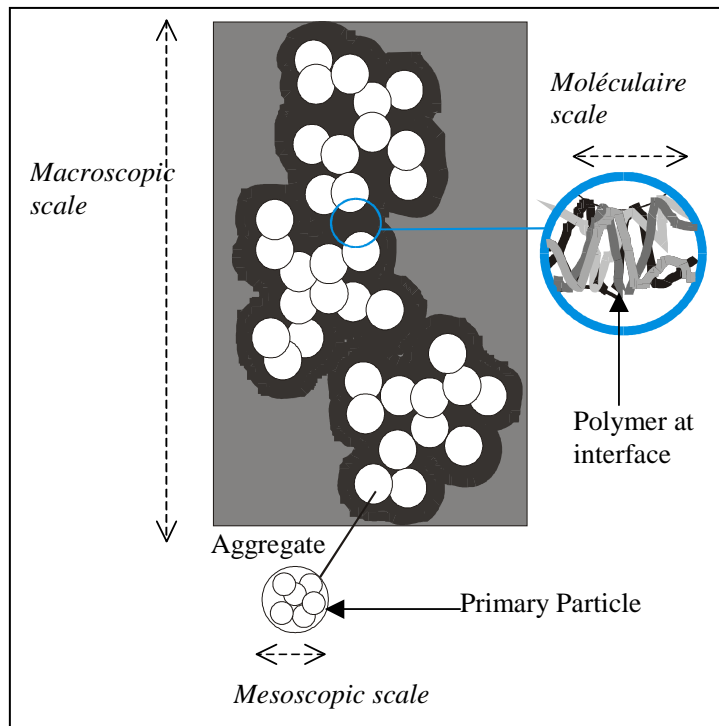

Figure 1 : Scheme illustrating the different scales of the microstructure in nanocomposites.

Thus, through this example, but also through the presentation of other works, I will present questions arising at each scale. I will show first that the comprehension of the behaviour o f the polymer matrix needs the examination of the molecular scale and of the heterogeneities met at this scale, including in their definition the role of interfaces, and their consequences on the global mechanical response of the materials. I will then discuss about the mesoscopic scale, i.e , that of the fillers and their impact via the mechanical coupling, in the different matrices. I will then have a look on the macroscopic scale of the structure of these fillers in a percolating network. At last, I will focus on the problem of solicitation heterogeneities, the latter leading to difficulties in the interpretation of the results when they are not controlled, or when they are too complex. I will finish this manuscript by a conclusion of the works and prospects.

Brief bibliographical recalls will be presented all along the manuscript when it will be judged necessary. However, for a more complete bibliography, I invite the reader to have a

look on the different publications written from the presented works. They will be indicated as bottom page notes in the text.

2. Heterogeneities at the molecular scale

For a composite or for a pure polymer, the behaviour of a material can only be understood if one examines the molecular scale, i.e. those of the polymer chains. Indeed, at this scale, relaxational processes at the origin of the macroscopic deformation occur, these processes depending on the molecular architecture of the chains and their interaction. It is then obvious that the introduction of molecules such as plasticisers or solvent, or the presence of interface introduced by the addition of fillers can influence these processes, and therefore the global response of the material to a mechanical solicitation.

We have been interested in theses aspects from an experimental point of view as well as a modelling one. The "Polymere Verres Matériaux Hétérogènes » group, whose I am member, work since its creation to the modelling of the mobility and response under solicitation of non crystalline solids, peculiarly amorphous polymers. The base of knowledge developed in this frame is in fact the common culture of all his actors. The modelling initiated by J. Perez is a powerful tool for the analysis of polymer mechanics (cf. bibliography recall further). As it will be detailed later, this model integrates the molecular mechanisms at the origin of the deformation in a description eventually homogenous of the material. Moreover, its last developments – we will see them in the chapter 4 – allow now the modelling of the behaviour of « structure » (in the mechanical sense of the term) in polymer.

So, we have confronted this model to experimental results obtained with two systems, a plasticised PVC, and cellulose solubilized in N-methyl morpholine monohydrate (NMMO/H2O). The interest of such a confrontation is first to estimate the modifications at the molecular level of the relaxationnals mechanisms of the polymer, induced by the plasticiser or solvent presence. But the model also enable, due to its homogenous formulation, to evaluate if these modifications are homogeneisable at the macroscopic scale of the material. The model being then, as seen with the example of plasticised PVC, as a tool for microstructural characterization.

We will see afterwards, that the understanding of the influence of molecules on the relaxationnal processes is very similar to that of the influence of the introduction of an important quantity of interface introduced in the polymer. Indeed, the polymer is then submitted to interactions with the molecules or chemical groups of this interface.

2.2 Polymer and plasticiser

2.2.1 Plasticised PVC

Plasticisers have been used for a long time in the formulation of polymer materials. The most significant example is the case of PVC plasticised by di-ethyl hexyl phtalate (DOP). This material is used in many applications. Literature on the subject is very abundant, however the important part of plasticiser usually used (it can be more than 50%) makes the

comprehension of the mechanical behaviour of the system difficult. In particular, the plasticiser is involved in the molecular mobility of the polymer in which it is introduced.
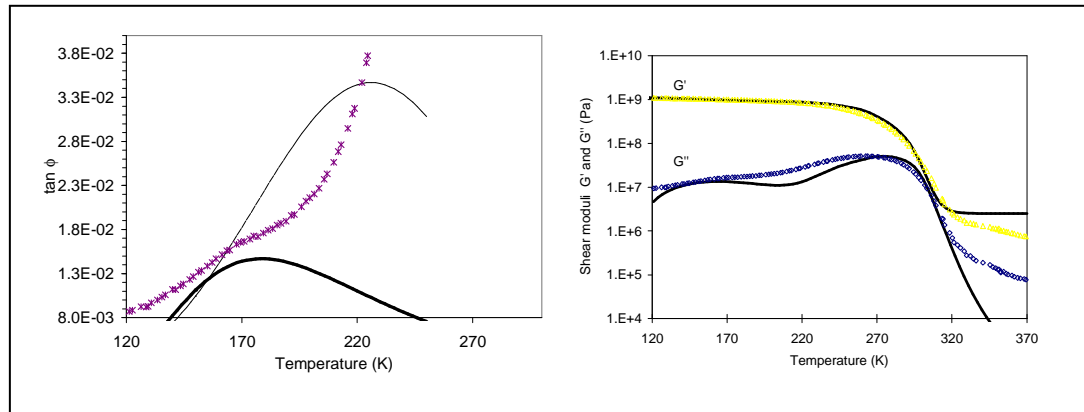

Figure 1: (a) β Relaxation of plasticised PVC by 30 phr of DOP, measured by mechanical spectroscopy (f=0.1 Hz, ε=10[-5]) . The experimental results have been compared to a modelling of the Nowick and Berry[1] type (bold line), as well as to experimental results of R. Flores Flores[2] obtained with PVC (dashed line). (b) isochronal curves of plasticised PVC (f=0.1 Hz). The theoretical curve (bold line) was obtained with the qpd model.

The addition of plasticiser modifies the glass transition temperature of the material. The study of the material by mechanical spectrometry enables the observation of the influence of molecules on the relaxational processes. As indicated on figure 1, the plasticiser decreases the intensity of the β relaxation for the high temperature part. Let us first consider this relaxation.

Bibliographical recall:

Amorphous polymers are made of macromolecular entangled chains. These chains can contain several hundreds of monomer units. During a cooling after the polymerisation, the material stays as an overmolten liquid down to a temperature, which depends on the cooling rate. This temperature is the glass transition temperature Tg. Below Tg, the high viscosity do not allow the reorganisation of the material needed to reach the thermodynamical equilibrium. Two behaviour domains are distinguished: the glassy domain (out of equilibrium) below Tg and the rubber domain (metastable equilibrium) above, Tg being the temperature at which the characteristic time for the structural reorganization is comparable to the experimental time of observation. This behaviour is not only seen for polymers but also for metallic glasses, or oxide glasses which have, like them, a glass transition temperature and an amorphous state below this temperature.

Polymer materials, like all the amorphous materials, show a viscoelastic behaviour strongly dependent on the temperature, the strain rate, and the stress level. The deformation has an instantaneous component, said elastic, and a differed part said not elastic. This anelastic part has a recoverable part in few hours, said anelastic, and a non recoverable part at the time scale of the experiment, said viscoplastic. The simplest mechanical test to evidence these different components is the creep test, which consist in applying to the sample a constant stress and in measuring the deformation as a function of time (cf. Figure R1). The characteristic times of the strain components are very dependant on the temperature, an increase of the latter leading to their decrease. Moreover, the effect of the stress enables to distinguish two domains, the one said linear (where it has no influence on the compliance r the viscoelastic modulus), and the other so called non-linear. In the linear domain, creep test and mechanical spectrometry lead to equivalent information since temporal compliance and complex compliance are linked by the Laplace-Carson transform.
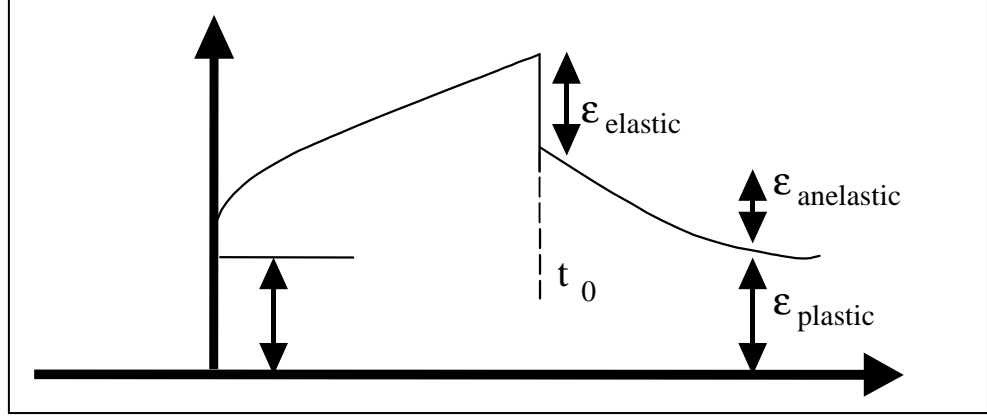
Figure R1 : Strain of an amorphous polymer as a function of time after a static stress is applied until time t_0. Different strain components.

A part of the processes at the origin of the anelastic strain are relatively rapid. They are the manifestation of local movements, either of lateral groups in the polymer (this is for γ, δ, etc… relaxations), either chain portion (generally speaking for the β relaxation). The times involved in these processes follow an arrhenian description. So for the τ_β time, one can generally writes: [3]

$$\tau_\beta = \frac{1}{2\pi f_m} = \tau_0 \exp\left(\frac{E_\beta}{RT}\right) \qquad \text{(R1)}$$

With τ_0 a time close to the Debye time, and E_β the activation energy of the relaxationnal process.

The temporal compliance can then be expressed as:

$$J_\beta(t) = J_\beta\left[1 - \exp\left[-\left(\frac{t}{\tau_\beta}\right)\right]\right] \qquad \text{(RE2)}$$

And the complex compliance:

$$J_\beta^*(i\omega) = J_\beta \frac{i\omega\tau_\beta}{1+(i\omega\tau_\beta)} \qquad \text{(RE3)}$$

With J_β the relaxation intensity.

In fact, τ_0 is often smaller than the Debye time because it integers the entropic part of the free activation enthalpy, or in other term the existence of a certain cooperativity of the movements involved in the relaxation. On the other hand, the local heterogeneities of the material lead to a distribution of the activation energy, leading then to a distribution of the relaxation times. The compliance is then the summation of a distribution of compliances associated to each distributed time.

A succession of isochronal measurements and then the application of the superposition principle enables the determination of the characteristic times of the secondary relaxation (i.e. the terms of the RE1 equation recalled above). Compared to unplasticised PVC, its activation energy is only slightly modified but its pre-exponential time (relaxation time at infinite temperature) is lower. This suggests an increase of the cooperativity of the involved movements. The decrease of the intensity of this relaxation for its high temperature part has the same explanation. Thus, the DOP shows an antiplasticising effect, since it creates intermolecular interactions. This effect can seem paradoxical if one considers the decrease of the glass transition temperature to which it also leads. For a better understanding of the plasticization mechanisms, we have tried to model the main relaxation of the material by the

"quasi-punctual defect" theory initially developed by J . Perez. [4] This model does not refer to the macromolecular nature of the polymer chains but to the disordered (amorphous) nature of their arrangement. [5] It is therefore also applicable to organic glasses or metallic glasses as J.M. Pelletier develops it in our team. This model already allowed the description of the glass transition, of the alpha relaxation and of the mechanical behaviour at large strain of numerous polymers. [6,7]

Bibliographic recall:

Before that, let us go back to the deformation mechanisms of the amorphous polymers: the components of the anelastic deformation (cf. Figure R1). That is not due to the β relaxation process (or more generally speaking secondary relaxations), and the component of the viscoplastic deformation involve large scale movements. They are responsible for the main or α relaxation easily measurable by mechanical spectrometry, whose the observed temperature during a dynamic applied strain at a frequency around 1 Hz s often confused with the glass transition temperature. The description of this relaxation is more difficult that that of the secondary relaxations since it does not accept an arrhenian description: the characteristic times can be described by equation ER1 only when temperature is below the glass transition temperature. Beyond this temperature, they are fitted by the empirical equation of William Landel Ferry. Moreover, the activation energy introduced in the equation is too high, of the order of 300 kJ, to have any physical meaning, and the preexponential time is too low.

A physical description has been proposed by Perez et al[3] (for a bibliography on the other model proposed in literature, the readers are invited to consult the references cited in this paragraph)) to explain these experimental facts. It is based on three main assumptions (cf. Figure R2):

Solid amorphous polymer contains enthalpy and entropy fluctuations, so called quasi point defects (qpd), in which the molecular mobility is higher than the average mobility of the polymer

The application of a shear stress leads to the nucleation of sheared microdomains (smd) which have their origin at the level of these defects. These smds grow and coalesce if the solicitation time or the stress are large enough. The growth of these smds is at the origin of the anelastic strain (with a characteristic time τ_{an}), recoverable at the time scale of the experiment, unless they had the time to coalesce. This last process is the origin of the viscoplastic strain (with a characteristic time τ_{vp}) only recoverable if the material is heated above the glass transition temperature, due to entropic force of the stretched molecular segments;

The growth of the smds is the result of hierarchically constrained molecular movements. That means that the movement of some structural units can only be done when their surrounding is in a configuration obtained by more rapid movements of other structural units. Therefore, the anelastic processes here described have characteristic times which spread from the time of elementary movements τ_1 up to a time τ_{mol}.

In many cases, the elementary time is associated to that of β process[8] and τ_{mol} is defined by:

$$\tau_{mol} = t_0 \left(\frac{\tau_\beta}{t_0} \right)^{\frac{1}{\chi}} \qquad \text{(RE4)}$$

Where χ is the correlation parameter. Its value is related to the concentration of qpd in the material. It is in between 0 and 1. The highest it is, the less important are the correlation effects.
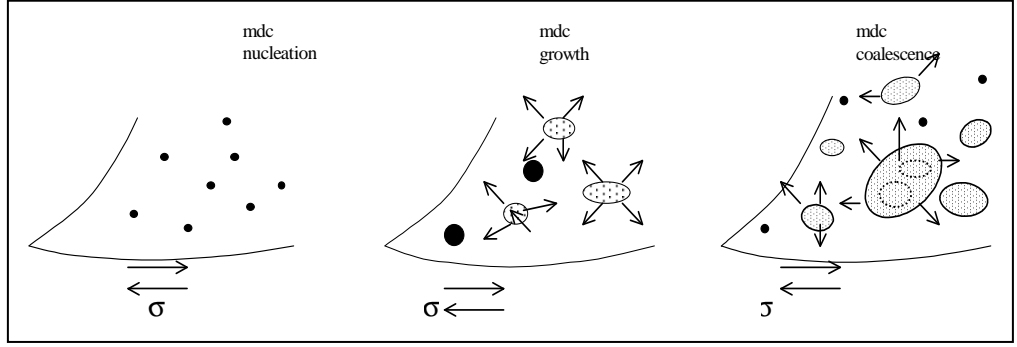
Fig. R2 – Effect of a stress applied : a) reorientation of structural units ; b) nucleation-growth of mdc ; c) nucleation-coalescence of mdc

This description has first lead to the expression of the temporal compliance in which the elastic, anelastic and viscoplastic contributions of the α relaxation are clearly distinguished:

$$J_\alpha(t)=J_{el}+J_{an}\left[1-\exp\left[-\left(\frac{t}{\tau_{an}}\right)^{\chi}\right]\right]+J_{vp}\left(\frac{t}{\tau_{an}}\right)^{\chi} \qquad \text{(RE5)}$$

$$J_{vp}=J_{an}\frac{\chi^{\frac{\chi}{\beta}}}{\chi'} \qquad\qquad \text{and} \qquad \tau_{an}=\chi'^{\frac{1}{\chi}}\tau_{mol} \qquad \text{(RE6) et (RE7)}$$

J_{el} is the compliance before the main relaxation, J_{an} and J_{vp} are respectively the intensities of the anelastic and viscoplastic relaxations, and χ' is a parameter which accounts for the distribution of the viscoplastic times due to structural heterogeneities initially present in the material (at the level of the macromolecular network). After simplification, a Laplace-Carson transform, then an inversion, this expression is equivalent to the biparabolic model often used to simulate the main relaxation measured by mechanical spectrometry:

$$G_\alpha *(i\omega) = G_c + \frac{G_{el} - G_c}{1 + (i\omega\tau_\alpha)^{-\chi} + Q(i\omega\tau_\alpha)^{-\chi'}} \qquad \text{(RE8)}$$

With $\tau_\alpha=(J_{an}G_{el})^{-\frac{1}{\chi}}\tau_{an}$ and $Q=\dfrac{\chi^{\frac{\chi}{\chi}}}{\chi'(J_{an}G_{el})^{\frac{\chi-\chi}{\chi}}}$ (RE9) et (RE10)

Where $G_{el}=1/J_{el}$, and G_c is the shear rubber modulus. The RE5 expression is also equivalent to that involving a Gumble distribution of the anelastic and viscoplastic times with the distribution parameter χ and χ' respectively:

$$J_\alpha(i\omega) = J_{el} + J_{an}\int_1^{+\infty} P_{an}\left(\ln(\tau_{an})\right)\frac{1}{1+i\omega\tau_{an}}\,d\left(\ln(\tau_{an})\right) + J_{vp}\int_1^{+\infty} P_{vp}\left(\ln(\tau_{vp})\right)\frac{1}{1+i\omega\tau_{an}}\frac{1}{1+i\omega\tau_{vp}}d\left(\ln(\tau_{vp})\right)$$

(RE11)

Where $\qquad \tau_{vp} = \tau_{an}\dfrac{J_{vp}}{J_{an}}$ (RE12)

With

$$P\left(\ln(\tau)\right) = \frac{1}{\displaystyle\int_1^{+\infty} P\left(\ln(\tau)\right)d\left(\ln(\tau)\right)} \exp\Big(B\cdot\left[\ln(\tau) - \ln(\langle\tau\rangle)\right] - \exp\Big(B\ \cdot\left[\ln(\tau) - \ln(\langle\tau\rangle)\right]\Big)\Big)$$

(RE13)

B being the parameter of the Gumble distribution.

Below the glass transition temperature, one can consider that, neglecting the structural relaxation (also called "structural ageing", i.e. an evolution of the out of equilibrium material toward its equilibrium state), the correlation parameter is constant. However, this same parameter is influenced by the temperature when the material is not in the glassy domain anymore. This influence is accounted for by a simple linear equation:

$$\chi = \chi_0 + a(T - T_g) \quad \text{pour T>Tg} \tag{RE14}$$

Where χ_0 is the value of the correlation parameter under the glass transition temperature and **a** an adjustable parameter. It is noteworthy that this equation enables the description of the evolution of the characteristic time below Tg in the same manner than the empirical equation of William Landel and Ferry.

The description of the non-linear domain needs to take into account the influence of the stress on all the characteristic times. It is accounted for by the introduction of a term in the expression of the elementary time τ_β:

$$\tau_\beta = \tau_{0\beta} \exp \left(\frac{(U\beta + \Omega_\beta P)\left(1 - \frac{\sigma_{cis}}{\sigma_0}\right)^{\frac{3}{2}}}{kT} \right) \tag{RE15}$$

Where P is the isostatic pressure, σ_{cis} is the shear stress applied to the material, σ_0 is the applied stress to overpass the energy barrier at 0K. Ω_β is the parameter traducing the influence of the hydrostatic pressure. The increase of P leads to an increase of the activation energy of the elementary molecular movements.

Besides, experiments suggest that the development of the anelastic strain creates supplementary defects, or, in other words the increase of the mobility, i.e. the increase of the correlation parameter:

$$\chi = \chi_0 + A_{def} \gamma_{an} \tag{RE16}$$

Where χ_0 is the correlation parameter before the development of anelastic strain and γ_{an} the anelastic strain.

At last, strain hardening of polymers, observed at large strain, suggests an effect of the orientation of the macromolecular chains on the relaxationnal processes. This effect can have two origins:
A decrease of the qpd number, or a non-linear evolution of the intensity of the viscoplastic processes. The latter would come from the finite extensibility of the chains between entanglement nodes (fixed at the time scale of experiments). The actual development of the model does not allow for the moment to choose between those two origins. This debate is presently justified by the experimental difficulties of large strain mechanical characterisation. [9,10,11] We will come back to this point later, in chapter 3.

To conclude, it is important to underline that all the parameters of the model have a physical meaning and can be individually determined from a restricted number of tests.

With few improvements, this model can provide constitutive equation of polymer materials useful in calculation code by finite elements, as we will see in chapter 4. However, this model leads to a macroscopically homogenous description of the deformation. This might explain its impossibility to correctly model our plasticised PVC by a classical application of the equations. Indeed, as shown in figure 1b, the main relaxation of the material is very wide. This, as we have shown it experimentally by ageing studies and neutron scattering

measurements[a], is due to the presence of concentration gradients of plasticiser in the material. It was therefore necessary to integrate this fact in our description. To do so, we have considered the material as the association in parallel of different plasticised phases, each of them having a specific glass transition temperature, or in other words, a different average relaxation time. This is expressed by the summation:

$$G_\alpha *(i\omega) = \int\limits_{-\infty}^{+\infty} G_{\alpha_i}(i\omega)\Psi\left(\ln\left(\frac{\tau_{\alpha_i}}{\langle\tau_\alpha\rangle}\right)\right)d\ln\left(\frac{\tau_{\alpha_i}}{\langle\tau_\alpha\rangle}\right) \qquad (EP1)$$

Where $G_{\alpha_i}*(\omega)$ is determined by equation RE8, with a characteristic time τ_{α_i}, distributed as the Ψ distribution. This leads to the distribution of the relaxation time at a given temperature, this being directly related to the plasticising effect of the DOP. This distribution is equivalent to a distribution of the correlation parameter (cf. Figure 2a). The latter is dissymmetrical and spread towards high values, significant of correlation effects less important. Thus, plasticiser allows less correlated movements of the polymer chain but this effect is distributed because of the concentration gradients of DOP in the polymer. Our approach has been successfully applied to the modelling of isothermal and isochronal curves (cf. Figure 1b) [b]. The modelling of the latter needed to take into account the evolution of the correlation parameter with temperature, which is related to the evolution of the correlation parameter of each phase at temperatures above the glass transition temperature of this phase. This coherent description of the material has been extended with a remarkable success to the non-linear domain, as shown on the modelling of compression tests at different temperatures with the same ensemble of parameters (cf. figure 2b). [c]

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[a] "Mechanical behaviour above Tg of a plasticised PVC reinforced with cellulose whiskers ; a SANS structural study", Chazeau L., Cavaillé J.Y., and Terech P., Polymer, 40, 19, 5333-44, 1999
[b] "Plasticized PVC reinforced with Cellulose Whiskers: I- Linear viscoelastic behavior analyzed through the "quasi point defect" or "qpd" theory", Chazeau L., Paillet M., and Cavaillé J.Y, J. Polym. Sci. pt-B: Polym. Phys., 37, 2151-2164, 1999.
[c] "Plasticized PVC reinforced with Cellulose Whiskers: II- Plastic behaviour." Chazeau L., Cavaillé J.Y. and Perez J., J. Polym. Sci. pt-B: Polym. Phys., 38, 3, 383-392, 2000.
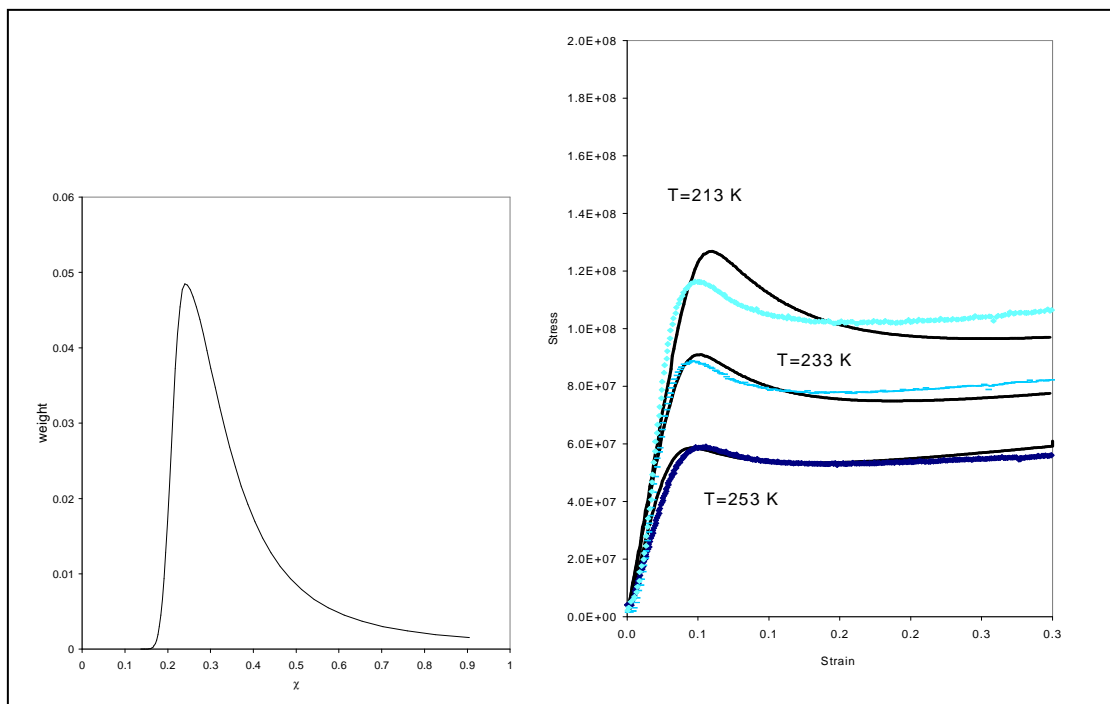
Figure 2 : a) Distribution of the correlation parameter deduced from the modelling of the data from mechanical spectrometry on plasticised PVC (30 phr of DOP), b) Compression curves at different temperatures of a plasticised PVC (30 phr of DOP), and theoretical curve (bold line) deduced from the « qpd » model.

Such modelling has allowed a better comprehension of the plasticizer role, as well as a confirmation of its heterogeneous distribution in the material. It leads also to the paradoxical conclusion that the plasticiser increases the cooperativity of the elementary movements at the origin of the beta relaxation, with decreasing in the same time the correlation effects. Thus, plasticiser, by specific interactions with polymer chains, blocks local movements, more difficult to proceed, but the larger scale movements conversely needs a less constraining succession of local processes due to the presence of a larger number of defects. These results should be confirmed by a molecular modelling.

2.2.2 Cellulose/ NMMO monohydrate solution.

The previous case has shown the existence of a critical concentration above which plasticiser domains exist. A work performed after the Ph-D thesis of Jean Francois Blachot[12] (at the Centre d'Etudes et de Recherches sur les Macromolécules Végétales) on the processing and the study of cellulose in a solvent, the monohydrate of N-methyl-morpholine N-Oxide (NMMO) presents the extreme case where the polymer is in small concentration in the solvent. This cellulose dissolution is the basis of a processing protocol, discovered fifteen years ago, which represents a very promising way much more environmentally friendly than the common processing (the viscose processing for instance). [13] The work of J. F. Blachot lead to the characterisation of the relaxations of a solution of 15% cellulose in NMMO/H2O on a temperature range going from the glassy domain up to the flow temperature. For instance, the material has been studied by mechanical spectrometry, in traction and torsion, in the glassy domain (T<Tg=245K) and below and above the glass transition temperature. This lead to the reconstruction of the complex modulus and the obtention of the relaxation

times as a function of temperature. It was therefore obvious to analyse these remarkable experimental data for their industrial interest as well as their scientific one.
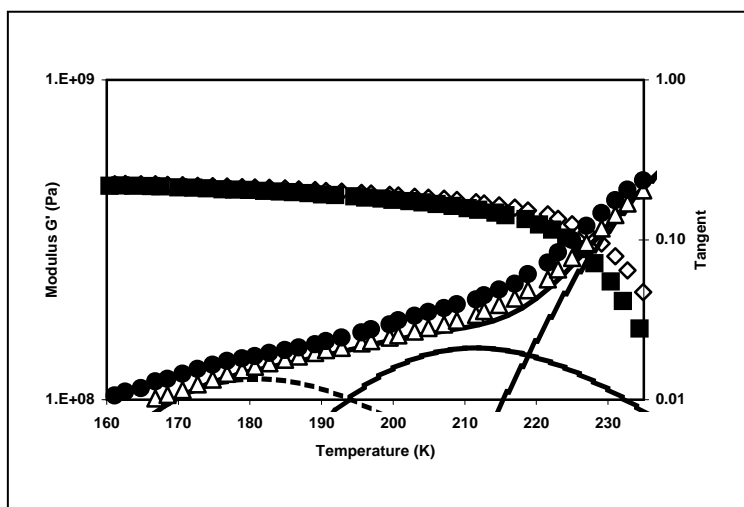

Figure 3a: Mechanical spectrometry in torsion of a 15 wt.% cellulose solution in (NMMO/H2O). G' (■ et ◊) loss factor (● et Δ) measured at 0.1 Hz (full symbols) and 1Hz (open symbols). Theoretical curves of both secondary relaxations γ and β and of the main relaxation α (dashed line), and theoretical curve resulting from a serial coupling of these three relaxations (bold line).
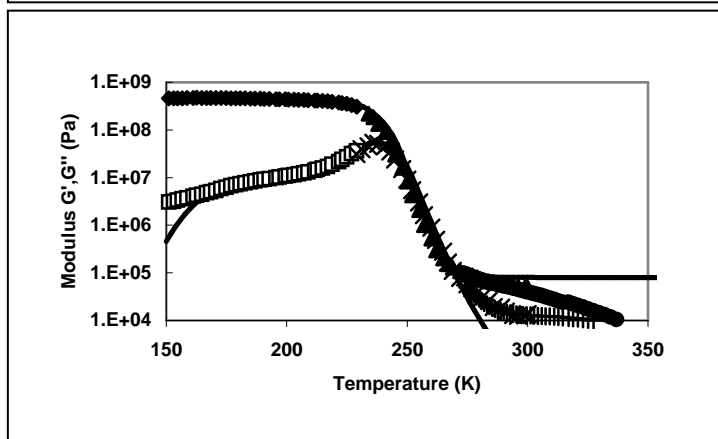

Figure 3b : elastic moduli G' (full symbols) and viscous moduli G'' (open symbols) obtained as a function of temperature by mechanical spectrometry with a cellulose solution (15 wt.%) in MMO/H2O. Theoretical curves (bold line) deduced from the qpd model.

The experiments show the presence of two secondary relaxations that have been attributed to the cellulose (cf. Figure 3a). The pre-exponential times of the beta relaxation as well as its activation energy (cf. equation R1 above) are very close to those found in literature for the cellulose in presence of a small quantity of water. [14] As seen previously with plasticised PVC, the value of the pre-exponential term is often discussed in term of activation entropy. The smaller is this one, the higher is the entropy and the more important the cooperativity of the corresponding molecular movements. It is noticeable that the water quantity in NMMO/H2O is more important than few percents; this should lead to activation energies smaller than those we found (70kj/mol). But it is also possible that like in the case of plasticised PVC, the strong interaction between NMMP molecules and cellulose lead to a movement of the main chain involving a largr number of repetitive units.

The gamma relaxation has been more difficult to interpret. The activation energy is higher than that of the gamma relaxation of the cellulose alone (65kJ/mole against 42 kJ/mole) and its pre-exponential time is smaller, suggesting a larger cooperativity. Again, these results can be explained by the inter-chain interactions via the solvent which have strong affinities with the methylol group involved in this relaxation.

The main relaxation is successfully modelled by the qpd model recalled in the previous paragraph. This modelling (cf. figure 3b) suggests that the main relaxation of the system is the result of the hierarchically correlated movements of the celluose chain in the solvent although its concentration in NMMO/H2O is low. This could come from the important rigidity of the cellulosic chain and its strong interaction in the solvent.[d]

A study with a smaller concentration of cellulose would have been surely very useful to confirm these results but could not be performed because of technical difficulties involved by materials with a so low viscosity at ambient temperature. However, the approach employed in this case like in the previous case allowed a better understanding of the influence of small molecules on the mechanical behaviour of polymers, introduced in small or large quantity in the material.

2.2   Interface …and interphase?

Besides solvents and plasticisers, polymer molecular mobility can also be modified by interaction with interface. Therefore, the extremely usual introduction of particles in polymer necessarily asks the question of the influence of the interface on the behaviour of the obtained composite. This question is particularly important when the fillers introduced – and this is more and more the case – are nanoscopic. The interfacial surfaces are then of the order of several hundreds of m^2 per gram of filler. They can perturbate a potentially important quantity of polymer at their contact. In fact, this important interface has already consequences during the processing. It is well known that the dispersion of nanoscopic fillers is more difficult than that of the same microscopic fillers. On the other hand, formulations involve small molecules such as plasticisers seen previously, or crosslinking systems in the case of elastomers or resins, whose adsorption sometimes important at the surface of the filler introduced can modify the crosslinking state of the final material. These same interfaces can also play the role of nucleating agent in the crystallisation, whose level and texture are then also modified. Moreover, surface treatments that can be performed on the fillers, by modifying the interactions involved, influence all these phenomena. Works that we have performed in the domain of nanocomposite materials naturally lead us to explore these different questions. One must notice that we will only discuss in this chapter the questions related to interfaces, the direct role of fillers being discussed in the chapter 3 since it concerns a larger scale.

[d] "Rheological behavior of cellulose/monohydrate of N-methylmorpholine N-oxide solutions. Part2: Glass transition domain", Blachot J.-F., Chazeau L., Cavaille J.-Y., Polymer, 43, 3, 881, 2002.

2.2.1 Interface and of crosslinking kinetic

J. Ramier's thesis (defended in May 2004) has the objective of studying the influence of filler-filler and filler-matrix interactions on the viscoelastic behaviour of elastomers filled by nanoscopic fillers.

> Recall:
>
> An elastomer is made of high molecular weight macromolecular chains, generally with a glass transition temperature above the ambient temperature, linked together by chemical bonds. This explains its large elasticity with reversible deformation up to 600%.

In the frame of this work, materials with poly(styrene-co-butadiene) filled by nanoscopic silica grafted with controlled interfacial agents (coupling agent and covering agent) have been processed. An interpretation of the experimental results needed first a precise characterisation of the material, in particular of the crosslinking state.[e] Thus, the influence of the huge amount of interface introduced by the presence of nanoscopic silica has been evidenced.

The matrix crosslinking by sulphur needs a complex formulation: activators (ZnO, stearic acid) and accelerators (n-cyclohexyl-2-benzothiazyl-sulfenamide (CBS), and diphenylguanidine (DPG)). These accelerators play a fundamental role in the crosslinking kinetic. The study of the kinetic can be made thanks to a rheometer measuring the torque evolution necessary to the shear deformation of the sample (characteristic of the increase of the material rigidity during the crosslinking) during the curing. As shown on figure 4a, the torque derivative as a function of time on samples without DPG or without CBS, CBS acts as a retardant of the vulcanisation, by delaying the time of the beginning of the reaction. This is because it has to decompose before reacting.[15] Once the process begun, vulcanisation is very rapid with formation of poly-sulphur bonds short and numerous. DPG reacts at short times but leads to a slow crosslinking kinetic. It leads to longer bridges, therefore less numerous. The simultaneous use, in equivalent proportion, of both accelerators leads to a vulcanisation process which begins early (due to DPG) and a rapid vulcanisation (due to CBS action).
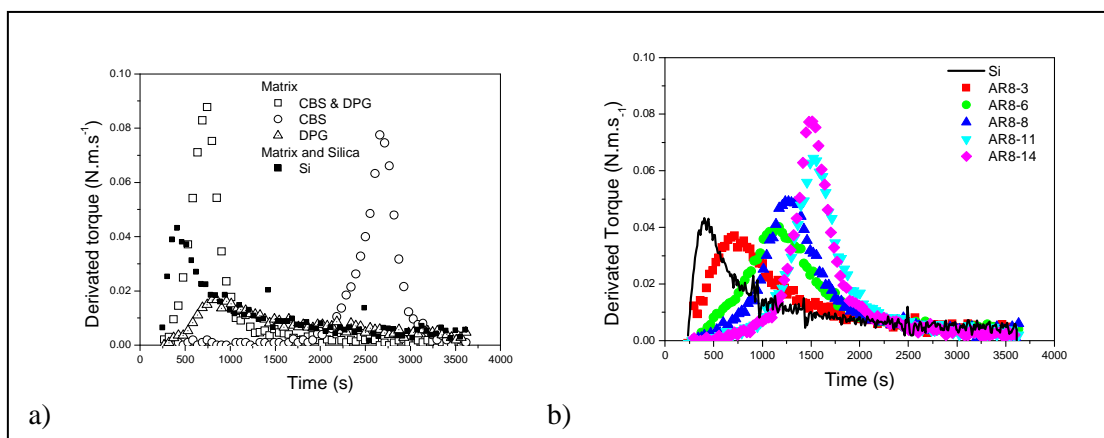
Figure 4 : a) Torque as a function of time during the vulcanisation at 150°C of the poly (styrene –co-butadiene) matrix with the CBS alone, the DPG alone, with CBS and DPG, and with the classical formulation (matrix, silica, CBS and DPG), b) influence on the crosslinking kinetic of silica and of the surface treatment of silica by a covering agent (tri ethoxy octyl silane), AR8, introduced in different quantities (the number written after AR8 indicates the content in phr).

The introduction of 50 phr of silica in the matrix, corresponding to 20% vol, leads to a crosslinking reaction which begins earlier with a slower kinetic (cf. Figure 4b). Literature shows there is a strong affinity between silica and common accelerators. [16] Adsorption measurements in solvent, performed with the same silica and the same quantities than that used in our formulations (50 phr silica, for 1.3 phr CBS and 1.45 phr DPG), show that the total amount of accelerators (CBS&DPG) is adsorbed on the surface. Therefore, the use of a silica treatment obviously leads to a modification of the crosslinking kinetic. As shown on figure 4, grafting of octyl triethoxy silane (noted AR8) leads to a kinetic close, at increasing grafting quantity, to that observed in the case of the matrix alone with CBS. Thus, grafting could limit, by steric hindrance, the adsorption of CBS during the processing, the CBS being totally adsorbed without grafting. The adsorption of DPG, because of the small size of this molecule, would be total and independent of the grafting, its desorption would be difficult, as suggested by the studies of Zaborski. [10] It is also possible that its desorption be delayed by the presence of grafting agents. This effect of the grafting is the same when using silane with alkyl chains of different lengths, the main parameter being the covering of the silica surface. The use of coupling agent has the same consequences with the difference that it contributes in the same time to the crosslinking kinetic (it accelerates it) by the coupling reaction.

Thus we have shown that the introduction of interface (via the incorporation of rigid particles) in a polymer matrix can have non neglectable effects on the crosslinking kinetic of this matrix. It is therefore necessary to characterise these effects before any analysis of the mechanical behaviour of the obtained material.

2.2.2   Interface and crystallisation

Creation of specific interactions between polymer and the filler interface can also have consequences on the crystallinity of semi-crystalline polymers. This question is important when trying to understand the mechanical behaviour of such a material since a modification of the crystallinity can sometimes explain by itself the measured reinforcement without invoking any other physical mechanisms. This problematic is present is the case of natural rubber. This polymer is atypical, on the one hand because of its natural origin, on the other hand because of its isoprene monomer. Thus, it is mainly constituted of poly(isoprene) [cis-1,4 99%] whose stereo-regularity authorises its crystallisation at rest at low temperature (-25°C)or under strain. From a strain level around 300%, its crystallisation is instantaneous.[17] This peculiarity gives to the natural rubber an original auto-reinforcing character. Like for synthetic rubber, natural rubber is often reinforced by nanoscopic fillers. It is well established that their addition can indeed strongly increase rigidity, abrasion resistance, tear strength, and stress at break…[11] It seems that these improvements of the mechanical properties are partly linked to the influence of the filler on the crystallisation under strain. However, even if the role of strain amplification of local strain is evoked in literature (this aspect, from my point of view, being relevant of the mesoscopic scale, I will discuss it in the second part of the manuscript), the impact of fillers on the material crystallisation is still not well known. [18,19] For instance, does the interface of nanometric fillers have a nucleating role, in particular when the surface is chemically modified ? A post-doc, J.M. Chenal, has been hired to study this question in the frame of National program "Réseau National Matériaux et Procédés" on "filled elastomers under severe solicitations" (2001-2004) that we have co-ordinated with our colleagues of the Centre des Matériaux d'Evry (Ecole des Mines de Paris).

We have first chosen to study the crystallisation of NR at low temperature. This has the advantage to dissociate the effect of interface from the strain amplification effect induced by the filler presence (still keeping in mind that crystalline morphologies induced by deformation and those created during crystallisation at low temperature are different and therefore that the link between the mechanisms at their origin have always to be considered with caution).

The crystallisation kinetic of crosslinked NR is slow. Its optimal temperature is –25°C and enables to reach a maximal crystallinity level around 40% (note that literature often indicates a maximal level of 30%, probably due to the impatience of authors in front of a very slow kinetic…). The spectrum of NR obtained in DSC presents the particularity to possess two melting endotherms (cf. figure 5), one at –2°C and the other at –17°C. The material melting at -17°C is seemingly unstable since its melting peak is sensitive to the heating rate. Conversely to what is written in some articles on NR crystallisation at low temperature[20], these two peaks do not seem, from our point of view, the manifestation of two types of crystalline lamellae with different lattice but could be, as suggested by the article of Strobl[21], the result of a multi-step crystallisation: creation of mesomorphic lamellae first occurs, then

these lamellae thicken up to a critical size, then solidify by a structural cooperative transition ; this transition leads to the formation of a granular lamellar structure which transforms in a last step in lamellar stable crystallite. The first peak traduces the presence of the granular crystalline phase, the second peak is characteristic of the eventually formed crystalline structure. The energy brought during the heating ramp performed in the DSC apparatus enables in a concomitant way the melting of the granular phase and the formation of the stable crystalline phase. [f]
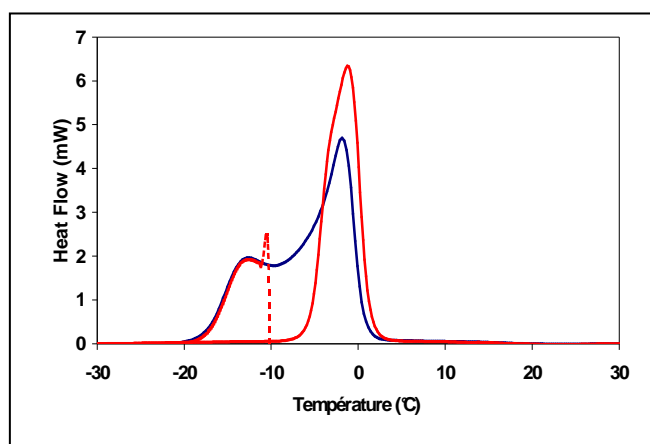

Figure 5 : Melting endotherms of NR measured by DSC (heating rate of 10°C/min). The blue curve is obtained during a simple heating ramp (The sample was previously stocked 16 h at –25°C). The red curve corresponds to heating ramp with an interruption of 1h at -10°C. During this interruption, the crystallites which have not melted associate themselves into larger crystallites which melt at higher temperature.
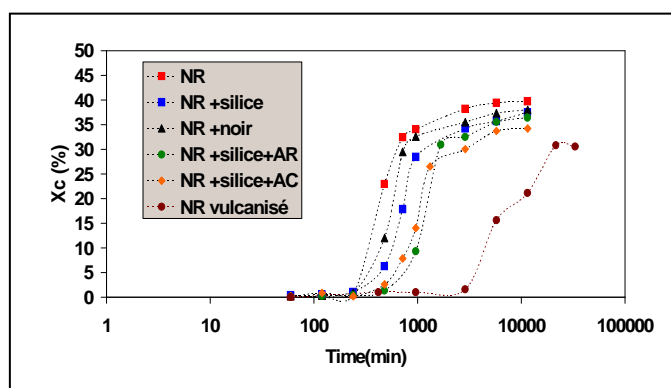

Figure 6 : Cristallinity level measured by DSC as a function of time of stay at 25°C, for an uncrosslinked natural rubber (NR), a uncrosslinked NR filled with 50 phr of silica treated by a covering agent (NR+silice+AR) or a coupling agent (NR+silice+AC), for a NR filled with 50 phr of carbon black and for a crosslinked NR (NR vulcanisé).

We have then evaluated the effect of the fillers on crystallisation (cf. figure 6). The introduction of carbon blacks or silica in NR favours the occurrence of the melting peak with the lowest temperature conversely to the melting peak at –2°C that decreases, even if the total crystallinity obtained at –25°C decreases only slightly. The interfacial surface did not show a significant impact (but it is true that the domain of surfaces explored is narrow). Moreover, the interface introduction has a limited influence on the kinetic of global crystallisation. Our assumption is that the crystallite growth is sterically hindered by the filler presence, the observed differences being the results of dispersion difference. Thus, interface lead to the formation of a larger quantity of mesomorphic phase, or of the phase with the intermediate morphology au detriment of that with the final crystalline morphology.

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[f] J.M. Chenal, L. Chazeau, C. Gauthier, Yves Bomal, «New Insights into the Crystallization and the Nature of Multiple Melting Endotherms in Filled Natural Rubber », Polymer, submitted.

Conversely, one cannot see significant difference of melting temperature, since, in all cases, NR crystallise under the form of small crystallites.

The effect of surface treatment on silica has also been studied (still with an uncrosslinked matrix). We have used different surface treatments, close to those used in J. Ramier PhD thesis and previously presented: silica was treated with a covering agent which limits the interactions between filler and the matrix and decreases the number of silanol. The second treatment is a coupling agent enabling the formation of covalent bonds between the fillers and the matrix (note that the coupling agent contains two more sulphur than the TESPD used in the PhD thesis of J. Ramier). These different treatments leads to a slight decrease of the final cristallinity of NR, due to the increase of the effective volume of filler and the decrease of the crystallisable fraction of NR. The crystallisation kinetic is slowed down at the beginning then is similar to that of the other samples. The time of beginning of the crystallisation is not modified. Thus, germination does not seem affected by the surface treatment in the crystallisable matrix zone but the crystallite growth is perturbed due to the global crosslink of the matrix (AC sample) or due to the presence of small molecules which are going to delay the chain organisation (AR sample). Like for untreated filler samples, one does not observe any significant variation of the melting temperature of the crystallite, for the same reasons than those given previously, i.e. crystallite sizes still small.

Note that the effect of small molecules on the crystallisation kinetic of Poly (ethylene oxide), that we have studied elsewhere is different.[g] Thus, plasticization of this polymer by polyethylene glycol decreases the melting temperature without modifying the final cristallinity level. The plasticiser molecules perturb the crystallite formation because it needs the "expulsion" of the plasticiser from the crystallizing zone. The crystallisation temperature (difficult to measure in the case of NR because its crystallisation is very slow) is also decreased, suggesting a modified germination. The germination kinetic is not completely changed in the case of NR because the surface treatments are only present at the periphery (at the interfaces) and not in the bulk matrix.

To go further in our analysis, we want to study the crystallisation at low temperature under X-ray diffraction. This needs the development of a low temperature chamber on our X-ray apparatus. This work is in progress.

2.2.3 Interface and viscoelastic properties

Thus, presence of important interface quantity can lead to structural modifications such as crystallisation state, or initial crosslinking state. These modifications are partly linked to adsorption mechanisms, more or less important, depending on the interface nature. It is therefore natural to evaluate the consequences of specific interactions between fillers and matrix on the mobility of polymer chains around these interfaces, this mobility being linked,

as seen previously, to the macroscopic mechanical behaviour of polymer. Controversial topic because the question is then to know at which distance this modification occurs and if this is significant compared to the mechanical activation of the relaxation times. Several studies indeed show that the confinement effects between fillers can increase this mobility[22], and it is obvious that surface treatments involving mobile chains at temperature below the matrix Tg, can lead to the same effect; However, we do not know studies clearly showing that an interface decreases the mobility of a polymer matrix below its Tg (is this surprising if one consider that in the glassy domain, the mobility is already reduced and very localised?). The question of a mobility modified above Tg is still pertinent… even is the importance of this modification is the object of a vivid debate: is there a mobility gradient? On which distance the polymer involved behaves like a glassy polymer?…

This debate is peculiarly nourished by the specific behaviour of filled elastomers, the latter being apparently linked to the nanoscopic character of the fillers they contain. The study of this behaviour was the topic of my postdoc at Rensselaer Polytechnic Institute (Troy, NY, USA) under the direction of Prof. Sternstein, performed just before I got the position at CNRS. The aim was to deduce from the study of many types of filled elastomers a general behaviour and, in particular to determine the kinetics involved.

Recall:

The energy dissipation measured during a strain cycle on a unfilled elastomer is low; in other terms, the elastomer shows a low sensitivity to strain solicitation, in particular at low strain (cf. Figure R3). This pseudo-elastic behaviour above Tg is relatively well described. Weak intermolecular interactions lead to consider the chains response to a mechanical solicitation only from an entropic point of view.
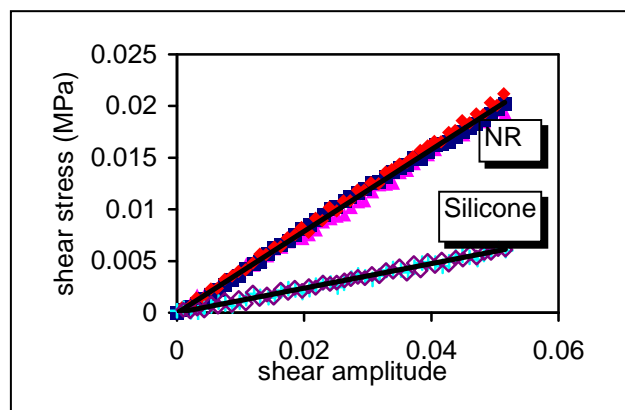
Figure R3 : Shear stress strain curve of two unfilled elastomers (NR, and silicone), at three strain rates.

This enables the modelling of the mechanical modelling of the material. [23] The accounting or not of the maximal extensibility of the chains (with the gaussian or Langevin formulation) and the integration of the response of the isolated chain in a more or less complex and representative volume element (5 chain models, 8 chains model, phantom network…)[24,25] lead to a more or less complete modelling of the stress-strain relationships in different loading paths. In particular, the stress measured in shear is proportional to the strain level up to a strain level of the order of 100 %: in other words, the shear modulus is constant in this strain range.

[g] Master Report (dernière année INSA-Lyon), F. Dalmas "nanocomposites à renforts cellulosiques pour électrolytes polymères. Application aux batteries en film mince." (2001-2002).
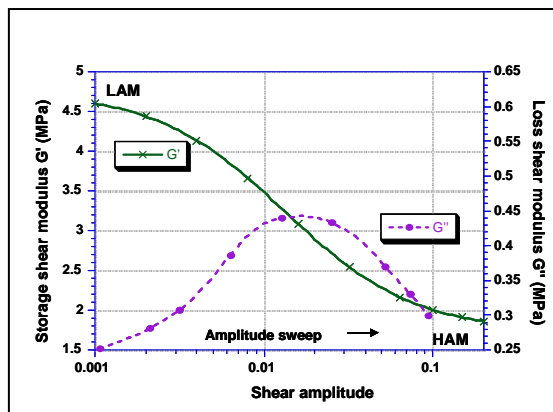
Figure R4 : Payne effect measurement of a carbon black filled NR : elastic (G') and viscous (G'') moduli as function of the shear amplitude. (at 1Hz). The measurements are performed at increasing shear amplitude.

The introduction of nanoscopic fillers strongly modifies this behaviour. A mean to show it is to submit the material in a dynamic mode to increasing strain levels. As shown on Figure R4, the modulus value measured at low strain levels is important (4.6 MPa for the material with filler, less than 1 MPa for the matrix alone). In fact it is more important than predicted by classical models used to predict the reinforcement. We will come back to this point in chapter 3. Moreover, the viscoelastic response becomes non linear (this is not the case without fillers) in the deformation range below 50%. This is the Payne effect, which is defined as the drop of the elastic modulus as a function of the applied dynamic strain, accompanied by a loss peak.

Works performed at RPI (cf. Figure 7) on natural rubber samples filled with different carbon blacks clearly show the influence of the filler size, or in other words of the specific surface on the phenomenon. The latter is mainly observed in the case of nanoscopic fillers. We have also shown the extremely general character of this behaviour by studying many different types of matrices. Moreover, we have focused our attention on the evidence of the very important role of the mechanical history of the material on the intensity of the Payne effect. Thus, the initial value of the modulus measured at low stain is measurable in a reproducible way only if the material has been not deformed during a given time (estimated in our experimental conditions of the order of half an hour), at deformation above which normally the non linearity appears. This value of the order of half an hour at ambient temperature has been experimentally estimated on different systems by the measurement as a function of time of the return to the initial value of the modulus (just after the solicitation of the material at a strain level needed to observe the Payne effect.). It depends on temperature. On the other hand, and to our mind, this is essential when one has the objective of modelling this type of material, the Payne effect is independent on the application of a static strain, even when it is above the strain necessary to observe the Payne effect, when again a stay time of the order of half an hour has been respected between the application of the static strain and the dynamic measurement (cf. Figure 8). [h]

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[h] " Modulus recovery kinetics and other insights into the Payne effect for filled elastomers", Chazeau L., Brown J.D., Yanyo L.C., and Sternstein S.S., Polymer Composites, 21, 2, 202-222, 2000.
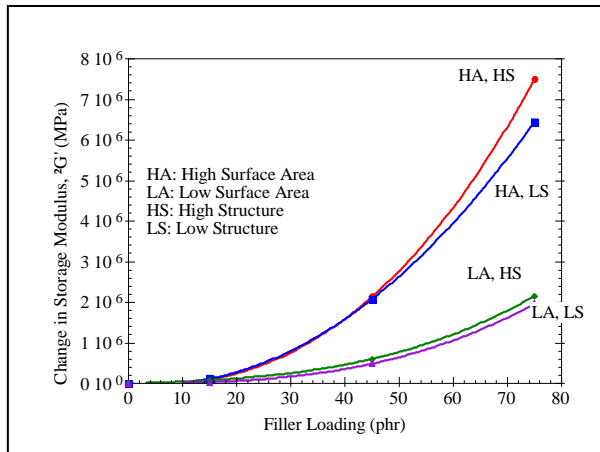
Figure 7 : influence of the filler content on the Payne effect amplitude (i.e. the modulus drop value). Carbon blacks with two specific surfaces (GSu for large surface, PSu for small) and two different DBP structures (GSt et PSt) have been studied. The influence of the structure is of second order compared to that of the specific surface.
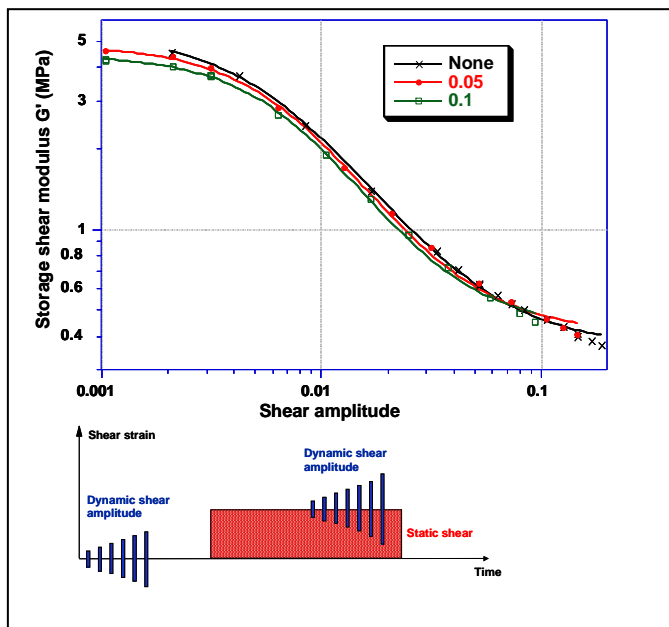

Figure 8 : Effect of a static strain on the Payne effect amplitude. The scheme describes the experimental procedure.

The influence of the filler size and the strongly viscoelastic nature of the phenomenon suggest that its origin is the interface. Then can we assume the existence of an interphase? The study of the influence of the filler surface treatment on the viscoelastic properties performed in the Ph-D thesis of J. Ramier brought new insight in this debate.

The different materials with a SBR matrix filled by nanoscopic silica with various surface treatments have been submitted to increasing dynamic strains in the range of the Payne effect. Figure 9 synthesizes the behaviour observed for the samples with untreated silica, with a silica treated by a covering agent with 16 carbons, or treated with a coupling agent enabling a covalent bond between the matrix and the filler.

The grafting (covering or coupling agents) leads to a decrease of the Payne effect amplitude (cf. figure 9), i.e. basically a decrease of the initial modulus, measured between the modulus drop. We have checked that this could not be due to a modification of the silica dispersion in

the material. [i] Bond rubber measurements, i.e. quantities of polymer non solubilized by washing the material in a solvent (these experiments are performed in the non crosslinked materials) have shown an expected decrease of the adsorption of polymer chains at the filler surface with the covering agent quantity (note that this characterisation also allowed to establish a equivalence between the quantity of covering agent and the length of this agent to cover the silica surface). [j] Bound rubber quantities are huge. They can represent, in the case of the studied materials, up to 40% vol. of matrix. Assuming a uniform layer, the thickness of this polymer can reach 30nm. Moreover, it exists a correlation between the bound rubber value and the initial modulus. The modulus drop in the peculiar case of the materials with coupling agents is very similar to that observed with materials with covering agents. This suggests that the formation of covalent bonds between fillers and the matrix do no counterbalances the decrease of the physical bonds induced by the covering of the silica surface. These physical bonds are key factors in the initial value of the modulus.
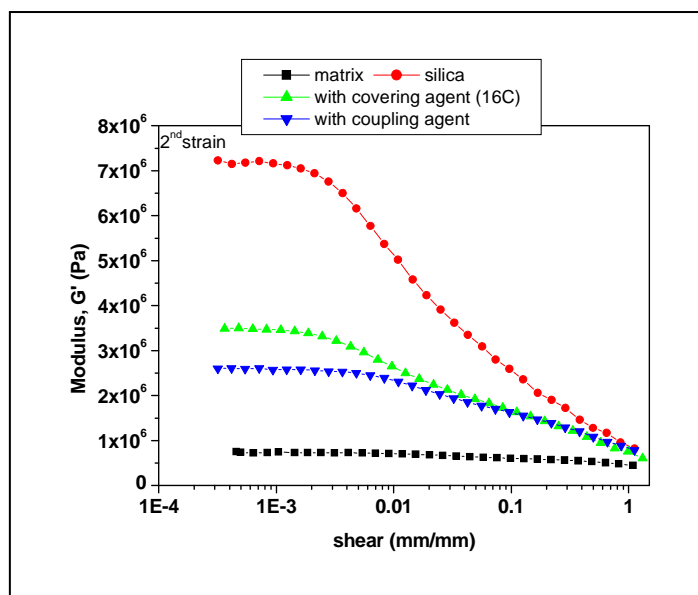

Figure 9: elastic shear modulus measured at 5 Hz of a SBR filled with untreated silica, or trated with a coupling agent or a covering agent.

In a purely entropic description of the viscoelastic behaviour of the material, Maier and Gortz[26] have then assimilated these bonds to supplementary crosslinks, the initial modulus being then the direct consequences of an increase of active chains in the elastomer, and its drop the consequence of a rupture of the bonds. This vision has the advantage to nourish the debate on the importance of matrix-filler interactions on the Payne effect but the model deduced from it is too global (homogenising) and leads to absurd theoretical crosslink densities. One could also conclude that bound rubber is also the indication of the existence of a polymer phase immobilised at the interface. It would have a glass transition temperature higher than that of the unfilled matrix. But DSC measurements do not allow to confirm this assumption. Mechanical spectrometry however shows, above the glass transition

[i] "Payne effect in silica filled styrene butadiene rubber : Influence of surface treatment", J. Ramier , C. Gauthier , L. Chazeau , L. Stelandre , L. Guy, J. Polym. Sci. PtB: Polym Phys, soumise.
[j] "Grafting of silica during the process of silica filled SBR: comparison between length and content of the silane", J. Ramier, L. Chazeau, C. Gauthier, L. Ladouce, M.N. Bouchereau, Journal of Polymer Science :Polymer Physics Part B, 44, 1, 143-152, 2005.

temperature, a second loss peak (characteristic of a drop of the rubbery modulus with increasing temperature). But there is no correlation between the intensity of this peak and the quantity of bound rubber value measured with the same sample. Therefore, the question is still controversial even if the argument of a mobility gradient is relatively convincing to explain the absence of DSC clue…

The most reluctant adversaries to this vision are those convinced by the direct role of the fillers in the phenomenon. In fact, on cannot consider the initial reinforcement as the only result of an interphase, i.e. without taking into account the filler role. The study of the material only at the level of the molecular scale is not enough, and one must also consider a more "mesoscopic scale, i.e. that of the fillers, still keeping in mind the phenomena described in this chapter.

2.3   Conclusion

The different examples presented in this chapter show that the study of materials at the molecular scale can be necessary if one wants to understand their mechanical behaviour. Indeed, a modification of the relaxational mechanisms involved at this scale can have important consequences on the observed macroscopic behaviour, as shown in the study of plasticised PVC or of cellulose in NMMO/H2O solvent. These modifications are unavoidable in the case of a formulation involving solvent or plasticizers, which influence these processes. They are also unavoidable when the introduction of an important quantity of fillers or filler with small size leads to the creation of an important interfacial area, which can interacts with the polymer. This is especially the case when these interfaces are also modified by chemical treatments. These interactions could lead to the formation of an interphase having a mechanical response different from that of the material far from the interface. Besides, these interactions can have consequences on the material microstructure if it can crystallise or crosslink.

3. Heterogeneities at the mesoscopic scale

However the interface created when introducing fillers has firstly the function of transmitting stresses between the fillers and the matrix. This aspect cannot be neglected for any discussion on the existence or not of an interphase. Fillers are first a rigid phase in an other phase, the matrix. And this has consequences in all the deformation range. At low strain, this effect can alone often explain the reinforcement, if all the filler parameters are taken into account. At large strain, the filler distribution, necessarily irregular, leads to strain heterogeneities which, depending on the interface quantity, will develop a more or less important damage. In the case of elastomer, they lead to a strain hardening, and when the elastomer can crystallise to more or less premature heterogeneities of crystallisation.

3.1   Fillers and their reinforcing effect at low strain

The introduction of fillers whose modulus is higher than that of the matrix leads to matrix deformation during a solicitation that is more important than that of the fillers. The global deformation of the material will then be smaller and therefore its rigidity higher. This is a simple description of the mechanical coupling. Different models enable a description of this coupling and its consequences on the global mechanical behaviour.

Recall:

These models have been first developed in the linear domain for experimental modulus of reinforced materials. We will not do an exhaustive review of all the existing models but will recall the most famous (we advise to interested readers the lecture of the books of Christensen[27] and of the thematic school organised by the Laboratoire de Mécanique des Solides[28])

The simplest models are the Voigt and Reuss boundaries, which assume a uniform stress (serial model) or a uniform strain (parallel model) in both phases respectively. Macroscopic strain and stress are then the average of strains and stresses of each phase, from which the composite modulus is deduced. The drawback of such models is their too large gap which does not allow a good estimation of the modulus, in particular when the modulus contrast of both phases is high. Both models can then be combined to give phenomenological models in which the distribution of phases serially or in parallel is controlled by more or less adjustable parameters. We will see later the Takayanagy model, or serial-parallel model which has been adapted by Ouali et al for the description of composites reinforced by cellulose whiskers. [29]
There are also geometrical models, which try to directly account for the composite microstructure. This needs the knowledge of the spatial distribution of fillers, which is not always well established. That is the reason why the system is generally simplified and described by a Elementary representative volume. A simple case is that of composites reinforced by spherical particles introduced at low concentration. One can then consider these particles as isolated inclusions. The analytical calculation of stress and strain field of a unique inclusion in a infinitely homogeneous matrix leads to the expression of the composite modulus as: [27]

$$G_c = G_m \left[1 - \frac{15(1-\nu_m)[1-G_f/G_m]\phi}{7-5\nu_m+2(4-5\nu_m)G_f/G_m} \right] \qquad \text{(RE16)}$$

Where the m, f indices are respectively for the matrix and the filler and ϕ is the filler volume fraction. In the case of infinitely rigid filler, the formula is simplified as:

$$G_c = G_m(1+2.5\phi) \qquad \text{(RE17)}$$

It is equivalent to the Einstein equation for the viscosity of an incompressible fluid containing infinitely rigid particles. [30]

The composites description with higher filler concentrations is more difficult. Guth has first proposed an extension of the previous formula by adding a quadratic term: [31]

$$G_c = G_m(1+2.5\phi+14.1\phi^2) \qquad \text{(RE18)}$$

More elaborated models have also been proposed, like for instance the 3 phase model initially proposed by Kerner[32] and corrected afterwards by Christensen and Lo. [33] In this model, the composite is seen as an inclusion surrounded by a matrix immersed in the unknown homogenous equivalent medium (cf. Figure R5). This is the reason of the name of the model, which is called "generalised self consistent scheme". This model must not be confused with the self consistent models initially developed for the description of polycrystalline materials. [34,35] In these models, each phase is alternatively immersed in the infinite medium with the researched properties submitted to the macroscopic solicitation. The composite properties are then deduced by considering the macroscopic strain and stress fields as the average of the strained stress calculated in each phase. The drawback of such models is that they exclude the continuity of one of the phase ; this can be a serious problem when one wants to describe a composite where the matrix is continuous. Therefore, from our point of view, the Christensen and Lo model is the most adapted for the description of our materials. Note that it has been extended to the description of materials with n phases, to account for, for instance, an interphase surrounding the inclusion. [36]
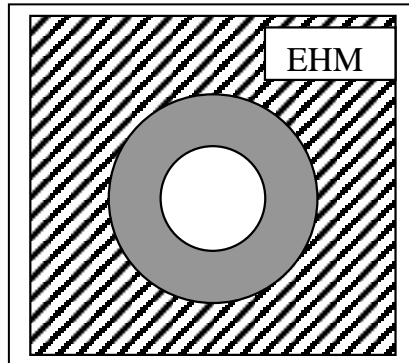

Figure R5: Generalised self consistent scheme (or 2+1 phase model) : the inclusion is surrounded by a shell of matrix immersed in the equivalent homogeneous medium.

This type of model developed for spherical inclusion has an equivalent in the domain of long fibres, then assumed with an infinite length. [37] When these fibres are short, the calculation is performed using the Eshelby calculation[38] for an ellipsoidal inclusion whose the form factor is that of the fibre, in a matrix taken as the homogenous infinite medium (this calculation was initially proposed by Mori and Tanaka). [39] The general solution for the modulus in the direction of the large axis of the ellipsoid has a strong dependence on the modulus contrast of both phases and on the form factor. One can define a reinforcement factor with the formula:

$$E_c = E_m(1 + A\phi) \qquad \text{(RE19)}$$

Its evolution as a function of the form factor ξ and of the modulus ratio is recalled on figure R6. One can notice that for a modulus ratio below 100, fibres with form factor above 100 have the same effect on the reinforcement than infinitely long fibres. Moreover, the highest the form factor, the largest the influence of the modulus contrast. These calculations can be applied to the simple case of composites with unidirectionnaly oriented fibres. The calculation for a transversely isotropic or totally isotropic material needs the calculation of

an average of the reinforcement on all the orientations, from the calculation of the reinforcement calculated in the unidirectional case, as proposed by Tandon and Weng. [40]
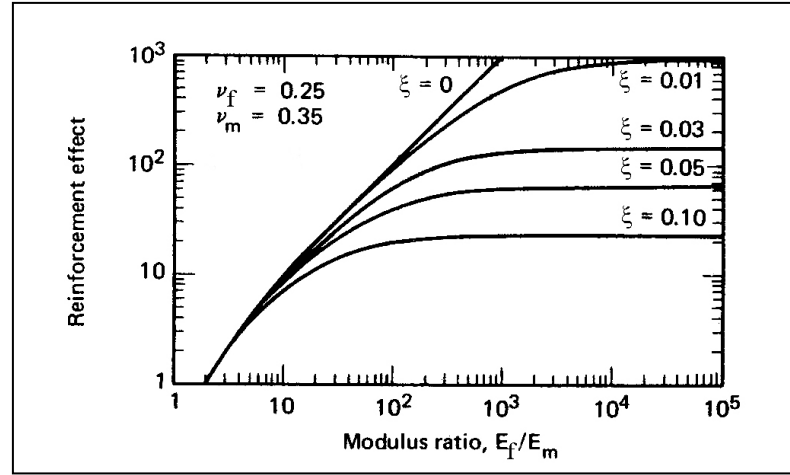

Figure R6: Influence of the fibre length on the reinforcing factor A ($E_{11}/E_m=1+\phi A$, E_{11} being the longitudinal in plane modulus, E_m the matrix modulus and ϕ the filler volume fraction) as a function of the filler to matrix modulus ratio. After R.M. Christensen, Mechanics of Composite Materials Chichester, UK: Wiley, 348p. 1979.

The absence of an analytical solution of such calculations lead Halpin and Tsai to propose an empirical equation equivalent to the Mori-Tanaka calculation: [41]

$$\frac{M_c}{M_m} = \frac{1+\zeta\eta\phi}{1-\eta\phi} \tag{RE20}$$

Where η writes:

$$\eta = \frac{\dfrac{M_f}{M_m}-1}{\dfrac{M_f}{M_m}+\zeta} \tag{RE21}$$

Where ϕ is the filler volume fraction, ζ is a factor depending on the filler form and M he researched modulus. Ashton and al. [42] have shown that the equations can be used for the reinforcement of unidirectional fibre composites. They advised the use of $\zeta=2a/b$ for the calculation, of the longitudinal modulus E_{11}, $\zeta=2$ for the transverse modulus E_{22} or E_{33}, $\zeta=1/(3-4v_m)$ for the shear modulus G_{23}, and $\zeta=1$ for shear moduli G_{12} or G_{31} with $v_{31}=v_{12}$.

This formula is often used for the modulus calculation of laminates. In this case, the modulus tensor is the orientationnal average of the moduli tensor of each ply, weighted by the volume fraction. The Halpin-Kardos model leads to the analytical formula of a laminate containing 4 plies in which fibres are oriented respectively at 0°, 45°, 90°, and 135°. From these calculations, Tsai and Pagano, have proposed a simplified expression of a transversely isotropic composite: [43]

$$E_{2D} = 0.375E_{//} + 0.625E_{\perp} \tag{RE22}$$

Where $E_{//}$ is the longitudinal modulus of the ply, and $E_{\perp}$ its transverse modulus. The modulus of an isotropic composite can be obtained by a tridimensionnal average such as that proposed by Van Es: [44]

$$E_{3D} = 0.184E_{//} + 0.816E_{\perp} \tag{RE23}$$

Even if his process is discussable, the results are equivalent to the calculation of Tandon and Weng.

Developed in the purely elastic domain, the equivalence principle of Hashin enables their extension in the linear viscoelastic domain. When an analytical expression is available, this is done by only replacing in the formula the moduli by their equivalent counterpart in the complex domain. [45] When it is not the case, the introduction of complex values is done at the level of the modulus tensors before their manipulation. Note that the extension of the models in the non-linear viscoelastic domain is more difficult; it is then necessary to perform a linearisation step, following different methods more or less elaborated. [27] The work of F. Saint Michel was the opportunity to explore this question; we will come back to this point in the manuscript conclusion.

The different models found in literature thus enable to account for the filler parameters in the reinforcement of the composite materials. However, they are adimensional and do not predict any effect of the filler size.

3.1.1   Filler size effect

There are however examples where the inclusion dimensions are involved in an obvious manner in the reinforcement. Among them, we will present that extracted from F. Saint-Michel Ph-D thesis (defended in March 2004). [k] The topic of this work was the process and the study of the mechanical properties of polyurethane composite foams. Polymer foams present very good mechanical and thermal properties in relation to their density and excellent energy absorption capacities, peculiarly useful for shock damping. However, these materials technologically very promising still present some problems for their processing and for the comprehension of their properties in relation to their microstructure. This topic complex by nature, involves two different characteristic scales: that of the cellular structure and that of the cell walls. The aim of F. Saint Michel was to optimise the formulation of polyurethane composite foams, used to make orthesis. The fillers in the studied material are mainly added to absorb heat generated during the the very exothermic chemical reactions occurring during the process. This needed their use in large quantity, with the problem of their possible sedimentation in the polyol, in which they are dispersed for their commercialisation. The technological solution that has been found needed first a study of the rheological behaviour of polyol mixed with different types of fillers. This work was performed in the Laboratoire de Rhéologie (UJF-Grenoble/INPG) that was co-directing the thesis. It needed in the same time a study of the mechanical properties of the final materials, to be sure that the properties still fulfilled the requirement of the industrials. This lead us to focus our study on the effect of the filler size.

Thus, we have shown that the increase of the material stiffness brought by the fillers mainly depend on the ratio of their size by the average size of the bubbles in the foam. Thus, in the studied range of the density and of the filler concentration, a foam whose characteristic size of the walls is below that of the characteristic size of the fillers can been seen, from a mechanical point of view like a composite material in which the inclusions are the fillers, and the homogneous matrix has the properties of the filled foam. Conversely, when the wall size is above that of the fillers, the foam must be considered like a composite whose

[k] F. Saint Michel, thèse de doctorat, Institut National Polytechnique de Grenoble, 2003.

inclusions are bubbles and in which the homogenous matrix has the properties of a polyurethane (without bubbles) reinforced by the fillers. Thus, Figure 12a presents the experimental moduli of foams with different densities filled with the same quantity of fillers. These experimental results are successfully compared to a 2+1 phases model applied in two steps with one or the other of both assumptions (cf. figure 12b). [l, m]
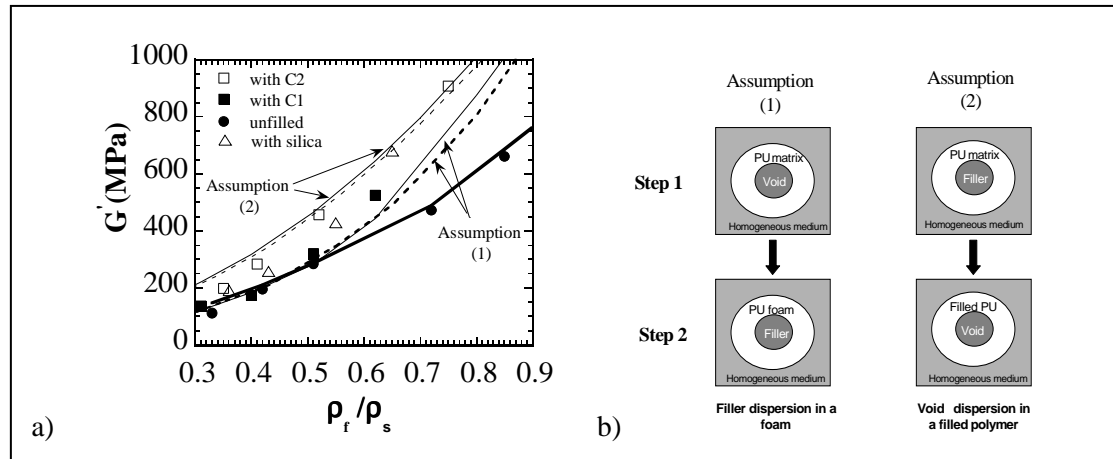

Figure 12 : a) elastic modulus G' as a function of the relative density of the foam for an unfilled foam and foams filled with small calcium carbonate (carbonate C2), large calcium carbonate (C1), or silica with intermediate sizes. Comparison with the model schemed on figure 12b. b) scheme of the model. In the first assumption, materials are seen as a matrix with voids (step 1), in which the filler is the inclusion (step 2). In the second assumption, foams are seen as a filled polyurethane (step 1) in which inclusions are voids (step 2).

3.1.2   Form effect

As seen previously, in the case nanocomposites, it is always tempting, when sing nanoscopic filler, to evoke the important interface quantity to account for the composite mechanical properties. However, this cannot be done without examining the aspect ratio of the nanoscopic fillers introduced. Indeed, as recalled previously, the models predict a strong increase of the reinforcement level when the fillers have a high aspect ratio.

During my Ph-D thesis on plasticised PVC filled with cellulose whisker (15 nm diameter and a form factor of 70), the reinforcement in the glassy domain was even overestimated in models taking into account the filler morphology. In fact, generally, nanocomposites moduli studied below Tg are, depending on the case, either in agreement, or overestimated by the models, this overestimation being the consequence of an overestimation of the filler aspect ratio (due either to a bad characterisation of the filler of a dispersion problem). [46,43] Conversely, in the rubbery domain, the same models (inclusion/matrix type) have the

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[l] "Mechanical properties of high density polyurethane foams: I Effect of the density" Fabrice Saint-Michel, Laurent Chazeau, Jean-Yves Cavaillé, Emanuelle Chabert, Comp. Sci. Technol., in press.
[m] "Mechanical properties of high density polyurethane foams: II effect of the filler size" Fabrice Saint-Michel, Laurent Chazeau, Jean-Yves Cavaillé, Comp. Sci. Technol., in press.

tendency to underestimate the nanocomposite modulus. For instance, in the case of cellulose whiskers/PVC nanocomposite above Tg, even, though the modelling enables to account for the reinforcement measured for filler content below 4% (the reinforcement reaching, though this low content, a factor 4!), , the same modelling largely underestimates the experimental moduli beyond this content. [n]

Besides cellulose whiskers, there is nowadays new fillers which have exceptionally high aspect ratio (it can reach up to several thousands), associated to very interesting physical and mechanical properties. Carbon nanofibres and cellulose nanofibrils are among them (cf. figure 13). [o] These fillers cannot be simply seen as straight fibres (like the cellulose whiskers where). Their aspect ratio provides them exceptional characteristic of flexibility, leading to a pronounced waviness, notably function of their processing conditions.
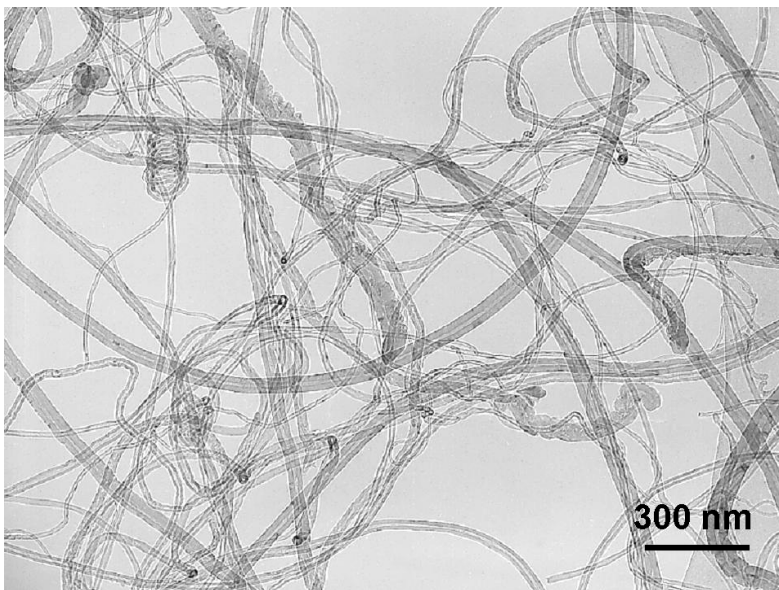

Figure 13: T.E.M. picture of carbon nanotubes.

In the frame of the CNRS Materials program "multi scale approaches of macroscopic properties of structure materials", and a "Jeune équipe chercheurs CNRS" 2005-2006 'behaviour of entangled fibre medium", we have the objective to process, to microstructurally and mechanically characterise composites filled with such filler. We wants to develop tools for mechanical modelling which can describe and quantify these effects of flexibility, but also (we will discuss it in paragraph 4) the multi-contact effects in the network that these fibres can form.

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[n] "Viscoelastic properties of a plasticised PVC reinforced with cellulose whiskers", Chazeau L., Cavaillé J.Y., Canova G., Dendievel R. and Boutherin B, J. Appl. Polym. Sci., 71, 1797-1808, 1999.
[o] " Multi-Walled carbon nanotubes/polymer nanocomposites : processing and properties", F. Dalmas, L. Chazeau, C. Gauthier, K. Masenelli-Varlot, R. Dendievel, J.Y. Cavaillé, L. Forro, J. Polym. Sci. Pt.B Polym. Phys., 43, 1186-1197, 2005..

The first works (A.T.E.R of P. Richard [p] and postdoc of T. Prasse[q]) concerned composites (i) with a filled epoxy elastomer matrix (epoxy prepolymer DGEBA – Jeffamine hardener D2000) whose glass transition temperature is below the ambient temperature (Tg~0°C) and (ii) with a crosslinked poly(styrene butadiene) matrix. The process, which needed a long work of optimisation, allowed to obtain a very good dispersion of nanofibres for filler content up to 10%vol. in the case of the SBR matrix. The measured reinforcement were however deceptive, but could be explained by the models (Equations RE21 and RE22). They have confirmed that (i) the nanofibres aspect ratio is low, of the order of 15, die to the presence of numerous defects in the initial fibres, and (ii) that the nanofibres modulus is small, of the order of 35 GPa, for the same reasons. Thus, these fibres did not show any size effect. They are however more interesting at low volume content (below 15%) than Carbon Blacks with the same specific surface, in particular for the improvement of properties at break, simply because of the form factor slightly higher (after the material processing) than that of carbon blacks.

This work was followed by the study of nanocomposites with poly(styrene-co-butyl acrylate) matrix reinforced by multiwall carbon nanotubes (MWNTs) and cellulose nanofibrilles. It was the topic of F. Dalmas Ph-D (defended the 18th of November, thesis codirected by GPM2 (INPG), and GEMPPM (INSA). The way chosen for the composite processing is an aqueous mixing. The polymer latex is mixed to the cellulose nanofibrils suspension or to a dispersion in water of MWNTs, stabilised thanks to an anionic surfactant (SDBS: $C_{18}H_{29}SO_3Na$) after a 5 minutes step of ultrasound sonication. Two different methods were then employed: the first consists in evaporating the mix in a oven regulated at 30°C for the latex film forming (coalescence of the polymer particles) ; the second consists in freeze drying the mix and hot pressing the obtained powder at 100°C. The dispersion homogeneity of the nano-fillers in the films was checked by transmission electronic microscopy on cryo ultramicrotome.

The mechanical characterisation at low strain was performed by DMA, in torsion mode, at 0.1 Hz, from 170 K up to 500 K, with a heating rate of 1K/min. The shear elastic modulus G' as a function of temperature divided by the main relaxation temperature T_α (measured at 1Hz, it is associated to the glass transition temperature, $T_g \cong 265$ K) is presented on figure 14.

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[p] "Reinforcement of elastomers by carbon nanofibres", Richard P., Prasse T., Cavaille J.-Y., Chazeau L., Gauthier C., Duchet J., Materials Science & Engineering A, vol 352/1-2 pp 344 - 348, 2003.
[q] " Reinforcement effects of Vapor Grown Carbon nanofibers as fillers in rubbery matrices", C. Gauthier, L. Chazeau, T. Prasse, J.Y. Cavaillé , Comp. Sci. and Technol., 65, 335-343, 2005.
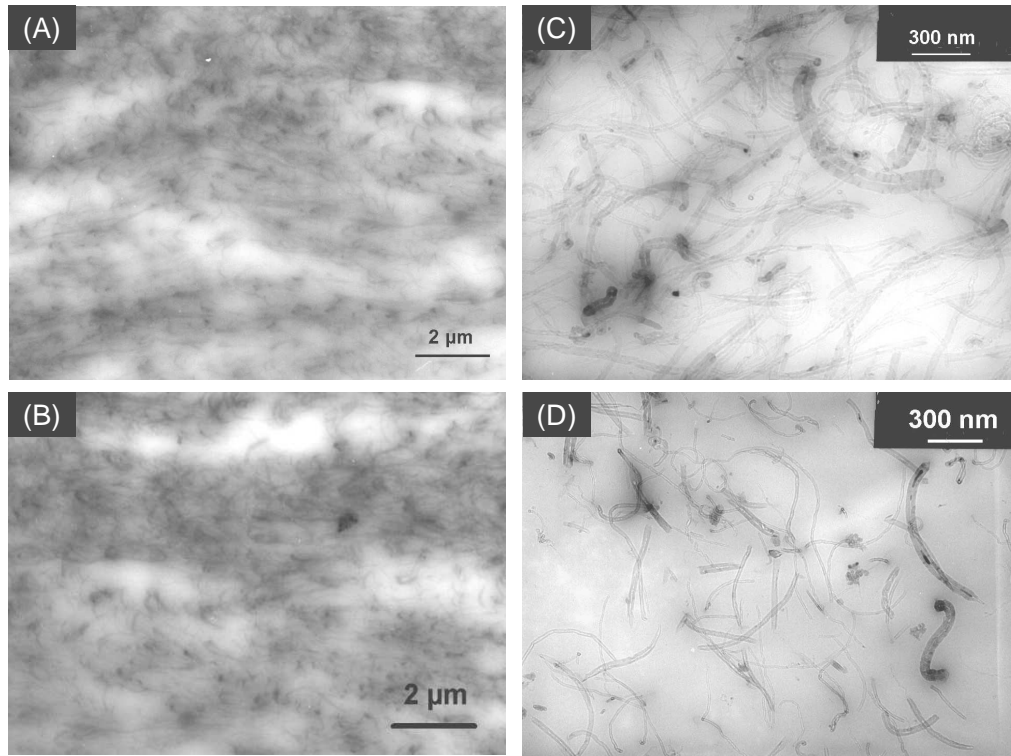
Figure 13 T.E.M. images from microtomes of P(S-ABu) reinforced with 4 vol% of cellulose nanofibrils processed either by evaporation (A) or by freeze drying (B), or reinforced by 3 vol.% of MWNTs E (C) ou FP (D). Image obtained with the help of J.L. Puteaux (CERMAV-CNRS) and K. Masenelli-Varlot (GEMPPM).

The modulus values measured at T/T_α equal to 1.15, were compared to a 3D Halpin-Tsai modelling (equations RE20, RE22 and RE23). The difficulty of such a modelling is that it assumes that the inclusions are straight fibres (like the cellulose whiskers were). The curved nature of the fibres is however clearly visible on the pictures of figure 13. We have used the same equations to estimate both their modulus and their aspect ratio. The best fit for the cellulose nanofibrilles composites processed by freeze drying and hot pressing (FP) is obtained for an aspect ratio of 310 and a longitudinal and transverse moduli of the fibres of 80 GPa and 15 GPa respectively. These moduli are in good agreement with literature. An estimate of the real aspect ratio is more difficult but the deduced value seems reasonable compared to the literatures estimations. [47] Thus, the description of the experimental results obtained with P(SABu)/cellulose composites processed by freeze drying/hot pressing is very satisfactory, meaning that the aspect ratio alone is enough to account for the observed reinforcement. The same approach was used for carbon nanotubes filled composites. The deduced longitudinal modulus of carbon nanotubes is below one TeraPascal, conversely to what is commonly said in literature. The model enables also to deduce an apparent aspect ratio of 240 whose value is the result of the fibre flexibility. The same model also shows that the reinforcement obtained in the case of cellulose nanofibril composites processed by evaporation (E) cannot be explained by the aspect ratio alone when the fibre content is above 2.5%. We will go back to this result in the following chapter.
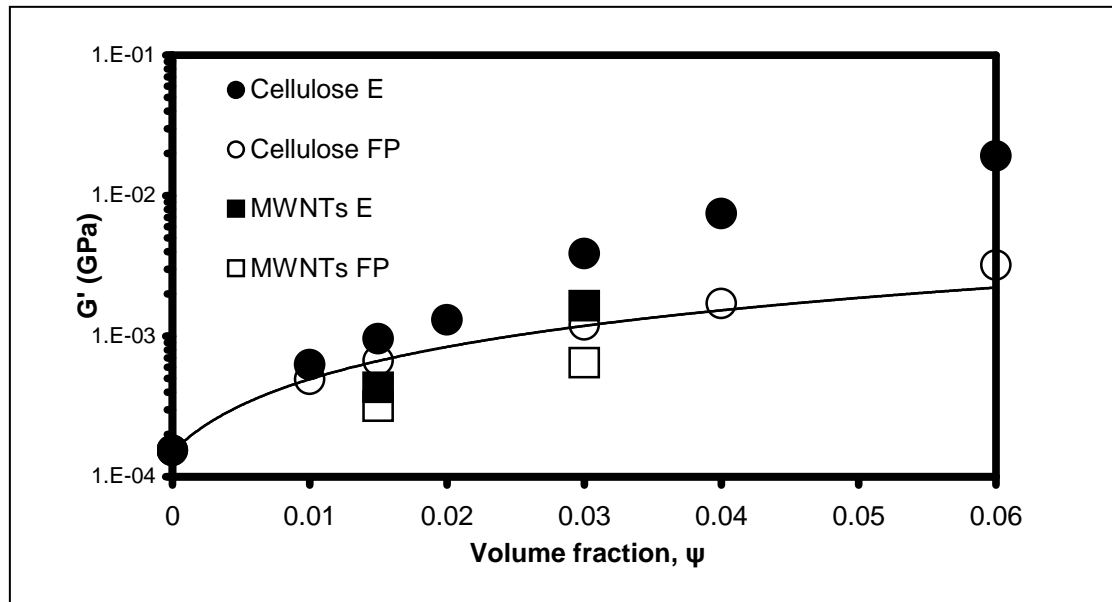
Figure 14 : G' at T/T$_a$ = 1.15 as a function of the filler content : comparison with the calculations from equation RE23. (—).

Thus, from these examples, it appears that for certain processing conditions and/or for limited filler content, the study of only the mesosopic scale and of the aspect ratio allows to understand the reinforcement of nanoscopic materials.

3.2   Influence of the fillers at large deformation

Introduction of heterogeneities at mesoscopic scale has also consequences on the mechanical behaviour at large strain. We will present here the peculiar case of elastomers.

3.2.1   Strain hardening and damage

The materials with SBR matrix reinforced by silica treated by different grafting agents (and presented in chapter 1) have been studied in the large strain domains. [r] Figure 15 presents their tensile behaviour. The plot of the tangent modulus as a function of strain shows an inflexion point corresponding to the beginning of the material strain hardening. It begins as soon as some chains between crosslinks are close to reach their maximal extensibility. [48] The introduction of silica leads to a decrease of the strain at the inflexion point, significant of the strain amplification induced by the fillers. The strain amplification deduced in the case of untreated silica is around 2.8. The silica treatment modifies this value. Thus, the grafting by covering agents leads to its decrease. One can assume that the use of covering agent leads to a narrower distribution of the chain lengths between crosslinks. When the grafting is

[r] "In situ SAXS and volume variation measurements during deformation of treated silica filled Styrene Butadiene Rubber", J. Ramier, L. Chazeau¨, C. Gauthier, L. Stelandre-Ladouce, E. Peuvrel-Disdier, Polymer, soumise.

performed with a coupling agent, strain amplification first decrease like for covering agents, and then increases when the surface is saturated in coupling agents. This result shows the existence of two concomitant effects: (i) the surface covering leads to a more homogeneous crosslinking (same observation as for covering agents), and (ii) an increase of the crosslink density due to the polycondensation of the coupling agent in excess (effect mainly visible for high content). However, these effects are still limited compared to the effect of the introduction of fillers.
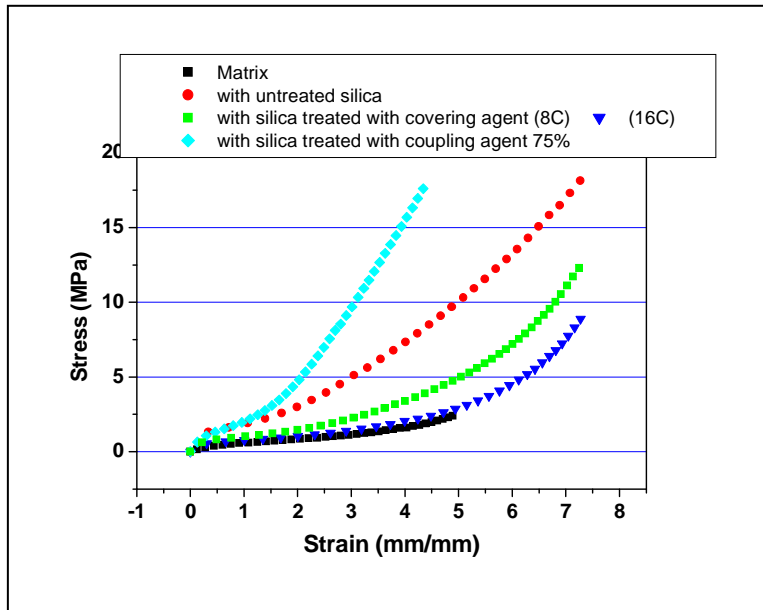

Figure 15 : tensile stress strain curves of silica filled elastomer for different silica surface treatments, T=25°C, ε= 0.4 s^{-1}.

The intensity of the strain hardening is however strongly influenced by the silica treatments. The use of covering agents leads to a decrease of the rate of the strain-hardening conversely to coupling agents, which increase it. In the latter case, the obvious explanation is a more important global crosslinking of the material, the fillers then playing the role of multifunctional crosslinking nodes. The role of the covering agent is *a contrario* to decrease the stress transmission between fillers and matrix and favour decohesion phenomena. This had been previously detected during the study of the Payne effect. Indeed, we had observed an increase of the loss energy during dynamic solicitation at strain level above 50%.
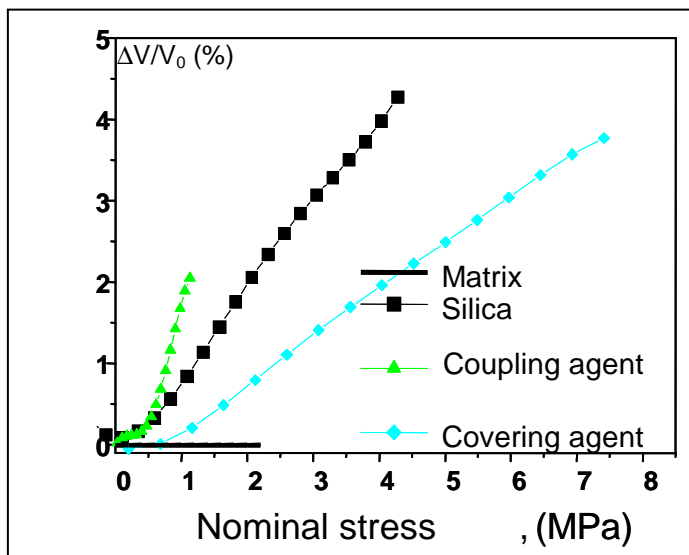

Figure 16: volume variation as a fuction of the strain level (tensile test) of an unfilled elastomer, and of an elastomer filled with silica treated by a covering agent or a coupling agent.

These decohesion phenomena have been studied by volume variation and small angle light scattering measurements during tensile tests (SALS performed in collaboration with E. Peuvrel-Disdier at CEMEF). Thus, the plot of the volume variation measurements on different samples as function of the stress shows a strong influence of the treatment of the silica surface (cf. Figure 16). A decrease of the filler-matrix interactions eases the material decohesion which occurs for smaller stresses. Conversely, the formation of strong covalent bonds between the fillers and the matrix delays this decohesion. Void formation has been confirmed by small angle light scattering. Figures 17 and 18 show the 2D SALS spectra respectively obtained for composite filled with untreated silica (the same spectra are obtained for covering agent treated silica) and for composites filled with coupling agent treated silica. In the case of untreated silica, the appearance of an ellipsoid perpendicularly to the stretching direction suggests formation of ellipsoidal voids, whose big axis is parallel to the stretching direction. With coupling agents, there is another phenomenon occurring in the same time: the formation of an ellipsoid parallel to the stretching direction (cf. Figure 18a). A first assumption to explain it is the spatial reorganisation of filler agglomerates during stretching leading to the formation of ellipsoidal clusters whose the large axis is perpendicular to the stretching direction. [49] The second assumption is, due to the presence of strain heterogeneities in the longitudinal direction, the revelation of new correlation length, increasing with strain (the strain in the perpendicular to stretching direction being to small to reveal any reorganization in this direction). Whatever the assumption, its origin is the delay of void creation by the coupling agents. A larger strain, when cavitation is the main phenomenon, both samples present the same scattering spectrum (cf. Figure 17b and 18b).
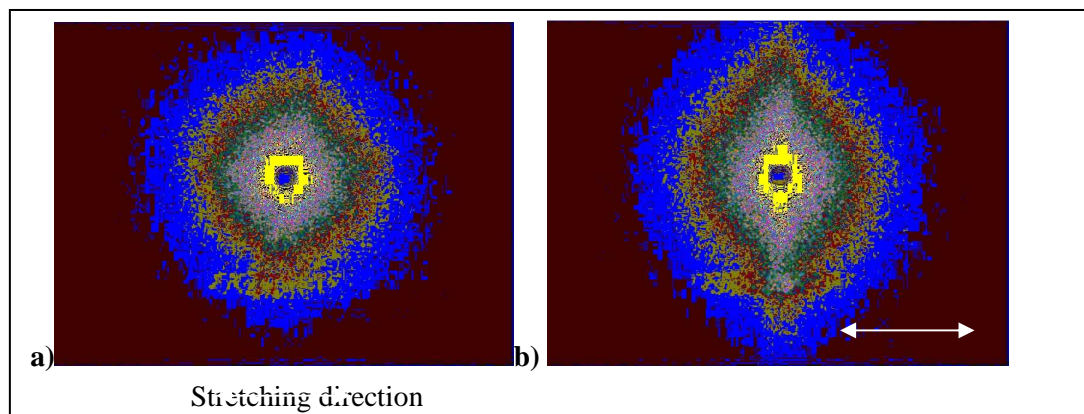

a)   b)

Stretching direction

Figure 17: light scattering spectrum of SBR filled with untreated silica at a) 75% nominal strain and b) 250% nominal.

Damage as volume variation as discussed here occurs already during the first stretching and increases with the strain level. Due to the hyperelastic nature of the material, and as checked experimentally, these volume variations are reversible. However, during the first stretching, irreversible damage can occur, such as a break of polymer chain having reached their extensibility limit. This rupture is eased by the filler presence, because of the strain amplification they create. A different readsorption of the desorbed polymer chain at the filler interface can also occur. This explains that the behaviour of a filled elastomer during a first deformation will always be different than that observed during the following deformations.

The difference between these two behaviours is commonly called the Mullins effect. It must be taken into account during the study of the Payne effect.
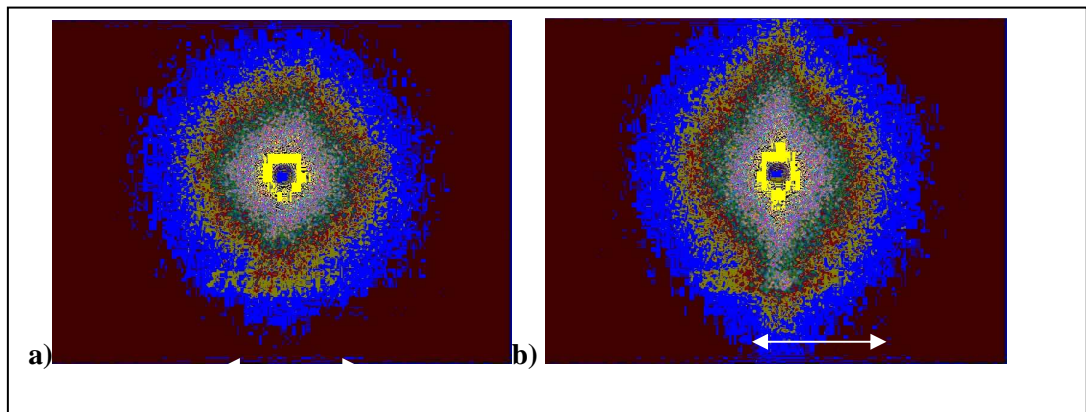

Figure 18: light scattering spectrum of SBR filled with silica treated with a coupling agent at a) 75% nominal strain and b) 250% nominal.

We have taken here the example of an elastomer matrix. Of course, this Mullins effect is not discussed during the deformation of a filled thermoplastic, because of the non reversibility of the plastic deformation in the experimental time scale. However, décohésion and cavitation also occur during deformation, as shown in our work on cellulose whisker filled plasticised PVC. Moreover, strain hardening of this material at large strain is also locally eased by strain amplification induced by the filler presence.

All this shows the complexity of the behaviour at large strain of heterogeneous materials as well as all the difficulty to take into account this complexity in a modelling which, generally, does not consider either the matrix degradation (chain break), or void formation by cavitation and or decohesion.

3.2.2   Fillers and crystallisation under stretching

To the phenomena previously described, one must add in certain cases crystallisation phenomenon, which occurs under stretching. We will take here the example of natural rubber filled with silica or carbon black. Crystallisation of the latter under uniaxial strain (post doc of J.M. Chenal) has been studied by in situ diffraction measurements but also volume variation measurementsunder strain.[s]

A first originality of this work was to show all the interest of volume variation measurement for the crystallisation characterisation. Indeed, crystallisation leads to a volume decrease measurable during the material stretching. Therefore this technique provides a quantitative

information in the case of an unfilled elastomer. In the case of filled samples, the negative volume variation generated by the crystallisation superimposes to the positive volume variation created by damage (as shown above). One can however observe a negative volume variation during the unloading of the material down to the zero strain, due to a slower melting of the crystallites than the disappearance of the voids created by the damage during the stretching. Thus, in that case, the technique provides quantitative information.

The formulation of the samples studied here has taken into account the problems generated by the different components of the vulcanisation system with the filler interfaces (cf. paragraph 2.2.1). Thus, accelerators and activators have been avoided. The chemical nature of the filler surface, and the structure have been the studied parameters. An example of the obtained results by Wide Angle X rays Scattering (with the laboratory apparatus) is presented on figure 19. Different spectra are shown during the loading-unloading path. The kinetic aspect of the phenomenon is underlined since it clearly appears that the crystallites are slow to melt during unloading.

Figure 20 presents the crystallinity index measured from WAXS spectrum (it is deduced from the evolution of the areas of the crystallisation peak [2 0 0] and [1 2 0]) as a function of strain with a NR sample, NR filled with carbon black, NR filled with untreated silica or treated with a covering agent or a coupling agent. Except a shift in the crystallinity index at a given strain, all the curves are superimposable. Completed by volume variation measurements, these results indicate the main influence of the local strain amplification on the crystallisation process. The filler-matrix interactions are only a second order parameter: on the one hand by the effect of these interactions on the stress transmission, and therefore on the strain amplification, and on the other hand, in the case of the addition of a surface treatment, by the perturbation of the matrix crystallisation in the neighbourhood of the fillers (as discussed previously with the crystallisation at low temperature). These interpretations are still to be confirmed by studies in progress.

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[s] "Strain induced crystallisation of carbon black filled natural rubber", Chenal J.M., Chazeau L., Gauthier C., - Eurofillers 2005, Bruges, Belgium (9-12 May 2005).
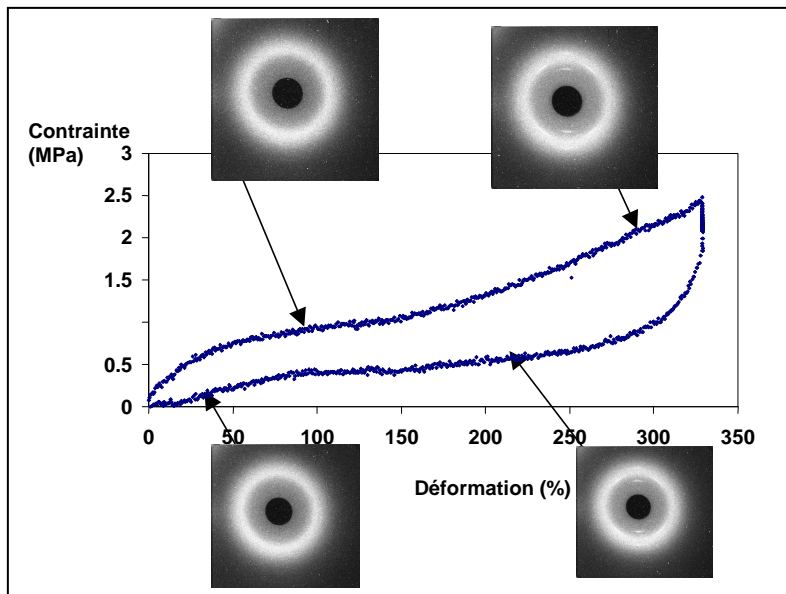
Figure 19 : cyclic stress strain curve of NR and concomitant evolution of the X ray spectrum.
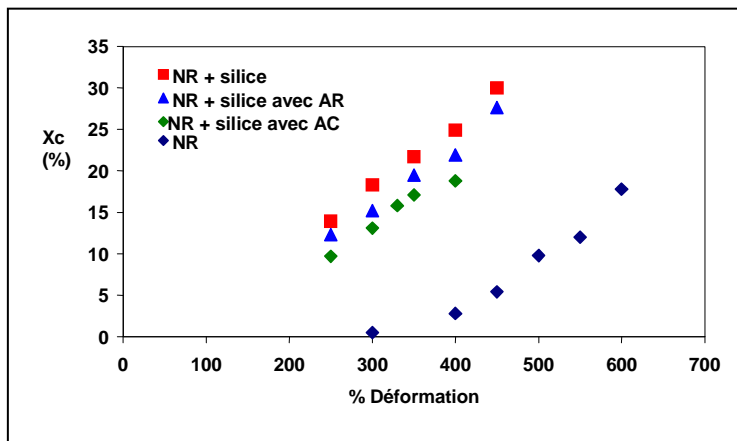

Figure 20 : Cristallinity index as a function of tensile strain of natural rubber (NR) filled with nanoscopic silica, nanoscopic silica with covering agent (AR) , nanoscopic silica with coupling agent (AC) (measurement on the GEMPPM apparatus).

3.3 Conclusion

The mesoscopic scale of fillers is important when studying their influence on the mechanical behaviour of materials. Thus, an account for filler intrinsic parameters such as morphology, modulus, mechanical properties of the interface, and relative size of the fillers compared to the material structure enables in many studied cases to explain the mechanical behaviour, without needing to evoke any modification of the molecular mobility of the matrix. However, phenomena occurring during deformation are complex and multiple, particularly at large strains. Damage by cavitation and decohesion is generally concomitant to an irreversible break of polymer chains in the matrix or at the interfaces, of a modification of the spatial organisation of the fillers, and in the case of crystallisable materials, of its crystallisation and texturation. Besides, these different mechanisms occur very heterogeneously in the material. Thus, if modelling sometimes enable to successfully describe the behaviour of polymer composite materials in the linear domain, modelling of

these same materials in the non linear domain, taking into account the ensemble of these phenomena, is still a challenge.

4. Heterogeneities at macroscopic scale

In certain cases, modelling of the mechanical behaviour of composite is also helpless to even describe the composite reinforcement in the linear domain. Thus, as seen previously, cellulose nanofibrils composite processed by evaporation cannot be described in the rubbery domain by models, even if they take into account the filler aspect ratio or its modulus.

> Recall:
> Works found in literature, among them those performed by V. Favier[50] on P(S-Abu)/cellulose whisker composites, lead to the same conclusion. The process of these material by evaporation of the mix latex/whisker suspension enable the formation of a percolating network whose stiffness is much higher than that provided by the reinforcement of the matrix by isolated whiskers. This networks appears at volume fraction which depends on the filler aspect ratio. Thus, in the case of cellulose whiskers with an aspect ratio of 70 and within the assumption of their random spatial distribution in the matrix, the theoretical volume fraction at which this network appears is only 0.8%. This threshold, so-called percolation threshold, is checked experimentally since the underestimation of the measured modulus by classical mechanical models (recalled previously) occurs at filler volume fraction above this threshold. The reinforcement can then be modelled by simply considering that it is basically the result of the stiffness of the whisker network, whose volume fraction is calculated from percolation theory, and whose modulus is that of a pure whisker sheet (obtained from evaporation of the whisker suspension). The process is a key parameter enabling (evaporation process) or disabling (freeze-drying and hot pressing process) the establishment of hydrogen bonds between fillers. My Ph-D work on the same type of filler has shown that the cellulose whisker reinforcement in a plasticised PVC matrix in the rubbery domain was also underestimated by a classical approach even if the process hinders, a priori, the formation of the whisker network. Our assumption is that a whisker network is formed, this time via filler-matrix-filler bonds, leading to a intermediary reinforcement, between that of stiff whisker network, and that predicted by the classical mechanical model.

Therefore, it seems necessary to consider a larger scale than that of the fillers, i.e. the macroscopic scale of the structure they can form inside the composite.

4.1   Impact of a macroscopic structure

In fact, the formation of a filler network inside a composite can be very similar, in its consequences at the level of the mechanical properties, to the formation of a second continuous phase in a multiphase material. Indeed, in both cases, there is formation of a macroscopic structure whose the role in the global mechanical properties will have often to be considered in an independent way (in parallel) from the properties of the other phases. The Ph-D work of A. Guimaraes on grafted natural rubber latex is an original way to illustrate this idea. The work is performed in the frame of a CAPES/COFECUB with the Chemical Engineering faculty of Lorena (FAENQUIL, Sao Paulo, Brasil). This thesis is

codirected by a brasilian colleague Dr. A. Martins Dos Santos, Prof. J.Y. Cavaillé and myself.

In many cases, the chemical structure of natural rubber has been predetermined since its extraction, and it is then difficult to modify it in industrial process. Therefore, it was appealing to proceed to a chemical modification of NR, prior to the industrial processing step, in order to control its surface energy, and this for three reasons: first, this open new prospects for the use of NR in applications where the hydrophobicity of the unmodified NR is a drawback. Secondly, this can ease the mix of NR with other polymers (for instance, for shock improvement of thermoplastics) by improving the chemical compatibility of the different constituents. At last, in the case of reinforcement of NR by hydrophilic particles such as silica, a chemical modification of NR such as that proposed in this project could replace that of the particles, and more generally could allow an optimisation of the filler matrix interactions, for the process as well as for the final mechanical properties of the composites. Thus, the objective of the Ph-D is to control the chemical modification technique of a natural rubber (this concerns the Brazilian team) and to use the modified latex in polymer mixes and as matrix of composites.

In this project, the wished morphology for the latex particles is of hairy layer type. The latex particles are then made of a core in poly-cis isoprene (NR) and a shell of grafted polymer. This morphology has two advantages: (i) the hydrophilic shell is going to sterically stabilise the colloidal latex suspension, (ii) the hydrophilic groups being accessible at the beginning of the processing, this can make easier the processing of blends either with polar polymers (PMMA or PVC) or with hydrophilic filler such as silica. The chosen comonomer is di-methyl-amine ethyl methacrylate (DMAEMA).

The lattices, once grafted, are evaporated as films and tested by mechanical spectrometry. Results are presented on Figure 21. Grafting by DMAEMA leads to a second plateau between –40°C and the ambient temperature, followed by a drop of the elastic modulus down to the level of the unmodified natural rubber modulus. The value of modulus on this plateau is quasi the same for the samples modified with 10phr and 20phr of DMAEMA but strongly increases when the used concentration of comonomer is 30 phr. We can rapidly compare these values to that predicted by Guth-Gold (seen previously). The disagreement with this very simple model becomes huge for the NR grafted with 30 phr DMAEMA. Conversely, the modulus of this sample tends toward that predicted by a simple parallel model. There is apparently a threshold around 25phr DMAEMA (or 0.2%vol. of DMAEMA) ; and this "threshold" effect indicates that the particles have indeed a core-shell type morphology, with a shell of poly-DMAEMA: as checked in complementary experiments this external layer presents a main relaxation at a temperature close to the ambient temperature ; the processing at temperature at 40°C is high enough for the DMAEMA chains grafted at the NR particle surface be able to interdiffuse, creating a continuous phase, or in other words a macroscopic structure of this polymer. These results are confirmed by the impossibility to form this type of film by evaporation at ambient temperature. They are also confirmed by tensile tests: NR grafted with 30phr DMAEMA has a behaviour, which is a combination of

the plastic response of the DMAEMA grafted chains forming a continuous phase and of the elastic response of the NR.[t]
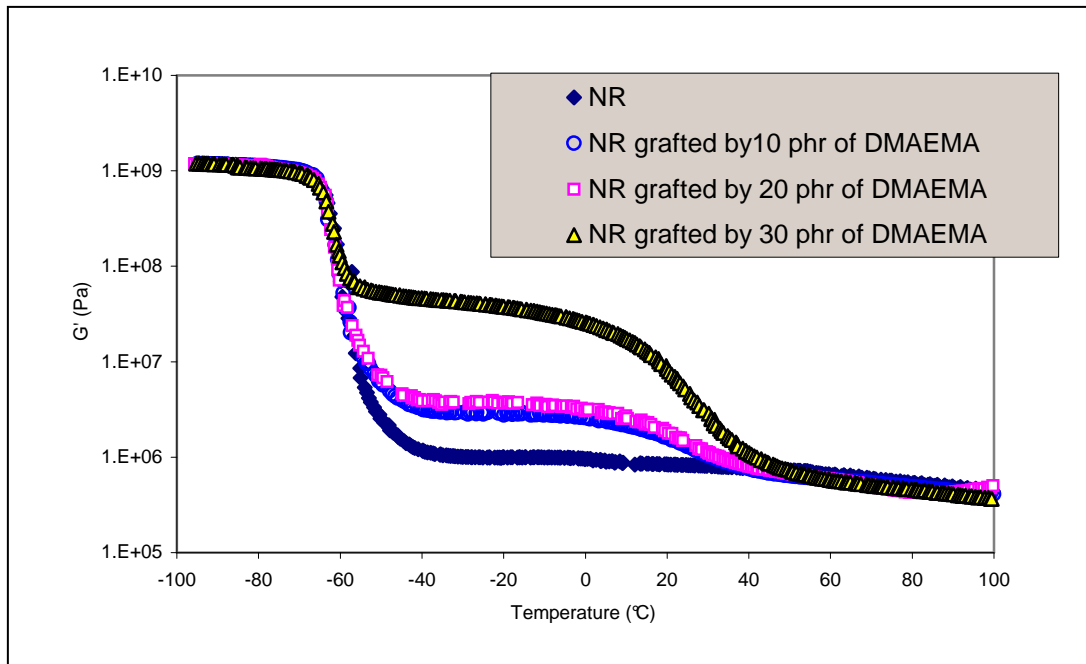

Figure 21: Torsion modulus G' measured as a function of temperature for a natural rubber NR ungrafted or grafted with DMAEMA (f=0.1Hz), the modulus of the different materials have been normalised at -100°C, to the modulus value of the non grafted NR).
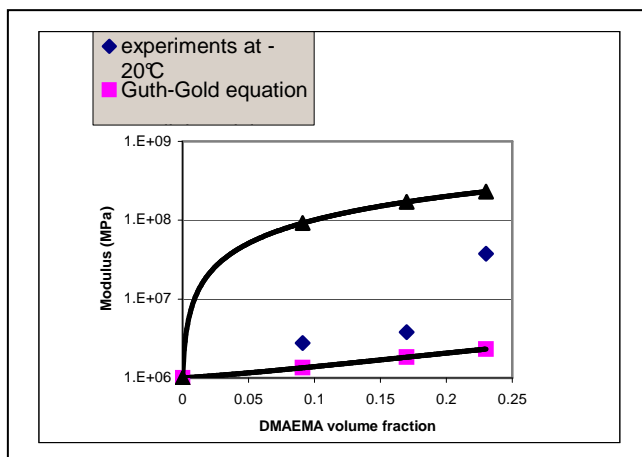

Figure 22 : G' measured at –20°C of NR grafted by DMAEMA as a function of the volume fraction of DMAEMA. Comparison with the Guth-Gold equation and a parallel model (the DMAEMA modulus is then its value at –80°C).

This example illustrates that mechanical spectrometry is a powerful toll for the characterisation of composite material when one wants to evidence the formation of a continuous phase whose mechanical properties are very different from those of the matrix.

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[t] " Poly(dimethylaminoethylmethacrylate) grafted natural rubber by seeded emulsion polymerization", P. C. Oliveira, A. Guimarães, R.G. Gilbert, J. Y. Cavaille, L. Chazeau, A. M. Santos, polymer, 46,4,1105-1111, 2004.

4.2   Formation of a filler network?

Let's go back to the stucture of fillers inside the composite. It is now obvious that if there is formation of a network, this will have mechanical properties which, like in the general case of a continuous phase, will depend on its morphology and the intrinsic mechanical properties of the constitutive material but also of the contact between fillers.

4.2.1   Evidence

The formation of such a network can, as seen above, be evidenced by mechanical spectrometry. Thus, as seen with cellulose nanofibrils/P(S-Abu) composite material, for filler content above 3%, the shear modulus in the rubbery domain draws a plateau, up to the temperature of cellulose degradation (cf. Figure 23). This plateau is very different from the flow which occurs at Tg in the case of the matrix alone, or when the material has been processed by freeze-drying.
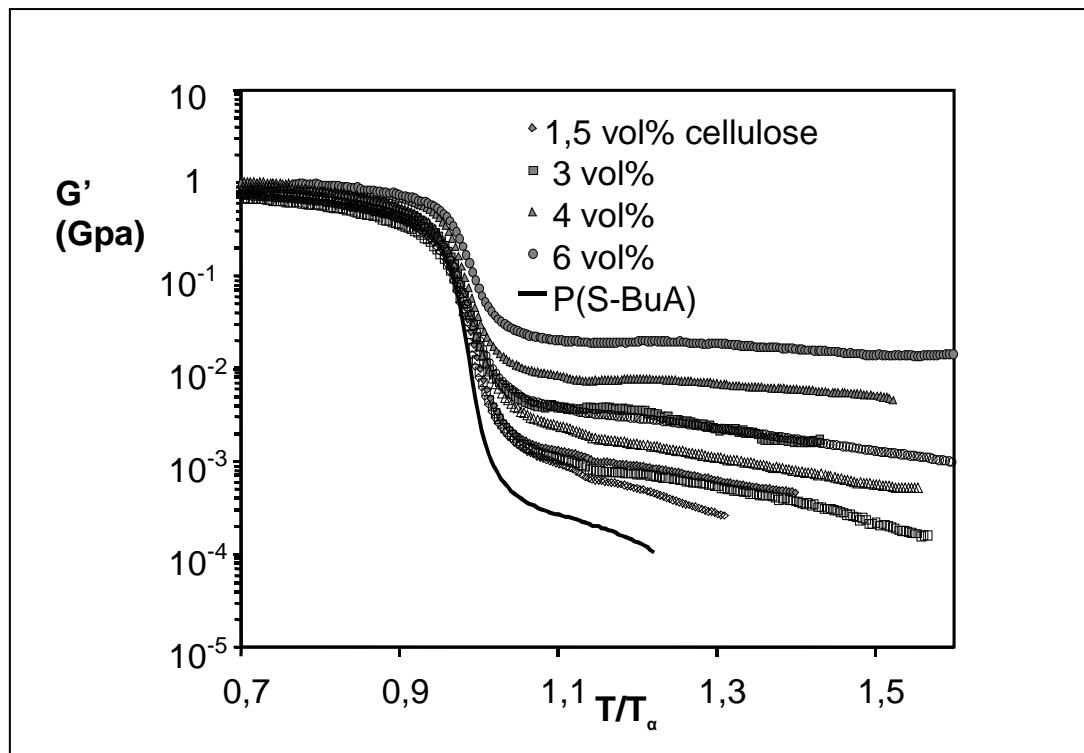

Figure 23 : G' as a function of temperature (normalised by the main relaxation temperature) P(S-ABu) filled by different volume fractions of cellulose nanofibrils. Full symbols for the materials processed by evaporation, open symbols for those processed by freeze drying (F. Dalmas Ph-D thesis).[u]

[u] .   "Viscoelastic behaviour and electrical properties of flexible nanofibre filled polymer nanocomposites. Influence of processing conditions" Florent Dalmas,   Jean-Yves Cavaillé, C. Gauthier, Laurent Chazeau, R. Dendievel, Comp. Sci. Technol., accepted.

The moduli measured at T/Tg=1.15 have been reported on figure 24. A model such as that developed by Ouali et al[29], and used afterwards by Favier[51] has been used. The material is considered as the parallel association of the matrix reinforced by non percolating nanofibrils and of a percolating nanofibrils network (cf. Figure 25). The volume fraction of the latter is calculated from the percolation theory like it had been done previously for cellulose whiskers. The percolation threshold is estimated equal to 0.3% vol. using the law established by Nan[52] for stiff fillers, randomly dispersed in the matrix and with an aspect ratio of 240. This aspect ratio is only apparent and was estimated from the modelling of the modulus of the freeze dried films (cf. paragraph 3.1.2.). The modulus of the nanofibrils percolating network was deduced from a tensile test measurement on a evaporated nanofibrils film.

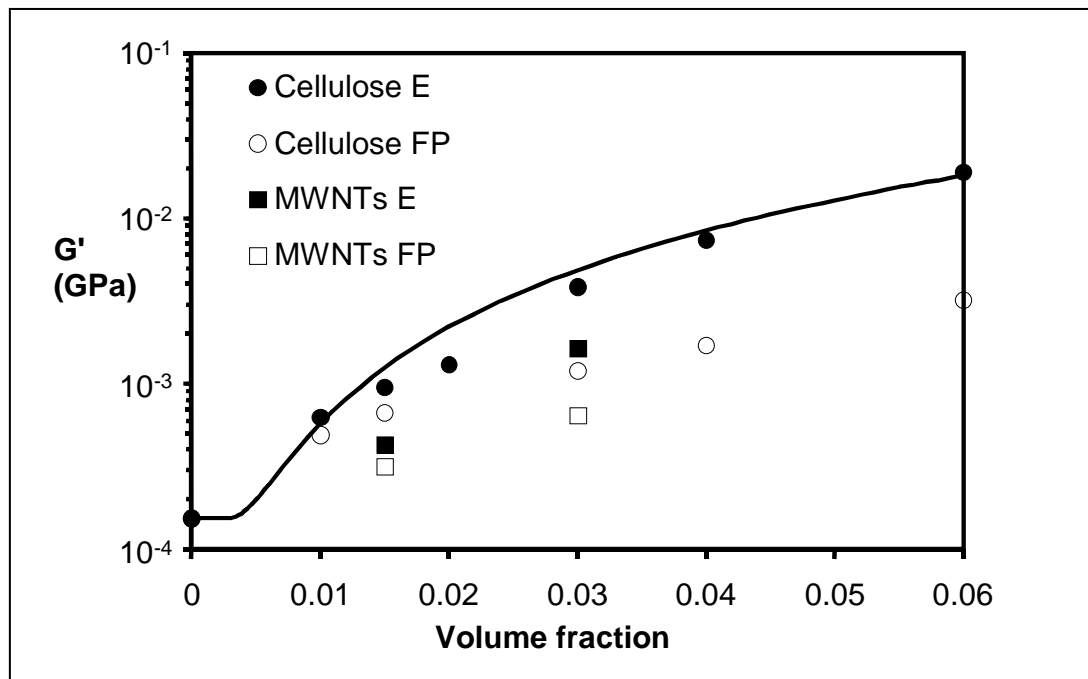**Figure 24 : G' at T/T$_g$ = 1.15 as a function of the filler content. Comparison with the theoretical curve deduced from the mechanical percolation model (━).**

Though its simplicity, this model can describe experimental data and indicates the validity of the assumption of the formation of a nanofibrils network in the evaporated material, the formation of such network being impossible in the case of the freeze drying process.

Takayanagi model with the
percolation approach

Percolation

$$P(\phi) = 0 \qquad\qquad \phi < \phi_C$$

$$P(\phi) = \left(\frac{\phi - \phi_C}{1 - \phi_C}\right)^b \qquad \phi \geq \phi_C$$

R
e

b=1.8

$$G = \frac{(1-2P(\phi)+P(\phi)\phi)G_sG_r+(1-\phi)P(\phi)G_r^2}{(1-\phi)G_r+(\phi-P(\phi))G_s}$$
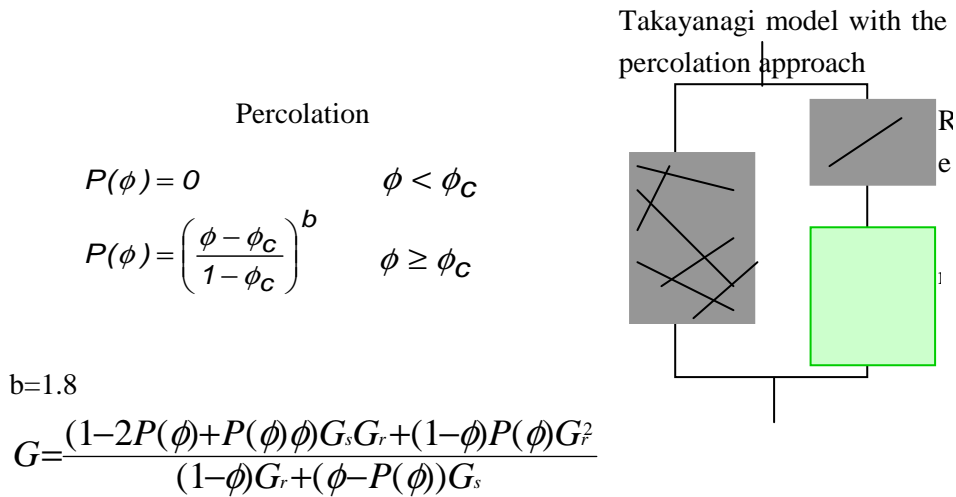
Figure 26 : mechanical percolation model used for the description of the reinforcement by cellulose nanofibrils of P(S-ABu) matrix composite processed by evaporation. G_s is the shear modulus of the matrix, G_r is that of the filler network. ϕ is the filler volume fraction, $P(\phi)$ is that of the filler network, and ϕ_c the percolation threshold volume fraction.

Thus, cellulose nanofibril composites are school cases to illustrate such a phenomenon due to the possibility of the nanofibrils to form or not strong hydrogen bonds. Carbon nanotubes reinforced materials did not show, above the glass transition temperature, reinforcement level as high as those measured with cellulose nanofibrils, since they cannot establish such bonds. However, this does not forbid the formation of a conductive percolating network. Figure 26 shows the real part of the conductivity of evaporated materials. Clearly, the material goes from a capacitive behaviour to a resistive one with the introduction of fillers. Moreover, the conductivity plot as a function of the filler content (deduced from the conductivity measurement at 10^{-2} Hz) shows an electrical percolation type behaviour with a threshold around 0.3%.

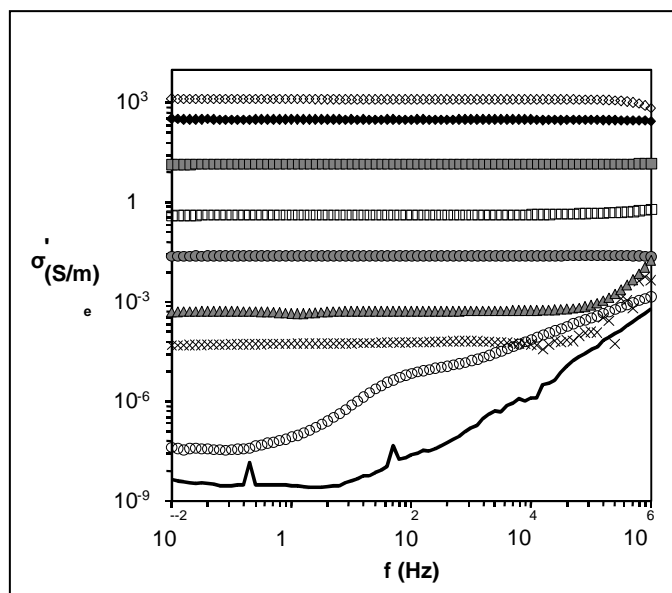**Figure 26 : real part of the conductivity as a function of frequency of the applied field for the for the P(S-ABu) matrix (—), the composite filled by 0.2 vol% (▲), 0.5 vol% (●) et 3 vol% (■) of MWNTs processed by evaporation (full symbols) or processed by freeze drying (open symbols). Experimental results also for SDBS surfactant (sodium dodecyl benzyl sulfate) (×), a SDBS/MWNTs film (◆) and a MWNT film(◆).**

So, there is indeed formation of a nanotube network inside the material but the contacts created are weak and lead to a filler percolating structure whose the mechanical properties are too weak to have a significant influence on the composite stiffness. The freeze dried materials have a low conductivity and a high percolation threshold; this indicates less good electrical contacts and a less random dispersion of the nanotubes (with less contacts), probably because of the process. The consequences are visible at the level of the mechanical properties since they are less good for the freeze-dried materials than for the evaporated ones.

Thus the examples presented here show the existence of a filler network in composite materials if the filler volume fraction is higher than a critical fraction. The nature of the contacts in this network is of main importance in the reinforcement level. Moreover, the critical volume fraction is very dependent on the filler aspect ratio. In the case of a random dispersion of spherical fillers, the percolation theory predicts a critical fraction of the order of 30%. This is of the order of the filler volume fraction commonly used in industry…

4.2.2   What about filled elastomers?…

…Let's go back to the modulus of filled elastomers described previously: the SBR/silica composites studied in J.Ramier Ph-D thesis. Different models can be tested to account for the modulus measured in the linear domain. The Guth Gold equation (equation RE18 of paragraph 3.1), using a filler volume fraction of 20%, largely underestimates the modulus measured at 300K (1.5 MPa for 9.5 MPa experimentally measured). With untreated silica, we have seen above that the bound rubber quantity represents 40% of the matrix. The most extreme assumption considers all this bound rubber as a shell around the filler, this lead to an increase of the filler content from 50phr (20%vol.) to 145 phr (58%vol.). However, the calculated value is still below the experimental value (5.2 MPa). Thus, this clearly appears that the hydrodynamic effect, even corrected of layer of bound rubber in the glassy state, cannot account for the experimental value of the modulus.

Given the large filler content, one can logically consider the assumption of a network formation. However, it is obvious that the contacts in the network are not hydrogen bonds, otherwise the reinforcement would be much higher than that measured experimentally. The elastic modulus value measured for this system is seemingly due to a network effect, but this network is not made only of direct filler-filler bonds. Besides, instead of the assumption of a completely immobilised bound rubber, we prefer the assumption of the stress transfer between particles via a polymer whose stiffness is higher that that of the matrix.[53] Figure 27 presents our vision of the material.

It is in agreement with the observed influence of the surface treatment, i.e. a modulus drop although the dispersion was found the same for all the samples. The surface treatments modify the bound rubber quantity. This influences the stress transmission between sub-

structures of fillers and therefore the network stiffness. Moreover, the Payne effect appears like a modification under strain of the polymer properties linking these sub-structures.
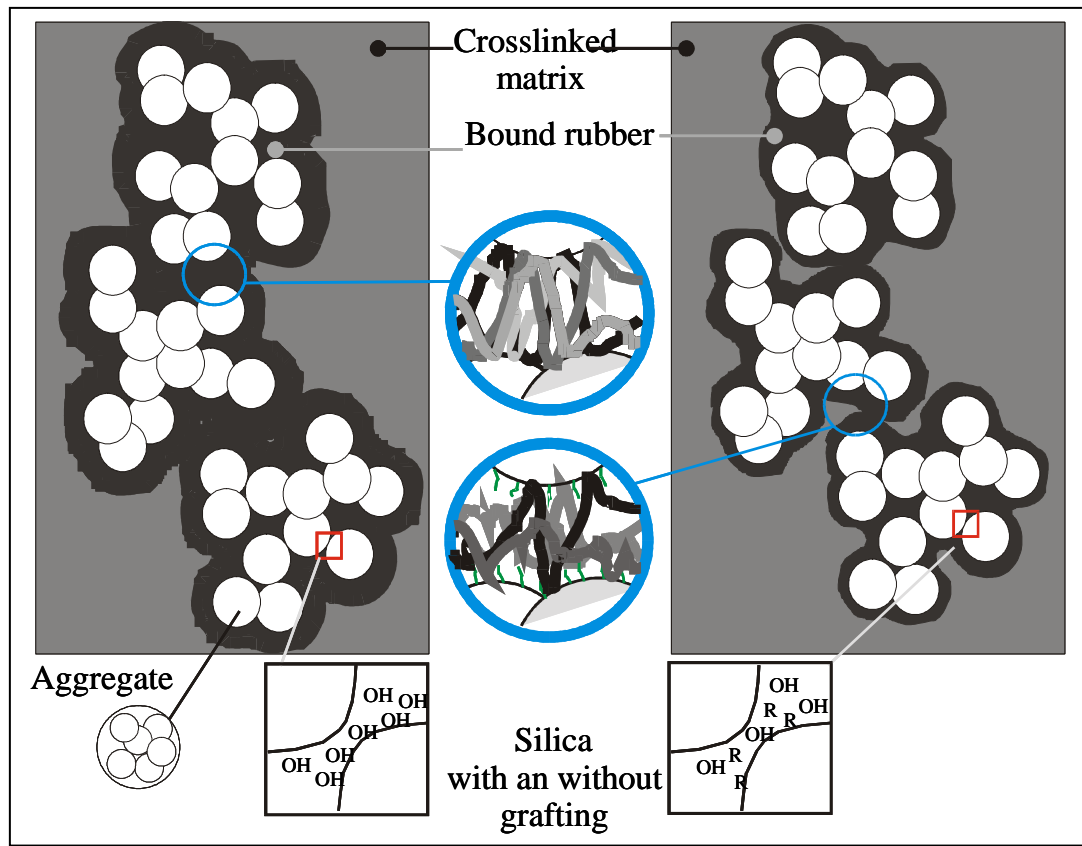

Figure 27 : Scheme of the network involving filler agglomerates and bound rubber as a function of the filler surface treatment : the use of covering agents leads to a decrease of the thickness of the bound rubber, which in turn decreases the stiffness of the agglomerate-bound rubber-agglomerate network.

4.2.3 Modelling

To support these assumptions, new modelling approaches have been developed. Indeed, classical mechanical models are unadapted since they assume the definition of a too simple R.V.E., and cannot correctly describe the connectivity between inclusions and the specific properties of the contacts. The approach we have explored is the modelling by Discrete Elements initiated and developed by the Groupe de physique et mécanique des matériaux (GPM2, INPG Grenoble), in particular R. Dendievel, whom I have collaborated with for a long time. As indicated in its name, this modelling consists, in a R.V.E. whose size is defined *a posteriori* (by a convergence of the calculation when the R.V.E. dimension increases), to discretize the microstructure in simple elements, and to define between these elements contact properties. The interest of such a method compared to Finite Element Modelling, is to allow the description of microstructures complex at the level of their morphology as well as at the level of the interfaces they contain.

This method has been adapted to the systems we wanted to model. The different fillers previously presented have various aspect ratios. They are of the order of unity in the case of silica particles, reaching 70 in the case of cellulose whiskers, or can be higher than several hundreds in the case of carbon nanotubes. Besides, carbon nanotubes are curved. Therefore the networks morphologies they lead to are also different. To minimize the calculation time, a simplification of this microstructure needs an important step of discretization adapted to the considered microstructure.

The modelling of the mechanical properties of a 3D cellulose whisker network has been first processed. This work is in the continuity of ph-D thesis of V. Favier, L. Flandin and myself on the behaviour of cellulose whisker reinforced nanocomposites. [24] The aim of the model developed was the evaluation of the mechanical properties of the filler network alone, the matrix being only present at the contact level. This model consists in generating a virtual fibre network for which the fibre centres and orientation can be random or follow desired anisotropy conditions (cf. Figure 28). Once the network is generated, filler intersections are calculated. Two types of elements are then defined: those linking the nodes of a same whisker, and those linking two whiskers, which intersect. This description is then introduced in a F.E.M. calculation (CAST3M, CEA) with the definition of two beam types, the whisker beam and the contact beam. The application of the boundary conditions on the virtual volume, a tensile test for instance, enables the calculation of the properties of the filler network. The originality of this approach is to accept the variation of the mechanical properties of the bonds and thus to determine their influence on the network properties.
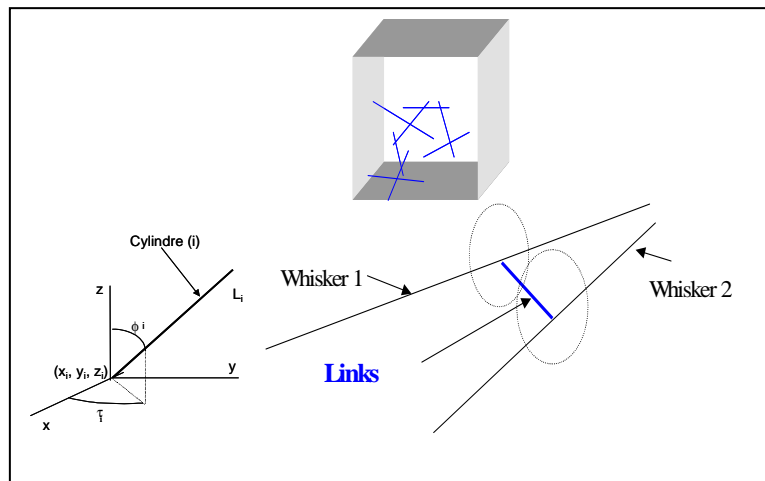

Figure 28 : modelling of a whisker network : generation of cylinders in a box, followed by the definition of linking beams at whisker intersections.

Figure 29 presents the network modulus calculated as function of the contact modulus and the filler volume fraction. The comparison of these results with the experimental moduli of the different cellulose whisker composite provide three information: [v]

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[v] "Polymer based nanocomposites: effect of filler-filler and filler-matrix interactions", Bréchet Y., Cavaillé J.-Y., Chabert E., Chazeau L., Dendievel R., Flandin L., Gauthier C., Adv. Eng. Mat., 3, 8, 2001.

As experimentally checked, the formation of a filler network, stiff or semi stiff, has no influence on the mechanical properties of a composite whose matrix is in the glassy domain (at least for small strain).

The creation of soft contacts made via the adsorbed matrix can explain the important level of reinforcement measured with composites for which the process inhibits direct contacts between fillers. Indeed, the model enables the description of the reinforcement of cellulose whisker/plasticised PVC composite for volume fractions above 4% ; this fraction corresponds to the value below which the reinforcement can be described by classical models.

At last, we have checked the assumption formulated by V. Favier, i.e. the presence of a stiff network can explain the mechanical properties of a composite whose processing enables direct contacts between cellulose whiskers, for filler content above the percolation threshold. Conversely, it does not correctly describe the mechanical properties measured just around the theoretical percolation threshold. Indeed, the calculation, like the mechanical percolation model used by the same author, predicts an abrupt increase of the modulus at that threshold, when the experiments do not show it. We will come back to this point later.
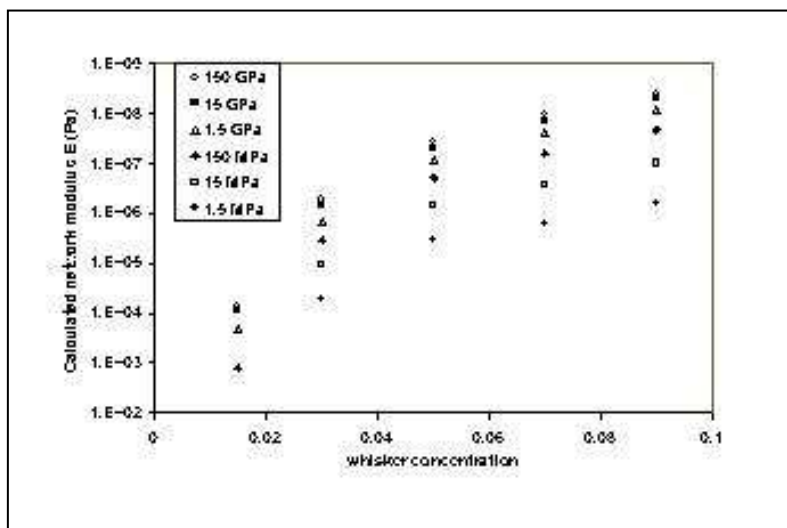

Figure 29 : calculated modulus of a cellulose whisker network as a function of the whisker concentration and for different moduli of the linking beams.

The case of the cellulose whiskers is a school case since they are comparable to stiff rods. A modelling of long and flexible fibres such as cellulose nanofibrils or carbon nanotubes is more difficult and needs the development of specific tools. [w] Each fibre is built from N elementary nodes, the first node being randomly generated in the volume, and the position of the following node being determined by three parameters, the distance between nodes, and the angles described by three consecutive nodes. For a better description of the fibre curvature and to limit the number of nodes for the calculation, the fibre segment between nodes is described by the Kochanek-Bartel formalism.[54] An example of the generated microstructure with 175 fibres is presented on figure 30. One can easily see the presence of entanglement in the structure and the important curvature of the fibres. It is then possible to study the mechanical response of such a network, or since the modelling is developed for

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[w] « Numerical simulation of electrical conductivity in 3-D entangled fibrous networks. Application to carbon nanotubes filled polymer composites. » F. Dalmas, R. Dendievel, L. Chazeau, C. Gauthier1, J.-Y. Cavaillé, *Acta Materialia*, sumitted.

carbon nanotubes network, the electrical response. Due to too long calculation time, for the moment, we have only focused on the conductivity calculated. In this case, it is possible to simplify the generated network by replacing the fibres between intersection nodes by equivalent conductivity beams. In a way similar to the modelling of the properties of a whisker network, contacts are simulated by beams whose conductivity is an adjustable parameter. The final step is then the integration of this network in the CAST3M software. The calculation uses the thermal module and the equivalences between thermal and electrical conductivity, and between temperature and electrical potential. Note that, like previously, the calculation does not take into account the matrix presence; this means that it has a meaning only if the network percolates.
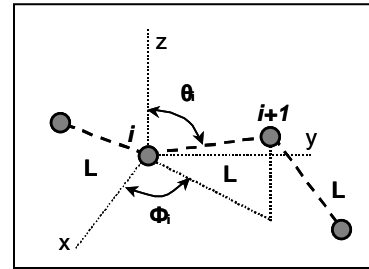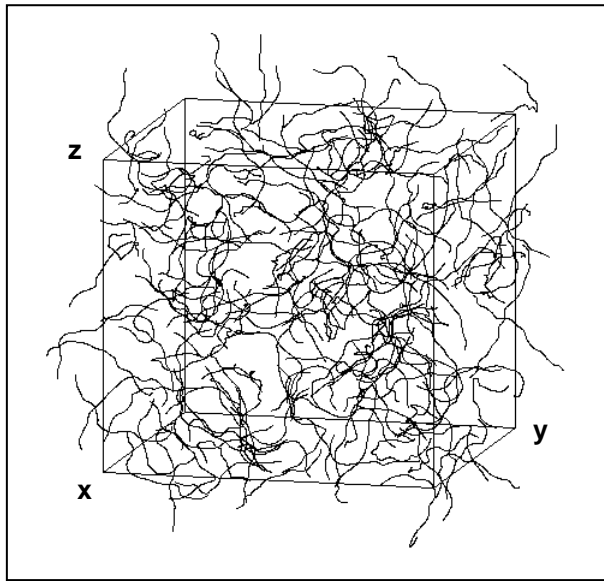

Figure 30 : Example of a 3D structure containing 175 fibres with 17 nodes by fibres and an angle made by three consecutive fibres below 45°.

This approach was devoted to the modelling of the electrical properties of the carbon nanotubes/P(S-Abu) composites. The morphological parameters needed for the generation of the microstructure were deduced from electron micrographs of the samples. Adjusting the conductivity of the fibre contact, it is possible to describe the experimental results (cf. Figure 31). The contact conductivity is low and between that of a nanotube and that of the surfactant used for the processing. Moreover, the evolution of the conductivity was adjusted by a percolation law:

$$\sigma \approx \left(\frac{\Psi - \Psi_c}{1 - \Psi} \right)^t \qquad\qquad \text{with t the critical exponent} \qquad\qquad (EP1)$$

In the case of composites processed by freeze-drying, the critical exponent is equal to 3.9, against 1.7 in the case of evaporated materials. This exponent is abnormally high and can be described in the modelling if one makes the assumption that the conductivity between fibres increases with the fibre level. Indeed, one cannot exclude that the surfactant, which can be involved at the fibre contact, has its concentration in the contacts, which decreases with the fibre content. This would increase the interfibre conductivity. The law traducing this evolution of the contact conductivity and which seems the most appropriate is a sigmoid:

$$s(\Psi)=\sigma_s+\frac{\sigma_{cE}-\sigma_s}{1+e^{-a\psi+b}}$$

(EP2)

Where σ_{cE} is the contact conductivity determined by the adjustment of the curves of the evaporated composites and σ_s the surfactant conductivity.

However, the percolation threshold is largely underestimated. Instead of considering an evolution of the average contact conductivity, perhaps one should consider the assumption of the existence in the composite of a distribution of conducting and non conducting contacts, which varies with the fibre content? The answer to this question still needs work, as well as the extension of the modelling to the simulation of the mechanical behaviour. Note that this last point will need to overcome the limitation introduced by the explicit absence of the matrix in the material description.
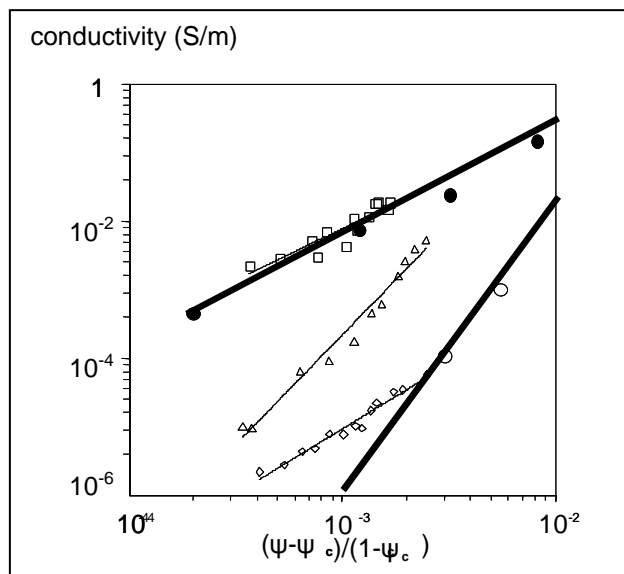

Figure 31 : Electrical conductivity vs. the reduced fibre volume fraction for microstructures simulated with an aspect ratio of 240, a contact conductivity of $\sigma_c = 10^{-1}$ S.m^{-1} and a maximum angle between three consecutive nodes θ_{max} of 45° (□), $\sigma_c = 5.10^{-5}$ S.m^{-1} and $\theta_{max} = 90°$ (◊), or $\sigma_c = s(\psi)$ (cf. equation EP2, i.e. following a sigmoidal law function of the fibre fraction) and $\theta max = 90°$ (△). Comparison with the experimental data obtained with P(S-ABu)/MWNTs composites processed by evaporation E (●) or freeze drying (○).

Conversely, the modelling (developed by R. Dendievel, then E. Chabert et al.) [x]used again for the silica/PS-Abu composites presents the main advantage to take into account the matrix presence. Instead of fibres, this modelling generates a sphere assembly. The composite is then simulated from a random run (or biased if one wants to describe a particle agglomeration or anisotropy), which attributes to each sphere of the R.V.E. the properties of the matrix or of the filler (cf. Figure 32). Like for a discrete modelling, the sphere assembly is then treated like a point network (for the sphere centre) and bonds between these points (representing contacts between particles).

[x] " Mechanical behavior of polymer nanocomposites : a discrete simulation approach", Chabert E., Gauthier C., Dendievel R., Chazeau L. et Cavaillé J.-Y., Mat. Res. Soc. Symp. Proc, vol 740, I6.1.1. , 2003.
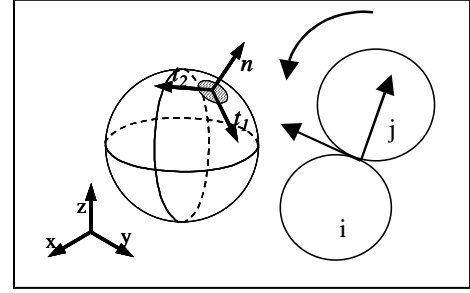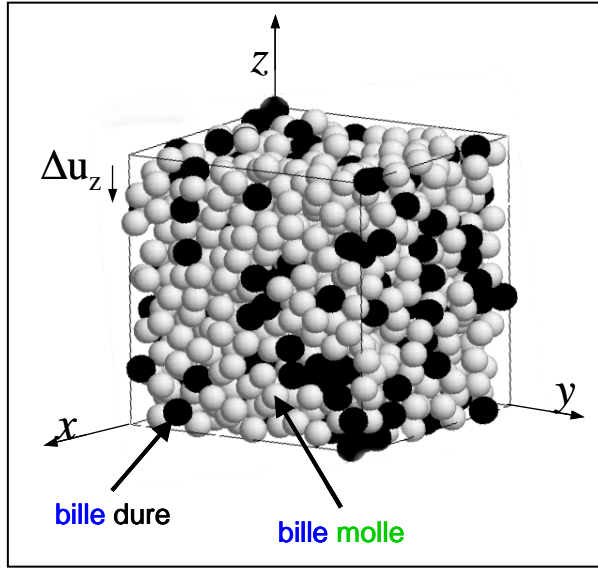
Figure 32 :a) scheme of the sphere assembly generated for the discrete modelling. The black spheres are the fillers; b) Coordinate system associated to each sphere, and scheme of the force and moments transmitted between two particle

Thus, a local orthonormal system of vectors $(\mathbf{n}, \mathbf{t_1}, \mathbf{t_2})$ at the contact level between two particles is defined (cf. Figure 32b). The forces F^{ij} and the contact moments between two particles i and j are expressed, in this coordinate system, as a function of the displacements $(\Delta\mathbf{u_i}, \Delta\mathbf{u_j})$ and of the rotations $(\Delta\boldsymbol{\theta_i}, \Delta\boldsymbol{\theta_j})$ between two particles, as: [55]

$$F_n^{ij} = k_n \left(\frac{\Delta u_n^j - \Delta u_n^i}{2R} \right) \tag{EP3}$$

$$F_{t1}^{ij} = k_n \left(\frac{\Delta u_{t1}^j - \Delta u_{t1}^i}{2R} \right) - \frac{k_t}{2} \left(\Delta\theta_{t2}^j - \Delta\theta_{t2}^i \right) \tag{EP4}$$

$$F_{t2}^{ij} = k_n \left(\frac{\Delta u_{t2}^j - \Delta u_{t2}^i}{2R} \right) - \frac{k_t}{2} \left(\Delta\theta_{t1}^j - \Delta\theta_{t1}^i \right) \tag{EP4}$$

$$\frac{M_n^{ij}}{R} = \frac{k_\theta}{2} \left(\Delta\theta_n^j - \Delta\theta_n^i \right) \tag{EP5}$$

$$\frac{M_{t1}^{ij}}{R} = -F_{t1}^{ij} + \frac{k_b}{2} \left(\Delta\theta_{t1}^j - \Delta\theta_{t1}^i \right) \tag{EP6}$$

$$\frac{M_{t2}^{ij}}{R} = F_{t2}^{ij} + \frac{k_b}{2} \left(\Delta\theta_{t2}^j - \Delta\theta_{t2}^i \right) \tag{EP7}$$

These contact laws involve different "stiffnesses" k_n, k_t, k_θ et k_b which have the dimension of a force. The normal stiffness k_n links the normal force at contact to the displacement between the sphere centres. The tangential stiffness k_t links the shear forces to shear, which depends on the relative tangential displacement and the rotations of both particles. The flexural

stiffness k_b and the torsion stiffness k_θ link the tangential and axial components to moments transmitted through the contact via relative rotations and shear forces.

The resolution of the system consist in solving equilibrium equations, for N spheres:

$$\sum_{j=1}^{n^{ci}} \mathbf{F}^{ij} = 0 \quad \text{and} \quad \sum_{j=1}^{n^{ci}} \mathbf{M}^{ij} = 0 \quad \forall i = 1,..N \qquad \text{(EP8\&9)}$$

This system can be summarised by equation:

$$\left\{ \begin{array}{c} \mathbf{F} \\ \mathbf{M} \end{array} \right\} = \left[\mathbf{K}_{tot} \right] \left\{ \begin{array}{c} \mathbf{U} \\ \Theta \end{array} \right\} \qquad \text{(EP10)}$$

Where $[K_{tot}]$ is the total stiffness matrix, $\{U\}$ and $\{\Theta\}$ are the displacements and rotations of each spheres, $\{F\}$ and $\{M\}$ are forces and momentums.

These equations are solved numerically. For each contact, the local stiffness tensor is estimated from equation EP2 and EP7. This matrix is then transformed to be expressed in a global coordinate system, and added to the total stiffness tensor $[K_{tot}]$ enclosing all the contacts.

In our study, we have considered a simple compression test: one impose a displacement for all the spheres of the top face of the R.V.E. The spheres of the bottom face are fixed in the horizontal plane, except one, which is totally fixed. The longitudinal modulus is obtained doing the ratio of the resulting force to the imposed displacement. [y]

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[y] Rigorously, to determine the longitudinal modulus M_l of the composite, one should apply an homogeneous displacement gradient u_z along the vertical axis and calculate the work of the external efforts. This work corresponds to the strain energy of the assembly and is proportional to the modulus M_l: $W_{ext} = \dfrac{1}{2} M_l u_z^2$. It was checked that the same results are found.

Thus, such an approach, since it enables the definition of matrix-matrix, matrix filler and filler-filler contacts, can take into account the matrix, the interface quality and the effects of aggregation (and of structuring) of filler as a network respectively.

First we have performed a calculation with a microstructure in which the beads are necessarily isolated and their content between 5% and 25% : the only contacts are those between the matrix beads (soft/soft contact) and between filler and matrix (soft/hard contact). [z] Stiffness of this last type of contact is obtained by a serial law with the matrix and filler moduli. The contrast between these two moduli is set to 10000. The results show an increase of the modulus, which follows the Einstein law (recalled previously).This validates the calculation. Another validation is the calculation performed for a microstructure generated by random run of hard spheres, allowing a stiff filler-filler contact. It gives, as expected, a curve with a percolation threshold around 20% volume fraction of fillers.

This modelling tool was then adapted to the study of the Payne effect and Mullins effect mechanisms. As evoked previously, our assumption for the Payne effect is that of a modification, in the mixed filler-filler and filler-matrix-filler network, of the link forces between sub-structures formed by the fillers, under the action of stress. This modification is due to the desadsorption of the polymer chains adsorbed at the filler-matrix interface. A way to evaluate the pertinence of such a scheme is to calculate the difference of the modulus of a initial undeformed structure and of a structure in which some interfaces have been destroyed ; this difference being related to the Payne effect amplitude. Calculation must be performed in several steps. Indeed one must firstly determine the most stressed bonds, consider them as broken (when is overpass a break criterion, for the moment arbitrary), then iterate this process up to the obtainment of a stabilised structure. Note that the broken bonds are replaced by bonds whose the stiffness is then a weak shear stiffness, simulating a friction. Preliminary results have been more simply obtained by successively simulating strong filler-matrix bonds (estimated by a Voigt model) and null filler-matrix bonds. The ratio of the filler modulus by the matrix modulus is 1000. Results are presented on figure 33 where we have plotted the modulus difference given by the two successive calculations. The curve shows an evolution of the Payne effect (i.e. the modulus drop, here maximal) as a function of the filler volume fraction similar to that experimentally observed, up to a filler content of the order of a percolating volume fraction. Above this threshold, the effect of the break of the filler-matrix bonds has less influence, leading to an inflexion of the curve which is not experimentally observed. Thus, it seems necessary to involve in the model the break of filler-filler contact. Indeed, during the first solicitation, the filler network can be damaged in an irreversible manner. This is evidenced by the Mullins effect whose a part is likely the consequence of this damage. The damaged network is less efficient in term of reinforcement and the modulus is afterwards more sensitive to the break of the interface. Moreover, the stiffness of the introduced bonds in the calculation is up to now arbitrary. It will be necessary to compare it to experiments, as well as to evaluate the rupture criterium.
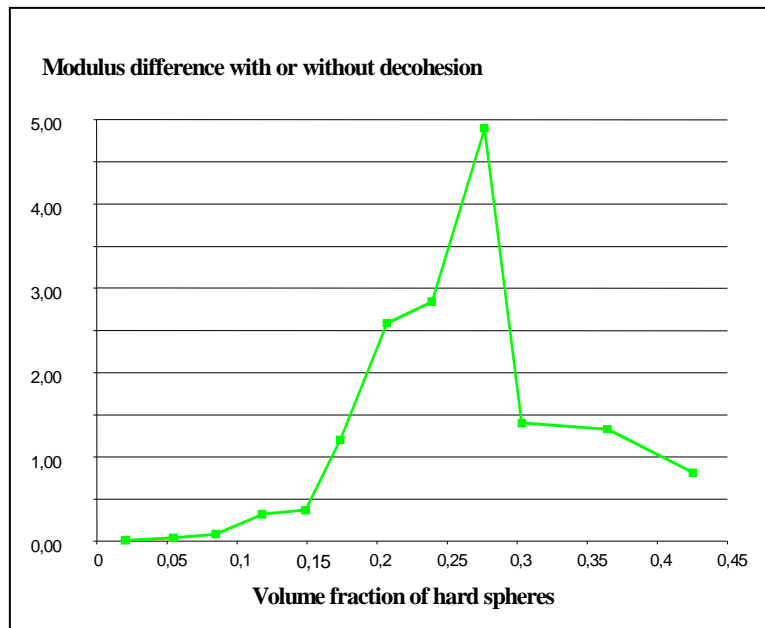
Figure 33: calculated difference between moduli with and without filler matrix decohesion as a function of the hard sphere volume fraction (i. e. filler volume fraction) : the soft/hard modulus contrast is 1000 and the soft modulus is 1.

Even if there is still a lot to do in this domain, in particular, in the determination of the different physical parameters of the description, the discrete type approach already seems to be a promising way for a better understanding of a mechanical behaviour still is in debate.

4.3   Heterogeneous solicitations

Up to now, heterogeneities discussed in this manuscript have always been intrinsic heterogeneities, or, when they develop during deformation (like cavitation or crystallisation), the consequences have always been implicitly considered like homogenous. In fact, if the characterisation in the domain of the simple solicitations at low strain can accept such a simplification (domain of the mechanical spectrometry), the large deformation and complex solicitation domain must be considered with caution. The variety of the initiated mechanisms at small strain and discussed along the previous chapters are for a large part responsible of it. Besides, the application of large deformation can lead to deformation localisation at the macroscopic scale, whose origin is in fact not necessarily in the presence of heterogeneities in the material but on a particular geometry of the solicited sample. Thus, samples submitted to simple compression tests will always show a barrel effect; thus a tensile test on polymer material will make appear, in certain experimental conditions, a striction, whatever the care taken during the test. Besides intrinsic heterogeneities of materials, it is therefore necessary to consider, in the analysis of the mechanical properties of materials, the extrinsic heterogeneities developed during solicitation.

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[z] Master report, « comportement visco-élastique non linéaire des élastomères chargés: caractérisation complémentaire et modélisation » , J. Toussan et M. Criton, 2003.

These strain heterogeneities which appear in samples during simple mechanical tests are therefore a real difficulty to overcome when one wants to determine constitutive law of materials. Up to now, the determination of a constitutive law, generally phenomenological, of a material (composite or not) was performed with simple tests, with the approximation of a homogeneous macroscopic response. For instance, the Polymere-Verres-Materaux hétérogènes group has used this type of experiment to develop the "qpd" model for the description of the mechanical properties of amorphous polymer (a relatively simple case compared to nanocomposites). One must acknowledge that this did not hinder the progression of this model, which, as recalled previously, offers the rare possibility of a complete description of the physical mechanisms of the polymer deformation, with the integration of the structural ageing aspects, and enables a description in the linear domain as well as in the non-linear one. The model limits appeared for the description of the strain hardening mechanisms since the strain heterogeneities, which are then developed cannot be neglected anymore. Moreover, the model provides a scalar formulation which neglects the consequences of the anisotropy development on the deformation mechanisms,.
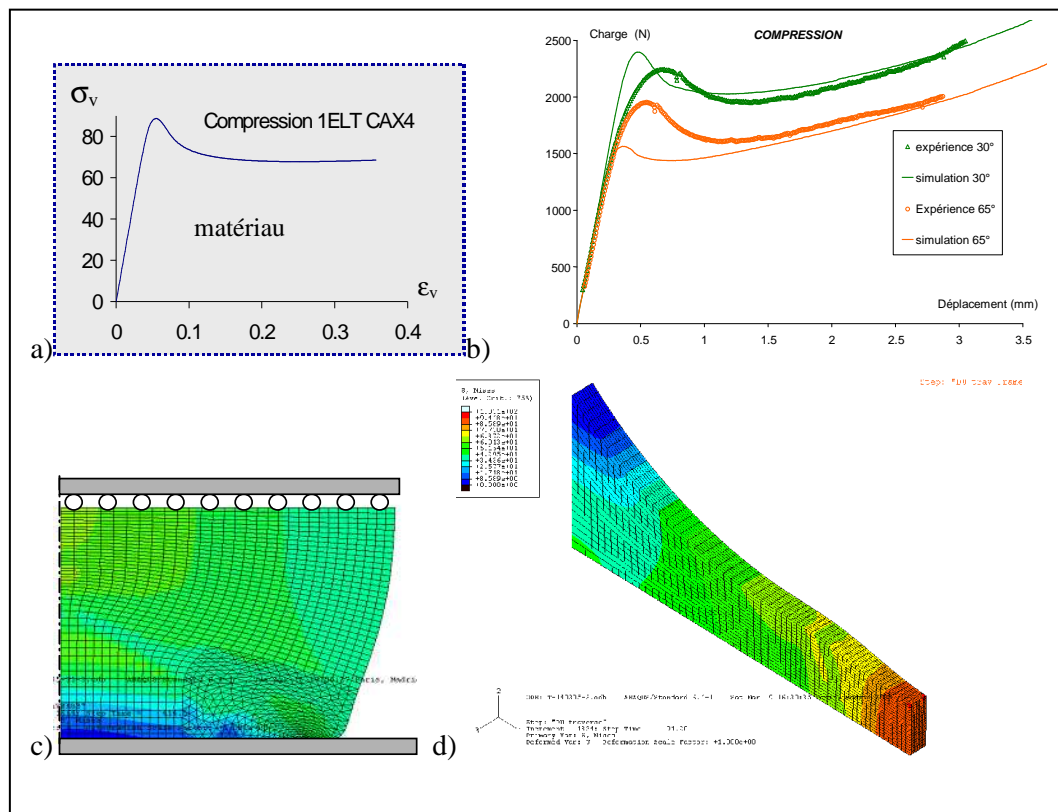

Figure 34 : a) Compression curve simulated on an element in the ABAQUS software with the use of the dqp model integrated in the software by R. Rinaldi, b) Simulated curve of a compression test performed on a cylindrical plot at two temperatures : experiments(symbols), in simulation (thin line) c) visualisation of the compression test, d) 3D simulation of a tensile test with the same parameters ; a defect was introduced in the sample, where appears the striction during the tensile test.

Two approaches can solve these problems: the model can be re-explored thanks to (i) on the one hand, a more local mechanical characterisation of the material, (ii) on the other hand, to the integration of this model in a finite element code to try to reproduce local strain fields

experimentally measured with simple mechanical tests. Then, the objective is to validate the tool of Finite Element modelling by a comparison with experimental results from complex mechanical tests, like for instance traction-torsion. To do so, the laboratory acquired a video-extensometry apparatus, and a traction torsion machine, and has initiated a collaboration with the Laboratoire de Mécanique des Contacts et des Solides (LAMCOS). In this framework, a Ph-D work is in progress (R. Rinaldi, defense forecast in March 2006) whose fellowship is provided by the Rhone-Alpes region (on an "emergence" program). The first phase of this project was the realisation of the passage from a scalar formulation of the model (as developed) to a tensorial formulation. The latter was then integrated in the ABAQUS software. [aa]

In the same time, a polycarbonate was characterised by mechanical spectrometry to determine the physical parameters needed by the model. Then it was solicited in simple tensile and compression test with the acquisition of local deformation. The different parameters describing the intrinsic behaviour of the studied polymer (on figure 34a) have been implemented in the Finite Element software. Figure 34c presents the simulation of compression test. One clearly see the development of strain heterogeneities and of the barrel form during the deformation. The simulated stress-strain compression curve is in good agreement with the experimental one. Besides, the temperature influence is well accounted for (cf. figure 34b). Figure 34d also presents a tensile test. The striction development experimentally observed is only reproduced when a defect is introduced in the sample drawing (via a element with a null stiffness). The actual state of the calculation code developed in the laboratory leads to a striction, which does not propagate in the sample. This is due to the fact that for the moment, the strain hardening is not introduced in the material. Different options to account for it are presently explored. The chain stretching, or in other words their ordering could lead to an increase of the correlation of the molecular movements. This could be simulated, as proposed in reference 6, by the addition of a term in equation (EP15):

$$\chi = \chi_0 + A_{def}\,\gamma_{an} - A_{dur}\,\gamma_{vp} \qquad\qquad (EP11)$$

With A_{dur}, a parameter traducing the decrease of the correlation parameter.

Another possibility is to consider that the plastic strain rate $\dot{\gamma}_{vp}$ is not constant at large deformation but depends on a gap to the equilibrium plastic strain γ_{vp}^{eq} :

$$\dot{\gamma}_{vp} = \frac{\gamma_{vp}^{eq} - \gamma_{vp}}{\tau_{vp}} \qquad\qquad (EP12)$$

This equilibrium strain is that of the polymer then considered like an elastomer. One can then use a Mooney-Rivlin type model or its equivalent (model with a Langevin function such as, for instance, the 8 chain model of Arruda-Boyce) to deduce, at a given stress, this equilibrium strain. It is then to early to conclude on this question. This can be helped by a

comparison of the experimental results with the simulation, which then appear like an aim but also like a tool to help the comprehension of the local mechanisms at the origin of the macroscopic mechanical behaviour.

4.4   Conclusion

Composite materials, in particular nanocomposite materials have sometimes modulus values, or more generally mechanical behaviours, which are badly described by classical mechanical models. These results invite us to reconsider the reinforcement of composite when a connected filler network can form, as for instance in the different examples presented in this chapter. In the general case of composites, it is therefore necessary to evaluate the impact on the mechanical properties of such a filler network, inevitably created when the filler content becomes important. In the case of nanocomposites, the introduction of nanoscopic fillers leads to an important interfacial surface, even for low filler content, that can modify the viscoelastic properties of the matrix. Besides, the interparticle nanometric distance can ease the formation of a stiff or semi-stiff structure whose nodes are made either of direct contacts between particles, or of a possibly modified matrix. In the case of an homogeneous filler distribution, the higher the aspect ratio, the lower the percolation threshold, i.e. the concentration at which this structure can appear. Thus, to understand the mechanical properties of such materials, it is necessary to explore new way of modelling; the discrete type approach is a very interesting approach. It enables the description of the connectivity of the filler structure and the specific interactions inside this structure, and in some ot its developments, between the structure and the matrix. Besides, extended to the large strain behaviour, it could help the understanding of the different complex mechanisms involved, such as reversible and irreversible break of different type of links.

Up to now, this multi-scale complexity has been discussed from simple mechanical tests performed in laboratory. However, these tests, though their simplicity, provoke the occurrence of macroscopic extrinsic heterogeneities, in particular at large strain. This makes difficult the use of the deduced stress-strain curves to establish intrinsic constitutive laws. Then, one must used, like in the study of amorphous polymer (previously presented), local characterisation tools, and a mechanical modelling whose development can appear not only as an aim but also as another characterisation tool.

5. General conclusion and prospects

A general conclusion can be done: polymer matrix materials have a multi-scale complexity. Besides, the heterogeneities they contain, or they develop – and this whatever their scale – generally have consequences on the macroscopic behaviour. Thus, no scale can be neglected in the macroscopic behaviour and a multi-scale approach must be adopted if one wants correctly describe this behaviour.

The nanocomposite case is exemplary. Indeed we have shown that at a molecular scale, the important interface quantity introduced by the nanoscopic fillers has consequences on the surrounding matrix, but also on the stiffness of the macroscopic network formed by these fillers. But one must not neglect the role of the individual filler and of their surface treatments on all the mesoscopic phenomena of reinforcement, strain hardening, and damage (mainly at large strain). Of course, the description of such a multi scale complexity still needs efforts from both experimental and theoretical points of view.

Thus, at the molecular scale, it is still necessary to characterise the contact force and resistance between filler and matrix, or between fillers via the matrix, peculiarly – as it is the case in nanocomposite – when the thickness of the latter in the contact becomes comparable to the size of the statistical polymer coil. A ph-D thesis has begun the 1st of October to explore theses questions. In collaboration with the Laboratoire de Physique de la Matière Condensée of the Université Claude Bernard and of the Van't Hoff Institute d'Amsterdam, its topic is the study of the influence of the interface and its treatments on the viscoelastic properties of polymer films when their thickness becomes sub-micronic. The chosen system is inspired from those studied in J. Ramier Ph-D work: a poly(styrene-co-butadiene) polymer and a silica glass substrate treated or not by silane.

The experimental data obtained in this thesis will be completed by the results of another Ph-D work financed by the CPR COPOLA. It has begun the 1st of October and is devoted to the study of the influence of ageing of these materials on their mechanical properties. This ageing is performed thermally or by irradiation. The interest is there a controlled modification of the different interactions involved in the material without modifying the filler dispersion. At last, the thesis in progress of A. Guimaraes on the grafting of NR and on its use as the matrix of a silica filled composite, as well as the new thesis financed by the Integrated European Project NAPOLEON, on the development of new materials by mini-emulsion technique will be an opportunity t explore the mechanical properties of new nancomposite systems: in both cases, the obtained systems will have peculiar interfaces and microstructure with consequences on the properties. Besides, the thesis on mini emulsion will allow a better study of the surfactant distribution and its influence on the mechanical properties of the material. Up to now, we have more or less neglected this aspect though our last works on carbon nanotubes have shown the influence of surfactant both on the matrix

itself (its glass transition temperature is slightly modified) and on the quality of the contacts between fillers.

Of course, the work on the NR crystallisation, with or without fillers, has to be continued. Experiments in progress on crystallisation at low temperature should help the understanding of the influence of fillers and of their surface treatments. The questions asked by the complexity of the melting endotherms of this material is by itself a topic which has also he interest of being transposable to other materials, such as poly(ethylene oxide) ; indeed the latter shows the same influence of the heating rate on the crystallite melting…the study of the role of fillers on the strain induced crystallisation must also go on. Experiments performed at ESRF are actually exploited, as well as DSC measurements on pre-stretched samples.

This study, or more generally those on the viscoelastic properties of filled elastomer, clearly show the main role of strain heterogeneities at the mesoscopic scale on the global macroscopic behaviour of the materials. The development of techniques to characterise them is therefore necessary. To do so, a new promising technique is currently developed in the frame of a collaboration GEMPPM/Laboratoire de Physique de la Matiere. The approach consists in deposing a grid of nanometric plots made of photosensitive resins. Then, the samples will be observed under strain in an Environmental Scattering Electron Microscopy of the GEMPPM equipped with a tensile test device: for each strain level, obtained images will show the grid distorsion and allow to deduce the local strains. The provided information could be very useful for the understanding and the modelling of the Mullins effect, generally observed in filled elastomers. They would allow to dissociate irreversible mechanisms of damage involved during the first strain, those occurring in the matrix and those linked to void formation. It would also enable, with the different materials available for this study, to evaluate the influence of the surface treatments on these mechanisms.

Such an observation at the submicronic scale could be completed by X rays tomography experiments on the same samples. The advantage of such a technique is to allow the observation of the entire sample volume. The tomography X could also provide useful complementary information on the void formation mechanisms of the materials until they break. Such a technique also allows to follow modifications of the filler network structure during the sample deformation. For the moment, the nanoscopic size of the fillers generally used in filled elastomers makes impossible a precise observation of this evolution. The X tomography allows it only in the case of micronic fillers. The observation of elastomers filled with micronic fillers can be a first step, that we will follow in the Ph-D work financed by the CPR.

This type of data is necessary to improve the modelling of the mechanical behaviour at large strain, when it cannot neglect anymore the development of an important modification, anisotropic and very heterogeneous, of the filler distribution, nor cavitation and decohesion phenomena. The qualitative evaluation of the influence of these modifications is difficult and cannot for the moment be performed by a discrete type modelling (such as that developed

by R. Dendievel at GPM2), limited to the behaviour a low strain. The collaboration with the Laboratoire de Mécanique des Solides (in particular P. Ponte Castãneda) in the frame of the Ph-D thesis financed by the CPR, is a good opportunity to treat this question. Note that this collaboration was initiated during the work of F. Saint Michel on the mechanical properties of filled and unfilled polyurethane foams. These materials, in particular unfilled foams, were indeed good candidates to compare our experimental results to the last developments in the domain of the homogenisation calculation in the non-linear domain. The first calculations, using a simple method of tangent linearisation of the stress-strain curves were deceptive. Other linearisation methods are still to evaluate, even if it appeared that the very localised deformations, which occur in the polyurethane foams, tested and modelled in the glassy domain, make difficult an homogenisation of the behaviour. We will see if the study of filled elastomers authorise better this homogenisation…at a scale that is still to be determined.

On the other hand, the exploration of these type of modelling does not mean a disinterest for the discrete type modelling. On the contrary, the development of the latter must enable a better comprehension of the local mechanisms, on which will depend the damage, and the possible reorganisation of the microstructure under strain. Moreover, the discrete modelling is still to be develop for a better understanding of the mechanical behaviour of network of entangled fibres such as carbon nanotubes and cellulose nanofibrils, since, up to now, we have only performed electrical modelling.

The aim of our works is to integer in the mechanical behaviour of the studied materials, the involved physical mechanisms. Then the objective is to develop a constitutive law fro a calculation code. The approach is ambitious and needs, if one wants chances of success, collaboration with specialists of finite element modelling. Our work with T. Barenger of the Département de Mécanique de l'Université Claude Bernard has begun. The approach that we will use is the inverse of that of the manuscript, i.e. to use the constitutive laws existing in Finite Element code, and to progressively modify them to account for our studies of the materials. This is an approach eventually similar to that followed in the Ph-D thesis of R. Rinaldi whose objective was to integrate the qpd model in FE code. This work, apparently very technical, provides new insights on the modelled polymers: it enables to re-explore the "qpd model" through the simulation of the polymer macroscopic behaviour. Even if there is still a lot to do, for instance to exploit the modelling of elastic, anelastic and viscoplastic strains, or to compare simulation results and observations of the macroscopic strain heterogeneities, the development of such a simulation tool, by this comparison between experiments and simulation, is another way to improve our comprehension of the material. Besides, the development of more "physical" modelling tools can be extremely useful to study materials submitted to solicitation as complex as those met in common applications[bb]…

[bb] We present in appendix the particularly difficult example of elastomer seal lip for ball bearings.

Appendix: surface/volume

We have previously seen that the mechanical solicitation seemingly simple such as traction or compression are already sources of strain heterogeneities. However, the main part of the applications of polymer materials involves much more complex solicitation, not only source of strain heterogeneities but also heating, ageing, damage, also very heterogeneous. For instance, the use of filled elastomer often involves both viscoelastic properties (volume) and friction and wear properties (surface properties) of these materials. This is made even more complex by thermal dissipation phenomena dependent on the viscoelastic properties and thermo-mechano-chemical damage activated by the heating they create and local stresses.
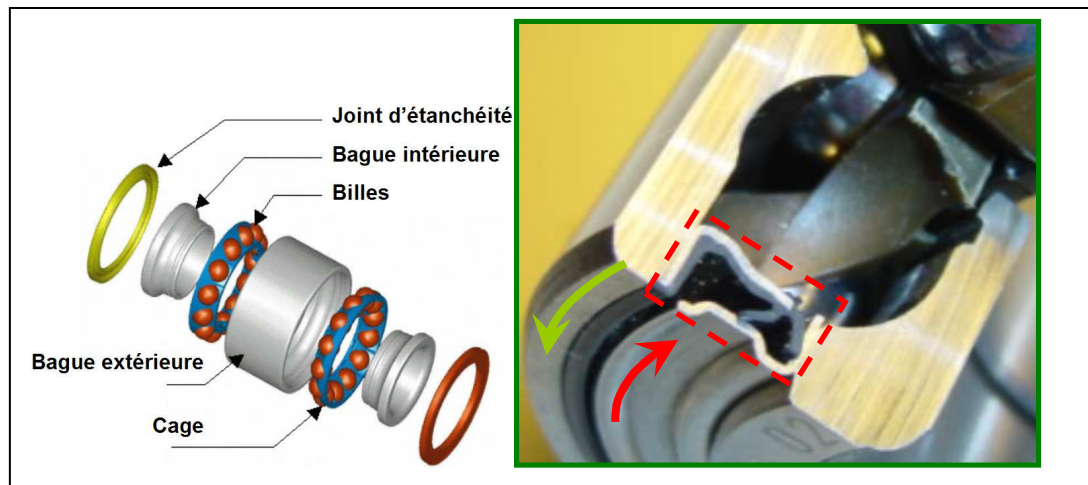

Figure A1: Scheme of a ball bearing and section of a lip seal in the device.

This complexity was met during the study In elastomer seals used for ball bearings. As shown on figure A1, these seals are used for maintaining etancheity of rolling cage from water and mud penetration. Their degradation is the first cause of failure of bearings during their use. The improvement of their performance needs a better understanding of the mechanisms involved, taking into account the heterogeneous and complex nature of the solicitations and the influence of temperature and of environment. The damage of these filled elastomers is visible as a local wear at the level of the contact surfaces (seal lips and their antagonist in steel), accompanied by a possible modification of the chemistry of the elastomer, and therefore of its viscoelastic properties, in the surface neighbourhood. In this frame, a study of the relationships between viscoelastic and tribological properties of the solicited material was the ropic of the Ph-D of M. Thomine (BDI CNRS, Paustra S.A., SNR S.A. fellowship) defended in Octber 2004, and of the Ph-D thesis of J.M. Desgrange (financed by the RNMP "elastomere sous sollicitations sévères, defended in October 2005). The aim was to evaluate the influence of the different constituents of the elastomer formulation on the durability of the seals. Both thesis were co directed with the Laboratoire de Tribologie et Dynamique des Systèmes of the Ecole Centrale de Lyon. The studied materials were Acrylonitrile Butadiene copolymer (NBR) reinforced either by carbon blacks, or "clear" fillers (silica and calcium carbonates).
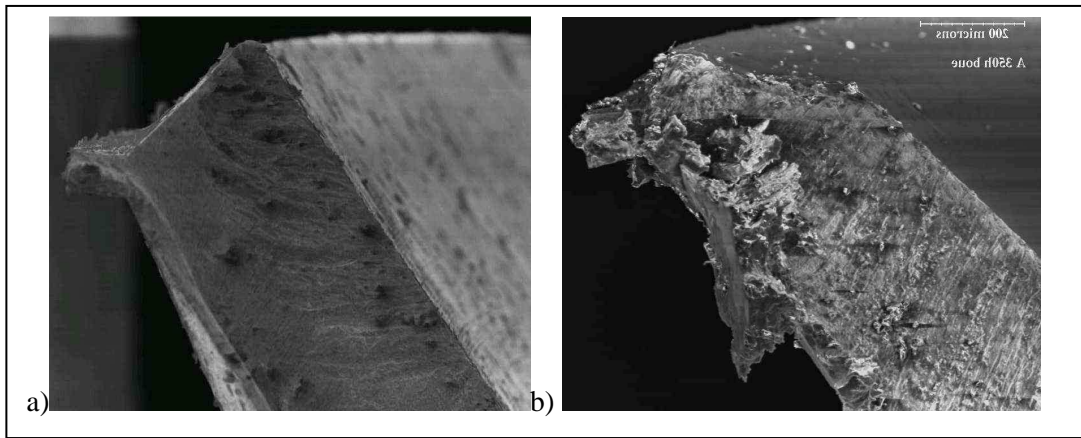
Figure A2: S.E.M. image of a lip seal for ball bearing (a) unused, (b) used after 300 hours of real test with external projection of mud.
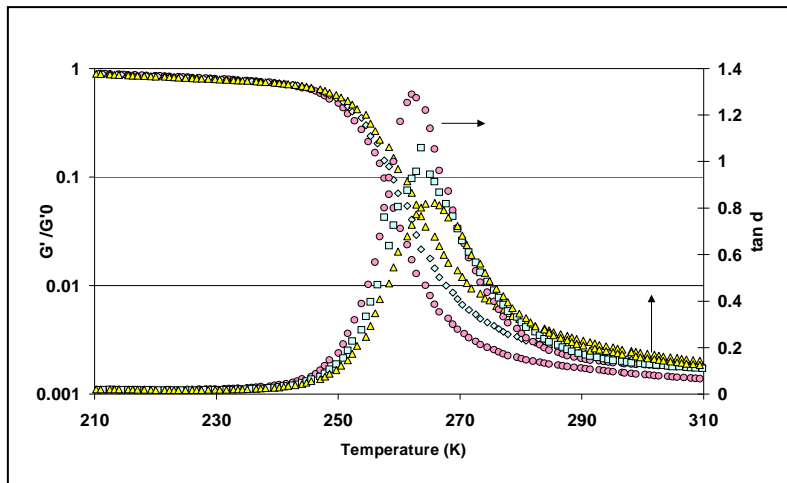

Figure A3 : viscoelastic properties of lip seal for ball bearings. G' is normalised by the modulus value at 210K; the evolution of the curves show the effect of wear on the viscoelastic properties of the elastomer lip seal.

Some samples, processed as elastomer seals, have been tested by SNR on their testing device reproducing the real use conditions, with and without mud (tests "BDJE" and "BFRE"). [cc] The influence of the filler type has been first evaluated. The lips and their antagonist (steel 100C6) have characterised after testing during different times by optical and scattering electron microscopy (cf. Figure A2). The presence of steel particles or of mud embedded in the elastomer was analysed by EDX analysis. The ensemble of these measurements enables the proposal of a damage scenario of the seals. Moreover, they showed that the lip wear occurs when there is a lack of lubricant, provoked by the beating of the lip in rotation and eased by the mud particles. The evolution of the material mechanical properties was evaluated by mechanical spectrometry. It showed an increase of the rubber modulus as well as a slight shift of the main relaxation peak toward higher temperature (cf. Figure A3). The assumption is a post-crosslink due to a heating of the material during solicitation. This post crosslinking explains the remnant deformation observed on the lips after their use. To confirm it, temperature ageing tests were performed on different samples. Besides a thermo-

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[cc] Rapport de projet de fin d'étude INSA de S. Deville (2001), Rapport de projet de fin d'étude INSA de F. Thevenet (2000), rapport de stage 4ème année ingénieur ISTG de J. Todeschini (2000).

mechanical surface degradation occurs that was characterised by local mechanical tests. The heterogeneous character of the evolution of the mechanical properties was characterised by nanoindentation measurements performed on the lips. They revealed the presence of a stiffness gradient from the lip surface toward the material core. [dd]

Concerning the influence of the different material parameters, we have observed that, in the material series tested for this application, carbon blacks or clear filler filled NBR, the filler characteristics have no real influence on the etancheity performance in real testing conditions. Of course, this result is only true when the global mechanical properties of the material vary a little (small gap of modulus or resistance at break). *A contrario*, materials presenting a matrix modification, this being essentially visible as a difference of the glass transition temperature, has shown very contrasted results on real system. Indeed, these materials have very different tribological behaviours, at the level of etancheity performance as well as that of wear resistance: the material with the lowest Tg (A) possesses a good etancheity performance though important wear, when the (O) material, whose Tg is higher of 15°C, though an important wear, shows a mediocre etancheity performance. The apparent contradiction of these results comes from the slight difference of viscoelastic properties of both materials, which lead to different contact area and dynamic responses. This response controls the etancheity function.

For a better understanding of the wear mechanisms, sphere plan tests were performed: plaque of materials have been submitted to friction of a steel bead in rotation and normal force conditions similar to those met in real tests. For the reasons discussed previously (wear originating in a stop of lubrication mechanisms), these tests have been performed without lubricant. Tests on materials A and O show a wear resistance similar to that observe in real testing: the O material, conversely to the A material, does not presence any wear trace (cf. Figure A4).
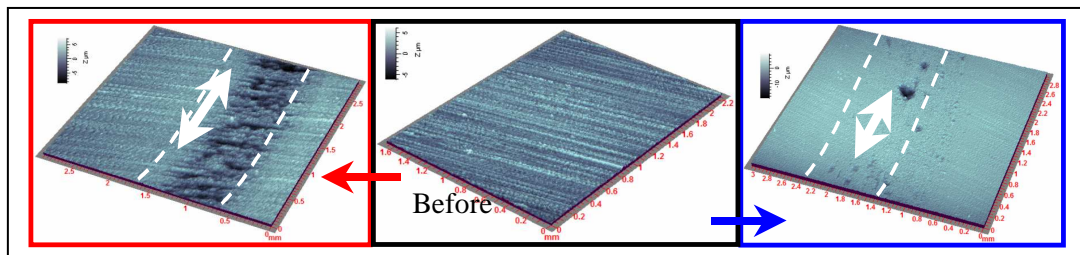

Figure A4 : 3D profilometry of samples before and after wear: from left to right, used sample A, unused sample A or O, used sample O.

ESCA analysis then allowed to evidence the presence of an oxidised layer. Its thickness is probably below few microns because it could not be detected by Infra Red spectroscopy, either mechanical test (AFM and nanoindentation) whose maximal resolution (in the imposed testing conditions) is several dozens of microns. Conversely, the A material surface is not oxidised and possesses the same characteristics of a new sample, except few neat wear

[dd] " Influence of viscoelasticity on the tribological behaviour of carbon black filled nitrile rubber (NBR) for lip seal application", J.-M. Degrange, M. Thomine, Ph. Kapsa, J.M. Pelletier, L. Chazeau, G. Dudragne, L. Guerbé, wear , 259, 684-692, 2005.

traces. The presence of the oxidation on the O material can be explained by the analysis of the real temperature at the contact level. This was the objects of different modelling approaches: one by Finite Element, one analytical, or the extrapolation from lcalised thermal measurements. This temperature is beyond the critical temperature of oxidation of the elastomer; thus the matrix oxidation can occur. This oxidation leads to a stiffer superficial layer, which decreases the friction coefficient and so enables in fine to avoid wear. In the case of the A material, oxidation kinetic is in competition wit the wear kinetic more rapid, due to an initial friction coefficient higher. The correlation between friction coefficient and wear is clearly established, as well as between friction coefficient and surfacial stiffness of the material.

This study has lead to the proposal of a technological solution for the industrial problem. It takes into account the very heterogeneous nature of the solicitation, and propose the processing of a property gradient in the material, the surface properties being close to that of the O material, and the volume properties being that of the A material. [ee]

The elaboration of other technological solutions would need to continue this study by focusing on three main points:

- Lubrication mechanisms: the absence of lubrication being, seemingly, the needed condition to begin the catastrophic wear of the lips, it would be useful to establish the optimal conditions of lubrication. This needs an experimental work which can be performed on a new testing device made during the Ph-D work of J.M. Degrange. This device enables the observation of the rotating lip at the contact level through the glass antagonist. It is also necessary to estimate, thanks to a viscoelastic modelling of the material initiated by J.M. Degrange, the pressure conditions on the lip.

- The heating of the material: a modification of the local temperature of the sample can strongly change its mechanical behaviour, and consequently its wear resistance. It would be useful to determine the kinetics but also all the parameters involved in the heating. To do so, one can use the modelling of the viscoelastic properties, useful for the calculated of the heat dissipated, and the thermal modelling, also initiated in the Ph-D work.

- The wear mechanisms: wear is related to mechanisms of local deformations involving different solicitation frequencies. These different frequencies are caused by different asperities, initially present or created during wear, with dimensions of the order of few nanometers. At these scales, the material response, as seen previously, can be influenced by the interfaces involved. In the case of both studied materials (A and O), it is possible that this influence has very different consequences on the mechanical behaviour, on the resistance, though the macroscopic properties do not show any significant differences. Thus, it is necessary to continue the study of these local properties.

Conclusion

Polymer materials, in their current application, are submitted to very heterogeneous solicitations. A large majority of the elastomer applications involves cyclic deformation and

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[ee] "Wear mechanisms of filled elastomers for leap seal application", M. Thomine, J.M. Degrange, G. Vigier, L. Chazeau, J.M. Pelletier, P. Kapsa, L. Guerbé, G. Dudragne, tribology international, acceptée.

friction. For instance, we have seen the example of elastomer seals, but we can also cite the example of tyres. In both cases, one must consider the volume viscoelastic behaviour, and the interfacial friction mechanisms (the latter having also a viscous component related to the global viscoelasticity of the solicited material), keeping in mind, as shown previously, that the volume solicitation has direct and indirect consequences on the friction behaviour. The directs consequences are visible at the contact: area and normal force, which are going to influence, when present, the lubrication quality. Indirect consequences are energy dissipation, which engender sometimes huge heating of the surface, and therefore the chemical modification of the material close to the interface. This can in turn modify the viscoelastic local response, and so the wear resistance. The comprehension and the material optimisation for this type of application need a rigorous approach which should dissociate mechanisms often interrelated. It must also be helped by a modelling of these mechanisms if it wants clarify their respective contribution.

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