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Propriétés de composites de polyéthylène haute densité et résidus de canne à sucre: effet de la délignification des fibres et d'un traitement de surface sur la résistance à la photo- et la bio-dégradation

Peyvand Darabi

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Mécanique et Génie Civil

Propriétés de composites de polyéthylène haute densité et résidus de canne à sucre: effet de la délignification des fibres et d'un traitement de surface sur la résistance à la photo- et la bio-dégradation

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Laboratoire de Mécanique et Génie Civil
860 rue de St Priest – 34090 Montpellier



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Properties of composites of high density polyethylene and bagasse flour: effect of fiber delignification and surface treatment on the resistance to photo- and bio-degradation

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Dedication

To my beloved family

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Abstract

The use of wood-polymer composites (WPC), combination of plastics and lignocellulosic fibers, is developing considerably. However, the effects of weathering, such as color fading and loss in mechanical properties, limit their performance in outdoor applications. WPC produced in Iran and made of high-density polyethylene and sugar cane fibers was studied. The effect of fiber pretreatments (delignification to various levels and, pigmentation) and clear coating on the resistance to weathering and biodegradation, and to their combination, was investigated. Chemical (NIR, ESR and FTIR spectroscopy), physical (color, roughness, wettability), mechanical (vibration, 3 points bending and indentation) and biological (resistance to fungi and termites) observations were made on extruded samples. Delignification generally reduced initial mechanical properties while not preventing degradation and color change due to weathering, except when combined with addition of pigments where the rigidity was stabilized to some extent. Clear coating showed very promising results: it prevented color changes associated to photo and bio-degradations, and reduced the loss of properties due to weathering. Although fungi and termites provoked some surface degradation of weathered samples due to the better accessibility of fibers, the resistance of the products to degradation was good. From the methodological viewpoint, the good correlation between various mechanical parameters suggests the applicability of non-destructive testing methods based on modal analysis or indentation techniques for in-situ characterization of WPC properties or evaluation of the degradation level.

Resumé

L'emploi des composites bois-plastique (WPC), combinaison de polymères plastiques et de fibres ligno-cellulosiques, se développe considérablement. Cependant, les effets du vieillissement, tels que l'altération de leur couleur ou la perte de résistance mécanique, limite leurs performances lors d'expositions/utilisations extérieures. Des composites produits en Iran, à base de polyéthylène haute densité et de bagasse de canne à sucre, ont été étudiés, notamment les effets de prétraitement des fibres (différents niveaux de délignification), de l'ajout de pigments et d'une finition transparente, ainsi que leurs effets combinés, sur le vieillissement et la biodégradation. Des observations chimiques (spectroscopie NIR, ESR, FTIR), physiques (couleur, rugosité, mouillabilité), mécaniques (vibration, flexion 3 points, indentation) et biologiques (résistance vis-à-vis des champignons et des termites) ont été réalisées sur des échantillons obtenus par extrusion. En général, la délignification réduit les propriétés mécaniques, bien que ne prévenant pas la dégradation ni le changement de couleur dû au vieillissement, excepté lorsqu'elle est combinée à l'addition de pigments auquel cas elle maintient la rigidité dans une certaine mesure. L'ajout d'une finition transparente a montré des résultats très prometteurs : la finition prévient le changement de couleur associé aux photo et biodégradations, et réduit la perte des propriétés mécaniques due au vieillissement. Bien que les champignons et les termites provoquent une dégradation de surface des échantillons vieillis étant donné l'accès plus aisé aux fibres, les composites ont montré une bonne durabilité biologique. Du point de vue méthodologique, la bonne corrélation entre les différents paramètres mécaniques suggère que l'utilisation de méthodes d'essai non-destructives basées sur l'analyse modale ou l'indentation est adaptée pour la caractérisation in-situ des composites et pour l'évaluation de leur degré de dégradation.

Contents

1. INTRODUCTION.....	15
2. LITERATURE REVIEW	17
2.1. WHAT IS WPC? STRENGTHS AND WEAKNESSES!	17
2.1.1. Advantage of wpc	17
2.1.2. Matrix part.....	17
2.1.3. Filler or reinforcement part.....	19
2.1.4. WPC Additives	22
2.1.5. Main factors of WPC properties.....	24
2.2. HISTORY OF WPC	24
2.3. MARKET SHARE FOR WPC AROUND THE WORLD	25
2.3.1. Market share in North America and Europe	25
2.3.2. Market share in Iran	26
2.3.3. Main challenge for developing the WPC Market	28
2.4. WPC DEGRADATION	28
2.4.1. Biotic Degradation	28
2.4.2. Abiotic degradation	31
2.5. PROTECTION OF WPC AGAINST DEGRADATION	41
2.6. APPLIED TREATMENTS	42
2.6.1. Usage of delignified fibers in WPC.....	42
2.6.2. Coating of Wood Plastic Composites	44
2.6.3. Pigment application in WPC.....	46
2.7. METHODS TO EVALUATE WEATHERING OF WPC	47
2.7.1. FTIR spectroscopy.....	47
2.7.2. CIE Lab colorimetry	51
2.7.3. Contact angle test.....	52
2.7.4. Roughness.....	52
2.7.5. Mechanical tests	53
2.7.6. Biological resistance test.....	54
2.7.7. Moisture absorption	55
3. MATERIAL	57
3.1. PREPARATION OF FIBERS.....	57
3.2. RAW MATERIALS OF THE COMPOSITE.....	58
3.3. MANUFACTURE OF WPC PROFILES.....	59
3.4. PREPARATION OF TEST SAMPLES.....	60
3.5. COATING APPLICATION	61
4. PROCEDURES AND METHODS	62
4.1. AGING PROCEDURE (WEATHERING).....	62
4.2. CHEMICAL TESTS	62
4.2.1. FTIR spectroscopy.....	62
4.3. SURFACE QUALITY	64
4.3.1. Color Analysis (Colorimetry).....	64
4.3.2. Contact angle test	64
4.3.3. Roughness.....	65
4.4. MECHANICAL TESTS	66
4.4.1. Three points bending	66
4.4.2. Vibration test	69
4.4.3. Indentation test.....	71
4.4.4. Statistical analysis.....	72
4.5. BIOLOGICAL TESTS	72
4.5.1. Fungal resistance test	72
4.5.2. Termites resistance	73

4.5.3.	<i>Moisture absorption</i>	74
5.	ANALYSIS OF CHEMICAL PROPERTIES	77
5.1.	CHEMISTRY OF FIBERS (BEFORE BOARD PRODUCTION).....	77
5.2.	CHEMICAL CHANGES ASSOCIATED WITH USING DELIGNIFIED FIBERS IN WPC STRUCTURE.....	79
5.2.1.	<i>Spectra of manufactured samples</i>	79
5.2.2.	<i>Effect of weathering on delignified samples</i>	81
5.2.3.	<i>Quantified study of delignified samples after weathering</i>	83
5.3.	CHEMICAL CHANGES ASSOCIATED WITH PIGMENTATION OF WPC	84
5.3.1.	<i>Spectra of manufactured samples</i>	84
5.3.2.	<i>Effect of weathering on pigmented samples</i>	84
5.3.3.	<i>Quantified study of delignified samples after weathering</i>	88
5.4.	CHEMICAL CHANGES ASSOCIATED WITH COATING	89
5.4.1.	<i>Spectra related to preparation of the surface before coating</i>	89
5.4.2.	<i>Spectra related to PU coating samples</i>	90
5.4.3.	<i>Effect of weathering on coated samples</i>	91
5.5.	GENERAL OUTCOMES.....	94
6.	ANALYSIS OF COLOR AND OTHER SURFACE PROPERTIES	95
6.1.	EFFECT OF DIFFERENT TREATMENTS ON THE COLOR	95
6.2.	EFFECT OF WEATHERING ON THE COLOR.....	96
6.3.	EFFECT OF BIODEGRADATION ON THE COLOR	100
6.4.	EVOLUTION OF THE RELATION BETWEEN COLOR INDEXES	103
6.5.	ROUGHNESS AND CONTACT ANGLE TESTS	107
6.5.1.	<i>Values of measured parameters</i>	107
6.5.2.	<i>Effect of weathering</i>	108
6.6.	GENERAL OUTCOMES.....	109
7.	ANALYSIS OF MECHANICAL PROPERTIES	111
7.1.	VIBRATION TEST.....	111
7.1.1.	<i>Values of measured parameters</i>	111
7.1.2.	<i>Effect of weathering</i>	113
7.1.3.	<i>Relation between rigidity and damping</i>	115
7.1.4.	<i>Relation between vibrational properties and density</i>	118
7.2.	THREE POINTS BENDING TEST.....	120
7.2.1.	<i>Effect of weathering on the value of parameters</i>	120
7.2.2.	<i>Effect of weathering on the relationship between parameters</i>	122
7.3.	INDENTATION TEST	125
7.3.1.	<i>Effect of weathering on the value of parameters</i>	125
7.3.2.	<i>Effect of weathering on the relationship between parameters</i>	128
7.4.	PROCESSING/ADJUSTMENT OF DATA ACCORDING TO DENSITY	129
7.5.	ANALYSIS OF THE RELATIONSHIPS BETWEEN VARIABLES	132
7.5.1.	<i>Direct correlations between variables</i>	133
7.5.1.	<i>Principal component analysis (PCA) for all data</i>	136
7.5.2.	<i>Separate PCA for data before and after weathering</i>	137
7.5.3.	<i>Simple linear regressions before and after weathering</i>	139
7.5.4.	<i>Multiple regressions</i>	142
7.6.	GENERAL OUTCOMES.....	143
8.	BIOLOGICAL DEGRADATION	144
8.1.	QUANTITATIVE RESULTS	144
8.1.1.	<i>Moisture absorption and fungal resistance</i>	144
8.1.2.	<i>Termite's resistance test</i>	149
8.2.	QUALITATIVE RESULTS.....	150
8.2.1.	<i>Fungal resistance test</i>	150
8.2.2.	<i>Termite's resistance test</i>	153
8.3.	GENERAL OUTCOMES	154

9. DISCUSSION ON THE EFFECT OF TREATMENTS	155
9.1. EFFECT OF DELIGNIFICATION AND PIGMENTATION	155
9.2. EFFECT OF CLEAR COATING	157
10. GENERAL CONCLUSION	158
REFERENCES	160
ANNEXES	174
ANNEX A: SUMMARY OF ALL QUANTITATIVE DATA	174
ANNEX B: ANALYSIS OF VARIANCE	177
ANNEX C RELATIONSHIP BETWEEN VARIABLES FROM MECHANICAL TESTS.....	179
ANNEX D: MULTI-REGRESSIONS BETWEEN MECHANICAL VARIABLES	185

List of tables

Table 1- Cellulose fibers - Properties.....	20
Table 2- Percent of Total Spectral Irradiance for UV, Visible, and IR Radiation.....	32
Table 3- Bond Dissociation Energies and Radiation Wavelength ^a	32
Table 4 - Relative Effect of Various Energy Forms on Wood (Brooks 2000).....	34
Table 5- Chemical Composition of Aspen wood before and after accelerated weathering (Brooks 2000).....	36
Table 6- Assignment of absorption bands of IR spectrum (Matuana et al. 2011).....	49
Table 7- General Characteristics of High Density Polyethylene	58
Table 8- Combination of variables used in the manufacture of bagasse/plastic composite boards. (Zero (0) and C, P, CP are the abbreviations for non-treated, coated, pigmented and coating pigmented samples, respectively)	59
Table 9- Compounding conditions for the base WPC material the cap layers.....	59
Table 10- The correlation between different mechanical variables.....	135
Table 11- Weight loss of different groups after termite's attack.	150
Table 12- General ideas about effectiveness of treatments.	156
Table 13- Total quantitative results from non-delignified samples (Control) accompany by pigmentation and coating (Means \pm STDV).....	174
Table 14- Total quantitative results from delignified samples with Ethanol accompany by pigmentation and coating (Means \pm STDV).....	175
Table 15- Total quantitative results from delignified samples with MEA (Means \pm STDV).....	176

List of figures

Figure 1- Hollow and solid WPC profiles	15
Figure 2- Global manufacturers of wood plastic composites.	25
Figure 3- WPC application in Europe excluding automotive part 2004, Source: Hackwell Group (Hackwell-Group 2006).....	26
Figure 4- The sugar mills spread based on the source of sugar production.	27
Figure 5- Increase of sugar production from sugar cane in Iran.....	28
Figure 6- Chemical structure of cellulose.	34
Figure 7- Monomer constitutive of lignin (coumarylic, coniferic and synapylic alcohol).	34
Figure 8- Mechanism of wood photo-degradation (Feist and Hon 1984).....	35
Figure 9- Lignin photo-oxidation mechanism (Anderson et al. 1991).	36
Figure 10- bond stretching and bending of Molecules	48
Figure 11- An attenuated total reflection (ATR-FTIR) system.....	48
Figure 12- The comparison of the HDPE/poplar composite spectra before and after weathering (Fabiyyi et al. 2009).....	50
Figure 13 - FTIR spectra of HDPE1.2 (for cap layer) and HDPE0.4 (polymer matrix for uncapped WPC and core layer of coextruded WPC). (a) before and (b) after exposure to 1952 h UV (Matuana et al. 2011).	51
Figure 14-Diagram of CIELab color space in 2D and 3D (http://learn.colorotate.org/color-models.html).	52
Figure 15- Scheme of the tests carried on un-weathered and weathered samples.	57
Figure 16- These pictures represent different parts of industrial extruder used for this study: a) Pre-mixer b) Feeder and Control Monitor of extruder; c) End part of extruder barrel and Die; d) Die and opened calibrator (Water pool).	60
Figure 17- Prepration of samples: a) Profil of samples; b) after cutting the sides; c) sanding.....	60
Figure 18- chematic diagram of the contact angle, θ angle between the solid-liquid interfaces...	65
Figure 19- Surface characteristics (Courtesy, ANSI B46.1-1962).....	65
Figure 20 – Surface roughness measurement.....	66
Figure 21- Position of the samples under the load.	66
Figure 22- Examples of the relationship between a typical stress–strain diagram and some mechanical properties obtain from it.....	68

Figure 23- Schematics of strain-stress relationship curve and its relation with ductility (D and D') and how ductility can be changed in relation to other variables.....	69
Figure 24- Experimental setup for BING dynamic tests (Brancheriau et al. 2006).....	70
Figure 25- Software of Bing software. The spectral representing the time-frequency relation of a typical sound obtained experimentally.	71
Figure 26- Diagram of relation between force and displacement of indenter into depth of 3 mm of the samples surface.....	71
Figure 27- Agar-block test plates for WPC samples and controls in beginning of the test.	73
Figure 28- Agar-block test plates for WPC samples and control after 1month.	73
Figure 29- Termite test plate in beginning of the test and two weeks after test started.....	74
Figure 30- FTIR spectroscopy of bagasse fiber in form of: Control (A0), delignified by ethanol until 9% lignin content (B0), delignified by MEA until 9% lignin content (B'0) and delignified by MEA until 5% lignin content (C'0).	77
Figure 31- The peak related to cellulose crystallization region and frequency of the aromatic structure vibration.	78
Figure 32- Three different IR ratios plotted for delignified fibers	79
Figure 33- FTIR spectra for non-delignified and delignified samples after baseline implement. U represents un-weathered samples.	80
Figure 34 - FTIR spectra region related to lignin vibration for non-delignified and delignified via MEA samples.....	80
Figure 35- FTIR spectra for non-delignified and delignified samples after baseline implement. U represents un-weathered samples and W represents weathered samples.....	81
Figure 36- FTIR spectra between 1800-600cm ⁻¹ for non-delignified and delignified samples before and after weathering.....	82
Figure 37- band related to HDPE crystallite (Left) and appears of extra peak for MEA delignified samples before and after weathering. Peak at 3350cm ⁻¹ (right); shows loss in O-H group for control samples and fix amount for Mea delignified samples	82
Figure 38- Lignin and Hydroxyl Index between different groups before and after weathering....	83
Figure 39- Wood and Carbonyl Index between different groups before and after weathering.....	84
Figure 40- ATR-FTIR spectra of non-delignified and delignified composites without with (Ap and Bp) and without (A0 and B0) pigment, before and after weathering.	86
Figure 41- Compare of ATR-FTIR spectra of all samples between 1800 to 1500 cm ⁻¹ , before and after weathering.	87

Figure 42- Peak related to OH band for pigmented samples and their pairs without pigments, before and after weathering.....	87
Figure 43- Comparing different index before and after weathering determined from ATR-FTIR spectroscopy.	88
Figure 44- ATR-FTIR spectra of sanded (UA0) and non-sanded (NUA0) surface of the bagasse/HDPE composites before coating.....	89
Figure 45- FTIR spectra of aliphatic polyurethane coating (RAE Engineering and Inspection Ltd).	90
Figure 46- ATR-FTIR spectra of coated on sanded (Ac) and non-sanded (NAC) composites.....	91
Figure 47- ATR-FTIR spectra of coated composites, on pigmented and non-pigmented samples.	91
Figure 48- ATR-FTIR spectra of sanded (A0) and none-sanded (NA0) surface of control composites, before (U) and after weathering (W).	92
Figure 49- Effect of weathering and fungi activity on average values of color indexes. U: un-weathered; W: weathered; UF: un-weathered samples expose to fungi test and WF: weathered samples expose to fungi test. Error bar: standard deviation.....	96
Figure 50- Color change in non-coated sanded and coated sanded samples (left) and on pigmented non-coated non-sanded and pigmented coated non-sanded samples (right). The upper part of the specimens was protected from weathering by the frame of the accelerating weathering device.....	97
Figure 51- Surface quality of Group A with different treatments: A0 (control), Ac (coated), Ap (pigmented), and Acp (coated and pigmented). First row representing un-weathered samples, second row are weathered samples, third row are weathered samples exposed to termites, and last row are the weathered samples exposed to fungal test.	97
Figure 52- Trend of changes in color indexes from initial values (U) to weathering (W) and fungal effect on un-weathered (UF) and weathered (WF) specimen by specimen calculations.	102
Figure 53- Distribution of color data in sanded samples from colorimetric test: before weathering (U), after weathering (W), after fungi attack (UF) and after weathering and then fungal attack (WF) for group A.....	104
Figure 54- Distribution of color data in sanded samples from colorimetric test: before weathering (U), after weathering (W), after fungi attack (UF) and after weathering and then fungal attack (WF) for group B.....	105
Figure 55- distribution of color data in sanded samples from colorimetric test: before weathering (U), after weathering (W), after fungi attack (UF) and after weathering and then fungal attack (WF) for groups A', B' and C'.....	106
Figure 56- Average Roughness (micrones) of sanded samples before and after weathering.	107

Figure 57- The value of θ for sanded A0 (non-delignified and non-coated), Ac (non-delignified and coated) and also for delignified samples with (Bp) and without pigment (B0) before and after weathering were depicted in this chart..... 107

Figure 58- Effect of treatment on the response to color change caused by weathering and fungal attack..... 109

Figure 59- Mean vibrational properties for all groups before and after weathering (error bar=STDV): (a) Modulus (E_{vib}); (b) Damping ($\tan\delta$); (c) density (ρ)..... 111

Figure 60- Graph representing the relation between density and E_{vib} for A0 and for A'0 before and after weathering 112

Figure 61- Relative change of vibrational properties induced by weathering: (a) Modulus (E_{vib}); (b) Damping ($\tan\delta$); (c) density (ρ)..... 114

Figure 62 - Relation between damping coefficient (or internal friction, $\tan\delta$) and the specific dynamic modulus of elasticity (E/ρ) and E_{vib} 116

Figure 63- Changes in internal friction and specific modulus relation due to wood compositions, after (Brémaud et al. 2010) 116

Figure 64- Schema of average values of internal friction and specific modulus position to general trend..... 118

Figure 65- Relation between density and E_{vib} of different groups before weathering..... 119

Figure 66- General trend between E_{vib} and $\tan\delta$ with density for all samples..... 119

Figure 67- relation between average per group of vibrational properties and density. Arrows join un-weathered to weathered value. Red color indicates coated samples, hollow line pigmented fibers, discontinuous line the B group, and gray color the 2nd set of samples (A'0, B'0, C'0). (a) Elastic modulus (E_{vib}); (b) damping ($\tan\delta$). 120

Figure 68- Mechanical Parameters measured by three points bending test: MOE, energy, strain max, MOR (max stress), D, and D' , for all group of samples before and after weathering. Error bar: standard deviation. 121

Figure 69- The percentage of changes in different three points bending variables caused by weathering..... 122

Figure 70- Regression between E_{3PB} with other three points bending test before and after weathering..... 123

Figure 71- Regression between other different variables of three points bending test before and after weathering..... 124

Figure 72- Regression between two different ductility with other different variables from three points bending test before and after weathering..... 125

Figure 73- Values of different measurements from f force-displacement relationship curve in indentation test..... 127

Figure 74- Linear regression between loading (K_L) and unloading (K_U) slope of indentation test.	128
Figure 75- Linear regression between loading (K_L) and unloading slope (K_U) with other variables from Indentation test.	129
Figure 76- Linear relation between density of same samples before and after weathering.....	130
Figure 77- Linear regression between density and different variables before and after weathering.....	131
Figure 78- Percentage of changes after weathering on different corrected variables.....	132
Figure 79- Illustration of stress-strain curves of two samples having the same MOE and different W due to changes in maximal strain and stress.....	136
Figure 80- PCA plan for two axis of Factor 1 and factor 2 for all variables and also for Factor 1 and Factor 3 (For Abbreviations see section 4, table 11)	137
Figure 81- PCA plan for axis of Factor 1 and factor 2 and factor 1 and factor 3 for un-weathered samples.....	138
Figure 82 - PCA plan for axis of Factor 1 and factor 2 and factor 1 and factor 3 for weathered samples.....	138
Figure 83- Relation between MOE calculated with two different methods (static test and NDT), for all samples before and after weathering.....	139
Figure 84- Most interesting relation of K_L with other variables from vibration and three oints bending test.....	140
Figure 85- Best Linear regression of different values of ductility with other variables.....	141
Figure 86- Linear regression between different values of ductility and $\tan\delta$	141
Figure 87- Linear regression between Density and other variables.	142
Figure 88- Equilibrium moisture content after 2 months placing the weathered and un- weathered samples at ambient conditions of 23 ± 2 °C and 75 ± 5 % relative humidity.	145
Figure 89- Weight loss and moisture content of all groups after fungal resistance test.....	146
Figure 90- Comparing of moisture absorption and weight loss caused by fungal attack in un- weathered and weathered samples.	147
Figure 91- Comparing of moisture absorption and Swelling caused by fungal attack in un- weathered and weathered samples.	147
Figure 92- Comparing of moisture absorption during fungal attacked density in un-weathered and weathered samples.....	148
Figure 93- Swelling of samples during fungal attack and density in un-weathered and weathered samples.....	149

Figure 94- Surface of sample without any treatment (A') before (on the left) and after expose to weathering (on the right) 151

Figure 95- Surface of Weathered of delignified samples: on the left B'0 and C'0 on the right. ... 152

Figure 96- Surface of un-weathered (on the left) and weathered (on the right) control samples attacked by fungal..... 152

Figure 97- Surface coated samples before (on the left) and after (on the right) attacked by fungal. 153

Figure 98- Surface of un-weathered (on the left) and weathered (on the right) of control samples (A') after Termites attack 154

Figure 99 - Relation between weight loss caused by biodegradation and color indexes for a and c) un-weathered and b and d) weathered samples. 156

1. Introduction

The purpose of producing engineered composites is to have products with enhanced properties for different end-uses. Wood-plastic composites (WPC) are engineered composites made from the combination of wood or any other lignocellulosic fiber/flour as a filler and plastic(s) as a matrix. WPC were first produced aiming to recycle polymers. However, after being introduced into the world market, their demand increased highly every year (Klyosov 2007; Stark and Gardner 2008). One of the reasons for this is the ability of these products to supersede wood in some of the applications, while also having the moldability of plastic. The latter advantage allows WPC products to have variety in shape, with or without simulated wood grain details, in different colors (Figure 1).



Figure 1- Hollow and solid WPC profiles

High resistance and durability of these products increase the preference of using them in outdoor applications instead of wood or other materials. However, they are not completely resistant against environmental factors and show some weaknesses. High demand for exterior application made researchers to work on enhancing their outdoor performances. Therefore, a variety of additives and modifications have been used. For consumers, quality of material is one matter and aesthetic properties are another matter. WPC may have a high quality aspect when manufactured but after short period of time of exterior use (Muasher and Sain 2006; Stark and Matuana 2006), they go through color change which is not acceptable for end users. Color is not the only property that changes due to weathering; other properties like mechanical properties are also subjected to some changes. Due to this phenomenon, manufactures and researchers are concerned about maintaining the WPC properties during weathering. Many researchers around the world worked and are still working on the ways to solve these problems. Although work has been done recently, there is still more to be achieved to fill the gaps in the knowledge of this field. However, in most of the studies it has been well proved that lignin is the main cause of color change and it is the main component that degrades due to photo-degradation.

Beside western countries, other countries like Iran are also progressing in WPC production, although it is a young generation of composites that still need to make their way through market, we can find 30 production lines scattered around the country. Manufactures in Iran are struggling with different difficulties: the main one the high cost of production, another one for a new product like WPC is to succeed in the market and gain credibility among new and unfamiliar consumers. Change of color or other problems due to weathering is a potential risk. One way to decrease the production costs is to use wastes from other wood production factories, however this alone cannot fulfill the demand of all the production lines. So, most of the factories use agricultural residual like bagasse (sugar cane) or rice hull which can be found in abundance in the south of Iran. In some of the Iranian paper factories, bagasse is used as the main raw material. The competition between paper producers and WPC producers is causing raise in bagasse price. Large amounts of under size delignified fibers are produced every year by the

pulping processes as a by-product of wood and delignification of other (non-wooden) lignocellulosic materials which remains unused. If WPC producers can use the waste material of these pulp lines, it can both help the financial costs and also lessen the color change due photo-degradation, as it has been claimed that color change is mostly due to lignin degradation.

Thus, our research will concentrate mostly on the consequences on properties of using delignified fibers as reinforcement into High Density Polyethylene (HDPE). If it could be demonstrated that it improves photo-stability and other properties of WPC, residual fibers from pulp and paper lines that did not go through bleaching process could be economically reasonable, and also could be considered for uses in exterior environment. However, even if it provided photo-stability, other properties like resistance against bio-degradation or water absorption would also be a concern. These matters will be examined in this study. In addition efficiency of other treatments like clear coating and pigment beside delignification will be investigated.

In summary, we tried to reduce the effect of weathering and bio-degradation changes on WPC by using delignified fibers, pigments, clear coating and combination of all these methods. At the end of this research the best combination of treatments will be suggested for better photo-stabilized WPC, and the efficiency of each treatment will be evaluated. Some methodological aspects will also be considered, in relation to the treatments efficiency evaluation.

In this regards, after “literature review” which mostly focused on importance of WPC, problematic aspect of using WPC outdoors and presenting some solutions, we will presenting some work which has been done until now, considering treatments and methods which have been selected for this study.

Then in the “materials” chapter after the short presentation of methodology, we will explain materials which have been used, the samples manufacturing process and procedures of treatments. Also In “procedures and methods” the basics of each used device and the method of properties evaluation will be explained.

Then after, we strive to present the results through a more comprehensive approach. Initially, we will explain the chemical changes for the reader to obtain the general idea about the basic information on each group and how their nature changes through weathering. Afterward, the effect of different treatments and how they change the process of weathering on different aspect of WPC properties will be discussed, individually in each chapter.

Each chapter is containing results and discussion of each aspect of WPC properties change due to the treatments and weathering and at the end of each chapter the general outcome of related measurements has been emphasized. In between, for each aspect of study, if any methodological study exists, it has been represented in related chapter.

At the end the general discussion which represents the combination of different aspects of treatments will be discussed and a final chapter contains main and new achievements of this study.

All the mean and standard deviation of quantitative results obtained for each part which will be discussed in different chapter are presented at the end in Annex A in three different tables. Also results of ANOVA which has been used to assess the significance of the effect of different treatment and weathering and their interaction on color and mechanical parameters presented in two different tables in Annex B. Annex C and D representing simple and multi regression between variables respectively.

2.Literature review

2.1. What is WPC? Strengths and Weaknesses!

“Wood plastic composites” (WPC) are composites that contain wood (as filler or reinforcement) and thermoset or thermoplastic polymers (as matrix). In fact WPC are mixtures of wood fibers and virgin or recycled synthetic resins. They can also be referred to as natural fiber plastic composites or natural fiber reinforced plastics. The ratio limits for mixture of wood with polymers varies typically from 50 to 70 % wood and 30 to 50 % polymer.

Possibility to incorporate waste agro fibers and recycled plastics in this industry is the one important aspect that has favorably impacted the development of these composite materials with the advantage of a positive eco-environmental impact. Using recycled plastic instead of urea formaldehyde resin as a bonding agent is a worthwhile alternative utilization of these residual materials. Such a product is less sensitive to moisture (Wolcott 1996) and does not require use of additional adhesives. It could thus compete successfully with similar products traditionally used by the local industry such as plywood, fiberboard and thin particle board.

2.1.1. ADVANTAGE OF WPC

WPC have many advantages of wood together with the processability of plastic materials. They offer the advantages of wood like ability to be sawn, nailed, screwed and to be worked on, and the flexibility of plastic. They also offer greater durability and moisture resistance than many types of softwood. Because of that these products can be used for outdoor applications (e.g., decking, cladding, window/door profiles, fences, playground equipment, roofing shingles...) as well as for indoor applications (e.g., floors, panels, door frames, furniture, shelving, storage equipment...). WPC combine advantages like high stiffness and recyclability. However they also have some drawbacks, such as a low bulk density, thermal instability and moisture absorption compared with net polymer. These defects can be solved by adding chemicals or applying some changes in production line. Since several decades WPC have been the subject of many studies. These studies mostly focused on: different sources of natural or organic material which can be used as filler in different thermoplastics matrix; improvement of WPC properties by different additives and mechanisms; and effect of photo-degradation on these composites. The latter issue became extremely important because, as we mentioned before, the properties of WPC change during exterior uses. Most studies concentrated on discoloration of WPC exposed outdoor because it is the first visual change and the main concern of manufacturers and consumers. There has been much effort to counteract this phenomenon, as will be discussed later.

2.1.2. MATRIX PART

Thermoplastic polymers are materials thoroughly used in emergent technologies having low processing cost and density, among other properties, such as transparency and possibility of recycling (Brandrup et al. 1999). Among synthetic resins, the only thermoplastics applicable in WPC are processed at temperatures below 200°C, because of the limitation in thermal stability of wood. Hence, according to processing temperatures, there is a small range of plastics available. Low melting point allows melts to mix well with fillers and reduce the risk of significant thermal degradation in cellulose fiber as filler. Therefore, thermoplastics such as polyethylene (PE), polypropylene (PP) (Sain et al. 2004; Zampaloni et al. 2007), poly-lactic acid (PLA)(Ochi 2008) and poly-vinyl chloride (PVC) (Zheng et al. 2007) have been compounded with natural fibers (such as sisal, jute, and sugarcane bagasse) to make composites. PE has a relatively low melting temperature (typically between 106 and 130°C, depending on density/branching of PE) compare to other polyolefins (polymer produced from a simple olefin

with the general formula C_nH_{2n} as a monomer) and can be produced in a very wide range of melt viscosities. Moreover, its higher resistance to photo-degradation compared to other thermoplastics (Ojeda et al. 2011) is another reason why it is widely used in decking industry. Therefore, it is used commonly in WPC industries.

Polyethylene (PE) is the largest volume plastic produced in the world. It is a semi-crystalline polymer. That means at ambient temperatures the polymer consists of two distinctive crystalline and amorphous parts, or phases. For polyethylene the glass transition point vary from very low to low (from -130°C to -20°C), thus making the plastic ductile at common temperatures. The lower glass transition point (γ -transition) is always present in the range of -130°C to -100°C , the higher one (β - transition, at -20°C) is manifested not in all PE materials. There is one more transition in polyethylene, called α -transition, commonly found between 10°C to 70°C , and it is associated with crystallinity of PE. For WPC the last two transitions (α - and β -) are less important (Klyosov 2007).

Moreover, polyethylene is rather soft, making PE-based composite easier to nail, screw, cut, and saw. Its moisture absorption, is near-zero (typically below 0.02% after 24h underwater immersion), and also it is high resistance to chemicals like strong acids. Only fuming acids can produce some staining of polyethylene. Because of its high resistance to oxidation compare to other polyolefins, it requires lesser amount of antioxidants for processing and for the outdoors service. These are its advantage over other polyolefins; however it has its own disadvantages. Polyethylene is rather flexible and not very strong. Its relatively low strength does not allow it to be used in long dimension. Another undesirable property of PE is its higher coefficient in thermal expansion- contraction compared to wood.

Depending on molecular weight and "linearity", polyethylene is manufactured in various polymeric forms. These characterize the density, or specific gravity of the polymer, which is used as the principal classification feature of polyethylene. The main forms of polyethylenes are High-density PE (HDPE), High-molecular weight HDPE (HMW-HDPE), Ultra high-molecular weight HDPE (UHMW-HDPE), Low - density PE (LDPE), Linear low - density PE (LLDPE), Very low - density PE (VLDPE).

High density polyethylene (HDPE), which is mostly use in WPC industry, is the most crystalline of the commercial PEs and its low cost, desired mechanical properties and processing facility make that acceptable for several industrial applications (Albano et al. 2005; Lei et al. 2007; Li et al. 2008). It is made from ethylene ($\text{CH}_2=\text{CH}_2$) by an ionic polymerization process, which gives a higher relative molar mass. In HDPE linear polyethylene can couple with its lower chain branching which increases the ratio of crystalline to amorphous polymer makes it much stronger than LDPE. HDPE density ranges between 0.950 and 0.965 g/cm^3 (Chanda and Roy 1998). However, the reduction in energy-absorbing amorphous phase also reduces its toughness. Due to its higher crystallinity compared to LDPE, HDPE is stronger and stiffer, but is more prone to warpage (Klyosov 2007). It shows a higher shrinkage, due to formation of crystalline, packed area upon transition from melt state to solid one. As it has high crystalline structure, in comparison to other kinds of polyethylene, it also results in a very high tensile strength performance. On the other hand, HDPE offers a good barrier for humidity and resistance to abrasion and corrosion, and it presents resistance to the most of chemicals.

Generally, the increase of density and the respective transition from LDPE to HDPE leads to an increase in abrasion resistance, chemical resistance, hardness, strength, stiffness, decrease in gas and water permeability, thermal expansion, and impact strength.

2.1.3. FILLER OR REINFORCEMENT PART

The materials which are loaded into the plastic matrix called filler or reinforcement. Cellulose fiber is good as reinforcing filler. In fact, it will make the composite material less expensive and will help to obtain material with overall better properties compared to neat plastic and wood, which are the two major motivations for producing WPC materials. For instance, adding lignocelluloses to rubber significantly improves Young's modulus and tensile strength (Bras et al. 2010) and improves the flexural and tensile stiffness (Clemons 2002) compared to net plastics. Also wood fibers offer higher specific stiffness and strength compared to inorganic reinforcing materials such as glass fibers, calcium carbonate, talc, and mica and also in terms of cost on a unit-volume basis, and flexibility during processing (Matuana et al. 1998; Bledzki and Gassan 1999; Mengeloglu et al. 2000). In addition, from the scientific point of view, there is a constant growing interest in green, environmentally friendly materials. Thus, the use of wood fibers as a loading constituent has drawn attention in the field of composites (Bledzki and Gassan 1999; Eichhorn et al. 2001).

Typical wood types used in WPC are saw dust of pine, maple and oak, however many other lignocellulosic materials like flax, hemp, bagasse, rice peel and other lignocellulosic agricultural by-products can be used in WPC production as well. The usages of these non-wood fillers are increasing every year due to growing demands and environmental problems which force the forest industry to harvest less wood from forests in some of the countries and some benefits of them over wood. These factors cause most of the manufactures around the world to prefer non-wooden raw material over wood. One example of these non-wooden lignocellulosic materials is bagasse.

Advantage and disadvantage of natural fibers in polymer composites

Many other cellulose-based fibers besides wood fiber, like those obtained from annual crops, can also improve mechanical properties (Neagu et al. 2006) and can be used to produce inexpensive low-weight composites. The primary advantages of using natural lignocellulosic fibers as additives in plastics are low densities, low cost, non-abrasive nature to the processing equipment, possibility of high filling levels, high specific properties, biodegradability, availability of wide variety of fibers throughout the world, and generation of agricultural economy (Sanadi et al. 1994; Dundar et al. 2010). In automotive sector, low density of natural fiber composite is the main reason why it has raised interest.

Natural fiber composites compared to other synthetic fibers (Table 1) have many other advantages: lower pollution level during production; lower energy necessary for production of fiber; healthier in use due to their natural origin. Beside these they can give a more environmentally friendly image of plastic and also they are renewable resources.

Table 1- Cellulose fibers - Properties

Fibre type	Density [*] (g/cm ³)	Stiffness (GPa)	Strength (MPa)
Hemp	1.5 – 1.6	30 – 60	300 – 800
Flax	1.5 – 1.6	50 – 70	500 – 900
Jute	1.3 – 1.5	20 – 55	200 – 500
Sisal	1.2 – 1.4	9 – 22	100 – 800
Cotton	1.5 – 1.6	6 – 10	300 – 600
Softwood	1.2 – 1.4	10 – 50	100 – 170
Cellulose fibres	1.5	50	800
Cellulose microfibrils	1.64	120	15,000 (max.)
Glass fibres	2.6	70	3,500
Carbon fibres	1.8	800	2,500

* Apparent density (i.e. including the fiber lumen) Source: Madisen 2004

Moreover, non-wooden fibers contain less lignin compare to wood fiber which has been shown that the less content of lignin reduce effects of photo-degradation (Chaochanchaikul et al. 2012).

Due to the presence of natural fiber, WPC become biodegradable. In other words, it can be attacked by wood destroying organisms, and can suffer degradation of mechanical properties, as well as experience color change after exposure to the outdoor environment (Morris and Cooper 1998; Rangaraj and Smith 2000; Silva et al. 2001; Verhey et al. 2001; Pendleton et al. 2002; Dawson-Andoh et al. 2004; Schirp and Wolcott 2005; Morrell et al. 2006; Manning and Ascherl 2007). Therefore it might seem as disadvantages for customers since it plays a negative role in the lifetime of the product as WPC are entering into the building and construction industries (Wolcott and Smith 2005). Durability issues especially degradation and structural failure of WPC are of concern for manufactures because of warranty claims (Klyosov 2007). But from an environmental point of view, using biodegradable polymers can lead to increase the recyclability of materials - although their use as fuel might be more satisfactory by some criteria (Klyosov 2007).

Another disadvantage of this product is due to weathering. As mentioned before, adding wood fibers and natural fibers as reinforcements in plastic remarkably increased mechanical properties such as tensile, flexural and compression strength compared with neat plastics (Abu-Sharkh and Hamid 2004; Bras et al. 2010). However, weathering which caused these products to discolor also caused severe loss in mechanical properties after UV exposure and water spray. For instance, research showed 30-40% loss in the bending strength and 40-60% in the ultimate strain after aging (Klyosov 2007). However, different reports have been published in this case. For instance, the mechanical properties of different WPC made from various polymers (PVC, PP, LDPE) were examined during a weathering and all composites showed decreased in mechanical properties (Parvatareddy et al. 1995). Nevertheless, another study showed that although composite samples exhibited greater discoloration than unfilled PVC samples, they retained all their original strength and stiffness properties even after 2600 hours of cyclic UV irradiation/condensation exposures (Matuana and Kamdem 2002). In fact in such studies, the different factors which can affect mechanical loss should be taken into account. Among these factors, we can mention the characteristics of additives and lignocellulosic materials used as reinforcement. Neagu et al. (2006) investigated quantitatively the influence of the kappa number (lignin content of pulp) on the stiffness of softwood Kraft and prehydrolyzed Kraft fibers, and the influence of different mechanical and chemical pulping processes on the reinforcing efficiency of the fibers. They concluded that the unbleached fibers are more suitable than bleached fibers for use as stiffening reinforcement. An apparent correlation between lignin

content and fiber longitudinal Young's modulus was observed, and an optimal lignin content range at which fiber stiffness attains a maximum was identified for softwood Kraft fibers (Neagu et al. 2006). In a similar study where the effect of additives and different reinforcements were surveyed, a little higher modulus but lower tensile strength and impact strength were obtained for the Recycled High Density PolyEthylene (RHDPE)/bagasse composites without coupling agents, compared to the RHDPE/pine system (Taib et al. 2010). Thus, there is important to know the characteristic and initial properties of reinforcement fibers, because they can have high effect on drop of mechanical or other properties of WPC due to weathering.

Bagasse, its market and potential as a reinforcement in composites

Sugarcane bagasse (or bagasse) is the fibrous residual material of the sugarcane stems left after the crushing and extraction process from sugar mills, which normally accounts for 20–24% of the cane. Sugarcane is one of the most important and abundant agro fiber resources with a worldwide annual production of 1170 million metric tons which has been reported in 2005 (FAO, 2006) and increase in production then after. Sugarcane grows well in hot and humid climate with the best height for optimum growth of 500m above sea level. Its original homeland is in Southeast Asia (India, Bangladesh, and China). Around 5–10% of paper production worldwide is produced from agricultural crops, valuing agricultural paper production between \$5 and \$10 billion (Rainey 2009). One of the most notable of these productions is from bagasse. Paper production is the second largest revenue stream from bagasse, after electricity cogeneration. As the main sources of sugarcane fibers, bagasse usually consists of rind, vascular bundles, and pith (the parenchyma). Fiber from bagasse are mainly constituted by cellulose, a glucose-polymer with relatively high modulus, found as fibrillar component of most plant natural composites (wood, sugarcane straw and bagasse) in association with lignin (Pandey et al. 2000; Alonso et al. 2007). Sugarcane stems consist of internodes, nodes, lateral buds, and leaf blades and sheaths. On the cross section of each stem, the outer portion mainly contains cortex or rind, whereas a large mass of storage tissue (parenchyma, mainly for sucrose storage) is the primary part of the internal portion. The sucrose content in the parenchyma (or pith) is as high as 14%, but the rind part contains relatively low sucrose. In the rind part, cellulose fibers account for 50%, while lignin and hemicellulose are 18 and 30%, respectively. In general, bagasse contains cellulose (46.0%), hemicellulose (24.5%), lignin (19.95%), fat and waxes (3.5%), ash (2.4%), silica (2.0%) and other elements (1.7%) (Sene et al. 2002). Since bagasse is a by-product of the sugar cane industry, the quantity of production in each country is in line with the quantity of sugarcane produced. For each 10 tons of sugarcane crushed, a sugar factory produces nearly 3 tons of wet bagasse. Bagasse fibers have properties similar to hardwood fibers such as length, hemicelluloses structure that mainly consist of pentoses (mainly xylose and arabinose sugars), and lignin nature which consists mainly of syringyl–guaiacyl units (Hans and Rowell 1997). Dimensions of bagasse fibers are on average of 1.2 mm length and 15 μ m width, yielding an aspect ratio (L/D) of 80. It is estimated that the output of bagasse fibers are 75 million metric tons worldwide per year (Bras et al. 2010).

As early as in the 1950s, bagasse has been extensively used as an industrial raw material. In general, bagasse can be used for cellulose, plastics, fermentation products, cane wax, paper and pulps, insulating board, particleboard, filter mud or cake as a field fertilizer, and sucrose and sucrose-based organic products. However, most of bagasse is burned as a fuel in sugar mills. Since the 1990s, more attention has been paid to the value-added applications of sugarcane fibers in biobased composites. In China and Pakistan small quantities of bagasse are employed by the particleboard industry (Berns and Caesar 1999), as well as in Cuba, Argentina, and Venezuela. Also sugarcane is an important agricultural crop in the Southern United States. It is estimated that the US sugar industry mills over 35 million tons of green cane each year to produce sugar and related products.

Works on the use of sugarcane bagasse clearly show the potentials, and also some disadvantages of these materials (McLaughlin 1980; Monteiro et al. 1998; Patil et al. 2000; Stael et al. 2000; Stael et al. 2001; Stael et al. 2001; Sousa et al. 2004). Using agricultural crops (non-wooden fibers) rather than wood has advantages like: reducing deforestation, requires fewer energy to collect (compared to harvesting of wood chips, as the fiber has already been transported to the factory for extracting the sugar), ease with chemical pulping, inquiry of less bleaching chemicals (since they have less lignin content compared to wood, it is easier to achieve a bright pulp or white sheet of paper), and consequently, bagasse mills tend to be smaller than wood-based mills.

At the beginning of this century agrobusiness is turning out to be one of the main important sources for the sustainable development of mankind. In this context, lignocellulosic reinforced resin matrix composites tend to share a relevant position among composite materials. These new generations of composite materials composed of lignocellulosic materials with thermoplastics have several benefits as mentioned before: low cost, low density, high toughness, acceptable specific strength properties, enhanced energy recovery and biodegradability (Mitra et al. 1998; Rana and Mandal 1998; Bledzki and Gassan 1999).

Nowadays, bagasse also is used in laboratories as a new agricultural residue for obtaining bio-nanoparticles (Bras et al. 2010). In the USDA Forest Products Laboratory (FPL, Madison, Wisconsin), many efforts have been made to combine wood and non-wood plant fibers (e.g. bagasse, kenaf, jute, and hemp) with thermoplastic resins to manufacture natural fiber/polymer composites by the non-woven process. Rowell and Keany (1991) studied the fabrication of bagasse board using acetylated bagasse fiber (Rowell and Keany 1991). So far, a number of research articles on sugarcane bagasse-based composites as value-added products have been published worldwide. Collier et al. investigated the potentiality and feasibility of using bagasse fiber as geotextile products (Collier et al. 1995). Lu et al. (2006) used a melt blending process to manufacture sugarcane fiber/HDPE composites. They investigated the effects of polymer melt index and fiber dimension and distribution on mechanical properties of the resultant composites. The fiber characteristics (i.e. the fiber type, morphology, and dimension) and polymer melt flow index (MFI) significantly affected mechanical properties of sugarcane fiber/HDPE composites, and HDPE resins with a low MFI value presented high tensile and impact strengths (Lu et al. 2006). Other researches showed that an increase of the bagasse content had a positive effect only on bending elastic modulus (MOE). On the other hand, a negative, statistically significant influence on modulus of rupture (MOR) was evidenced (Fuentes Talavera et al. 2007). Raj and Kokta (1991) used PE as a binding material to improve the mechanical properties and dimensional stabilities of steam exploded bagasse composites. However from the polymer aspect, it has been indicated that presence of bagasse whiskers in polymer matrix resulted in an increase in moisture sorption of rubber films up to 5% whiskers loading, nevertheless at higher whiskers' loading the moisture sorption tended to decrease. Also barrier properties to water vapor decreased on increasing cellulose whiskers up to 7.5% whiskers loadings, and then increased with further increase in whiskers loading. In addition, presence of cellulose whiskers increased the rate of degradation of rubber in soil (Bras et al. 2010). The results obtained from researches enable the selection of the best combination of bagasse origin, size, and molding pressure in WPC (Sousa et al. 2004).

2.1.4. WPC ADDITIVES

Many chemicals are used in WPC for different purpose. For example chemicals called lubricant is added in WPC for obtaining better surface quality. For WPC, the incompatibility between lignocelluloses fibers and thermoplastics, responsible for most of mechanical properties of the resulting product, is related to differences in polarity. Indeed, high content of hydroxyl (OH) groups gives hydrophilic nature to lignocelluloses (wood and wood polymers – cellulose, hemicelluloses, or lignin) and high polarity. On the contrary, thermoplastics matrix (polyethylene, polypropylene, or polyvinyl chloride) commonly have low polarity. Thus, in order

to obtain a composite based on non-polar thermoplastics with competitive final properties, it is necessary to achieve a good compatibility between filler and matrix. Generally, this is possible by means of filler surface modification (Hon and Ou 1989; Clemons et al. 1992; Gauthier et al. 1998; Marcovich et al. 2001; Iwamoto and Itoh 2005; Nenkova et al. 2006) or by adding chemical like coupling agents.

For chemical modification, the esterification of the lignocellulosic fibers with maleic anhydride has been examined (Clemons et al. 1992; Mishra and Naik 1998; Iwamoto and Itoh 2005; Nenkova et al. 2006). Delignification can also be considered as a filler surface modification, since by removing lignin, more OH groups will be available to take part in bonding. Another solution is using additives as coupling agent which nowadays is very common in industry. Anhydrides such as maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PHA) are popular coupling agents in WPC (Bodîrlă et al. 2009). Maleic anhydride polypropylene (MAPP) appears to be the most common choice as chemical additives for good compatibility between filler and matrix (Sombatsompop et al. 2005). The maleic anhydride present in the MAPP provides polar interactions such as acid-base interactions and can also covalently link to the hydroxyl groups on the lignocellulosic fiber. Coupling agents play a very important role in improving compatibility and bonding strength between polar wood (lignocellulosic) fibers and non-polar thermoplastics in WPC (Anonymous 1999). Mechanical analyses have illustrated improved impact strength, breaking strength and tensile modulus for blends containing PP and low density poly-ethylene (LDPE) with 1% maleic anhydride (Douglas et al. 2004). So mostly it has been used in 2% of total dry weight of the materials. Thus, with these explanations it can be assumed that lignin removal which rise free accessible OH of cellulose for connection, can increase the efficiency of coupling agent and result in increase of mechanical properties.

Also for obtaining better photo-stability or improving other properties of WPC, variety of additives have been used. However, these additives could not completely be efficient and to some extent have failed. For instance, lubricants, pesticides, ultraviolet (UV) absorbers, pigments and more on, which are used to improve WPC properties, have an effect but not as much as expected. The additives used in WPC, typically, are used only in very small quantities, but all together they constitute around 5% to 6% of the weight of the mix (Klyosov 2007).

One example is the additives for reducing the photo-degradation in WPC. Investigation of five HALS (Hindered Amine Light Stabilizer) (low, medium, and high molecular weight diester, and tertiary and secondary amine triazine) and combinations of HALS and UVA on the color changes of HDPE-based WPC indicated that the molecular weight of diester HALS played an important role in the color changes of WPC (Muasher and Sain 2006). It has also been expressed that low molecular weight diester HALS showed high effectiveness in the initial stage due to their fast diffusion to the surface but alternatively, low effectiveness with increased exposure time due to their loss by surface evaporation (Muasher and Sain 2006).

In addition to UV irradiation, the effect of water absorption also should be considered as it can have negative effect on mechanical properties and increase the effect of weathering. Each additive can have different effects on water absorption. There have been several efforts to treat the composites to reduce the water absorption by means of additives or chemical treatments. These efforts involve chemical modification(s) of wood fiber, for example with acetic anhydride which will results in tremendous improvements in moisture resistance (Rowell 1997), but requires pretreatment of the wood fiber, toxic catalysts and it is too expensive; so in this case using additives like a coupling agent which is cost effective can be reasonable, but it is not as efficient as it should be (Panthapulakkal et al. 2006).

2.1.5. MAIN FACTORS OF WPC PROPERTIES

In addition to melting temperature of polymer, the hydrophilic nature of wood fillers depending on moisture content and temperature also influences the physical and mechanical properties of WPC (Marcovich et al. 1998; Lin et al. 2002). Beside biodegradability of WPC which will explain later, other properties of the WPC like thermal stability, degree of color change and lightness which increase by weathering (Fabiya and McDonald 2010), and water absorption (Najafi et al. 2006) are species dependent. It means that the filler properties have high effect on resulted WPC properties.

2.2. History of WPC

WPC industry was born by connecting the forest products industry and plastics industry. Historically these two industries had no expertise, perspectives and scientific issues in common. In wood industry the typical methods are sawing, veneering, chipping, flaking, and gluing, while processing in plastic industry involves mainly extrusion, compression-molding, and injection-molding technologies. Window manufacturing companies were first to manufacture WPC since they had experience with both wood and plastics (Clemons 2002; Rowell 2005). The original use of WPC can be traced back to thermosetting molding compounds in the 1960s. The earliest of them was invented in the beginning of 1900s (Rowell 2005) and is still called by some “wood composites”. In 1920s, wood flour was first used as a filler. It was then that an early commercial composite composed of phenol-formaldehyde and wood flour with trade name of Bakelite was created (Rowell 2005). Afterwards, transition of adhesives from thermoset to thermoplastic polymeric materials happened. During and after this period of time, the issues which became the center of attention were the improvement of uniformity of cellulose fiber and plastic mixture, of mechanical properties, and of the compatibility of the filler with the polymer matrix by means of coupling agents.

Further improvements in properties of WPC by using plastics other than polyethylene (PE) started in 1990s. It was then that the newest history of WPC in the current understanding of this term has begun, contemporaneously with production of solid WPC consisting of 45-55% wood fiber in PE by the means of advanced environmental recycling technologies (AERT). Afterward, international market of WPC decking has grown rapidly from 2% in 1997 to 18% in 2005 (Smith and Wolcott 2006). The importance and growing potential of WPC were evident in 1991 by the advent of the international conference on wood fiber-plastic composites, a forum on the science and technology for the processing and development of these materials (Smith 2001). These examples serve to illustrate the growing level of interests in wood-plastic composites from both research and commercial standpoints (Eckert 2000).

The first important WPC application in United States was the production of flat sheet made from polypropylene (PP) with approximately 50% wood flour using extruding machine for interior automotive panelling (Schut 1999). The decking market which first appeared in 1990s (Youngquist 1995), is the largest and fastest growing WPC market (Klyosov 2007). In 1993, Andersen Corporation (Bayport, MN) began to produce wood fiber-reinforced PVC subsills for French doors. Further development led to producing windows in which wood-PVC components were used (Schut 1999). The market for WPC windows and door profiles has continued to grow. Since mid-1990s, activities in the WPC industry have increased dramatically. Although the WPC industry is still only a fraction of a percent of the total wood products industry (Smith 2001), it has made significant inroads in certain markets. However, the application of WPC in outdoor environment is still a major concern despite the progress in the processing technologies of WPC. The physical and biological degradation of the wood and polymer constituents of WPC is promoted through exposure to humidity, temperature, and UV light.

2.3. Market share for WPC around the world

2.3.1. MARKET SHARE IN NORTH AMERICA AND EUROPE

Differences exist between North America's more mature WPC market and Europe's smaller market. WPC materials as they are known today have been in production for over 30 years in Europe, in other words, Europeans were ahead of the United States in the production of wood plastic composites (Rowell 2005), but in the last few years North American's market has showed more rapid growth (Figure 2). In the U.S., the market has been dominated by rail and decking products, while in Europe more emphasis has been placed on automotive applications¹. Europe is reasonably well provided with timber, but nowadays the balance between supply and demand is being upset by rising demand in most countries (Winandy et al. 2008). One of the attractions of the WPC industry is that it can utilize wood that would otherwise often have been wasted, and can turn the waste into durable and useful products without causing any environmental complications.

The market share of WPC in total wood product consumption in Europe was estimated at far less than 1% in 2006, but annual growth rates in WPC consumption were estimated at over 10%. Other references reported growth of averaged 23% per year between 2003 and 2007, which was ten times as fast as the plastics industry as a whole in European region in that period (Satterthwaite and Nash 2008).

European WPC production was estimated at approximately 100,000 tons in 2007. The leading countries were Germany, Austria, Belgium, Netherlands and Scandinavia (Wahl 2008). The biggest sector of profiles and tubes were in European market for plastic use intended 56% for windows and 34% for construction purposes. The advantages of window profiles made of wood-plastic instead of plastics are the low cost, good stiffness and recyclability. The disadvantages are that compatibilisers (additives) raise the costs.

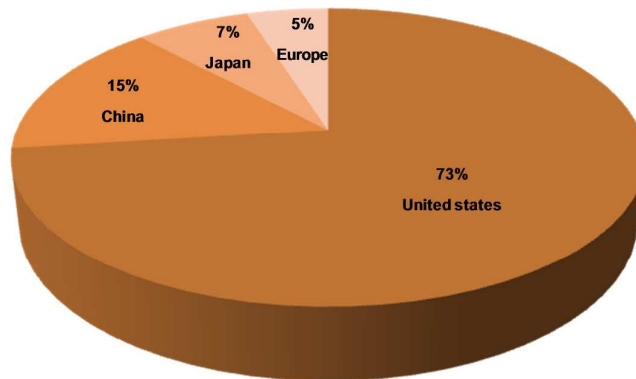


Figure 2- Global manufacturers of wood plastic composites.

Major applications for WPC composites on a weight basis can be summarized as follows: building products, 70%; other (including marine uses, infrastructure) 13%; industrial consumer, 10%; and automotive, 7% (Eckert 2000). However, from beginning growth in WPC market has been mainly due to a very high demand for decking (Figure 3), the market for which is ten times as great in North America as it is in Europe. But other applications are now becoming common in North America as well; most of them are related to the construction industry (Hackwell-Group 2006). Smith and Wolcott (2006) attributed the growth of WPC decking to four factors; first, a

¹ Wood Plastic Composites: Building Supply and Demand, 2010, AccuVal Associates, Inc, <http://www.accuval.net/>.

favorable value proposition in terms of life-cycle cost; second, it is perceived environmentally benign when compared to chemically treated solid wood products, third, the general acceptance of new wood composite building material solutions; and forth, the highly effective combination of push-pull marketing communications employed by WPC manufacturers and their distribution partners (Fabiya 2007). The European market also has great potential, but is developing differently from that in North America. WPC are rapidly expanding in many countries of Europe for applications different from decking (García et al. 2009). While decking accounts for over half of WPC volumes consumed in North America, WPC end-uses in Europe are more varied and there is no single dominating end-use application for WPC (Wahl 2008).

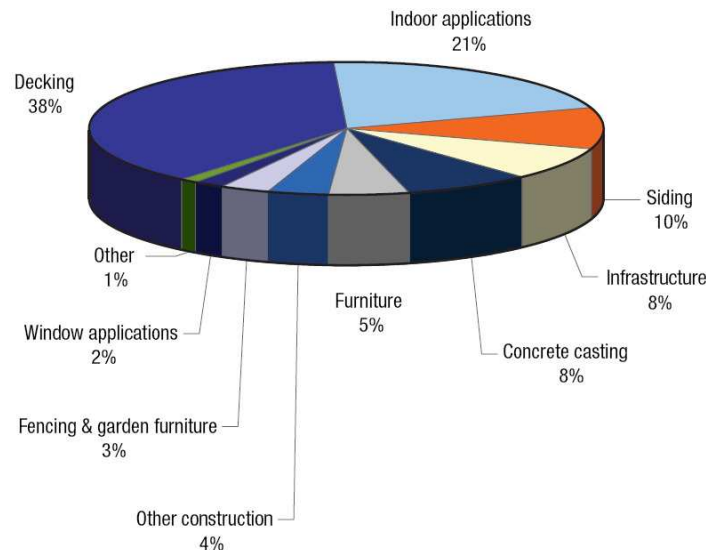


Figure 3- WPC application in Europe excluding automotive part 2004, Source: Hackwell Group (Hackwell-Group 2006).

Nevertheless, in 2007, a quality assurance label for WPC decking was introduced in Europe, to establish standardized performance values. Eight companies from Belgium, Germany and the Netherlands have applied to have their WPC products certified under the new quality label (Eder et al. 2007). There is also considerable interest in wood-plastics composites in other parts of the world, including South America, China, India, Japan, Malaysia, South Africa (Eder et al. 2007), and of course Iran. In China and other parts of Asia, wood plastic composites are beginning to experience considerable growth along with a wider variety of product offerings including pallets, doors, and architectural moldings.

However, surveys have shown that there are still countries like Austria and Germany where consumers preferring wood materials to WPC for decking, even considering maintenance and product lifetime (Eder et al. 2007).

2.3.2. MARKET SHARE IN IRAN

In Iran which has 7.3 million hectares of forests, forestry production industry is fragment and is facing numbers of challenges that hinder success in domestic and international markets, including lack of access to raw materials with quality, problems with production quality control, and access to markets. Sixteen percent of the biggest forests in Iran called Hyrcanian forests are located in the North, bordering the Caspian coastal plain and on the northern slopes of the Alborz mountain range which are protected from harvesting. Harvesting capacity for Hyrcanian forests are regulated by the government. The Forestry and Range Organization (FARO), under the Ministry of Agriculture, has responsibility for forestry in Iran, prepares and submits forestry

plans and projects to the Ministry of Agriculture for approval (Arian et al. 2007). Because of severe climatic conditions and forest degradation, forests in other parts of Iran are not exploited for industrial wood production. Ultimately, around 60 percent of Iran is arid desert or semi-desert. As a result of limited production of solid wood in Iran and high domestic demand, wood related factories face shortage of raw materials. Yet, in recent decade over a thirty factories are established for WPC production, some of which are built next to the wood industries manufacturers in order to use their wastes. However, most of them found new ways to overcome the shortage of raw materials and potential ways to increase raw materials supply by expanding domestic plantations and using nontraditional residuals; such as bagasse (sugar cane waste) and rice hull. Thus, in countries like Iran, the use of WPC, based on agricultural by-products, increase yearly. According to Iranian Sugar Factories Syndicate² the mills producing sugar from sugar beets and sugar cane spread as indicate in the Figure 4.

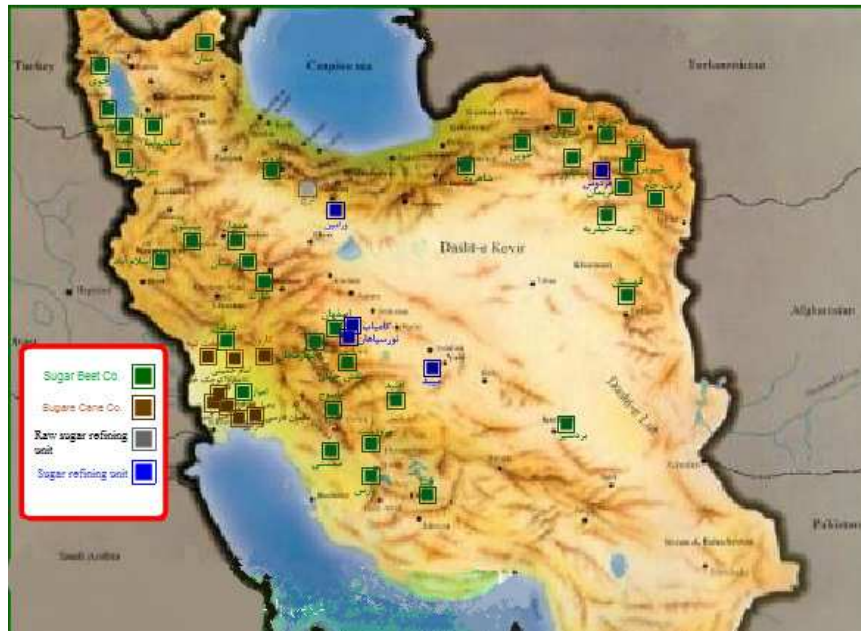


Figure 4- The sugar mills spread based on the source of sugar production.

Overall, sugar cane is grown in southwest of Iran and the total sugar production from cane increase yearly (Figure 5). It means that more land used by farmers to plant sugar canes, more sugar cane production implying more bagasse production. This bagasse is mostly used for pulp industry and small part of that use for WPC industry.

² www.isfs.ir/amartakhassosi1.htm

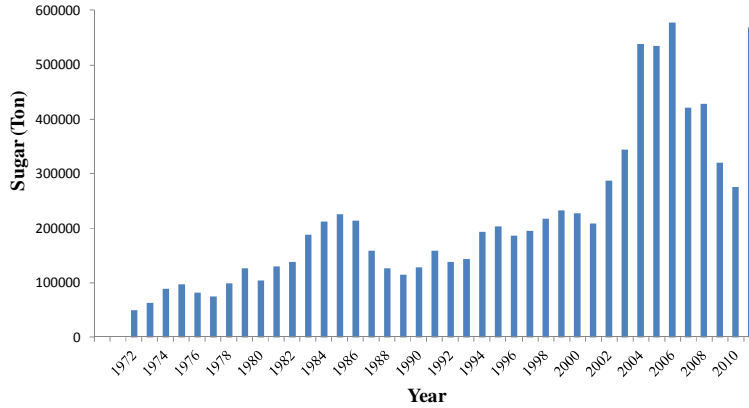


Figure 5- Increase of sugar production from sugar cane in Iran.

2.3.3. MAIN CHALLENGE FOR DEVELOPING THE WPC MARKET

Besides challenge of raw materials which is very important for final price, in order for WPC products to keep their market and to continue to grow, customer's acceptance is one of the major factors. Kadant Composites Company (USA) received 466 warranty claims relating to its GeoDeck products (decking products) manufactured in 2002 and 2003 due to WPC crumbling, degradation, and board failure (Fabiyyi 2007). Therefore, a path to find permanent solution to improve WPC' quality should be sought. Meanwhile, there have been several groups formed around world with the purpose of studying the WPC to improve its properties. The wood materials and engineering laboratory at Washington State University was one of that groups which has directed an interdisciplinary and inter-institutional research program for the development of HDPE- and PVC-wood composite materials to be used in waterfront structures (Smith 2001).

2.4. WPC Degradation

Due to the presence of both wood and plastic matrix, WPC materials are subject to several possible degradation processes (Schirp et al. 2008). Major factors in WPC degradation are water absorption, biological decay, and UV radiation. Combination of all these factors called weathering. This study mostly concentrates on abiotic degradation caused by UV radiation called photo-degradation beside water spray. Also intensity of biodegradation followed by weathering is noted in this study.

2.4.1. BIOTIC DEGRADATION

While there are evidences that WPC products can be attacked by decay fungi, many researcher emphasized on the advantages of them over wood which relates to their good dimensional stability in lifetime, i.e. lower water uptake, and durability against fungi and insects (Wang and Morrell 2004; Schut 2005; Morrell et al. 2006). Nevertheless there are strong indicators that show moisture uptake happened over time in WPC products, but far more slowly than in solid wood (Naghypour 1996; Morris and Cooper 1998; Mankowski and Morrell 2000; Rowell et al. 2000; Silva et al. 2001; Ibach and Clemons 2002; Pendleton et al. 2002; Verhey and Laks 2002).

In fact, variety of biological agents can attack wood and plastic, either as a food source (primarily the wood) or as shelter (both wood and plastic). The most common biodegradable agents associated with WPC are fungi, insects, and marine borers. Other organisms that colonize the

surface without degrading the material, such as lichens, molds and algae might also be considered due to the influence they have on the surface appearance that reduces product quality (Klyosov 2007). Fungi, molds, bacteria and algae are the groups of microorganisms which can stain, deface, and degrade wood, plastic, and WPC materials. Bacteria often cause staining of surface by their metabolic products. Microorganisms damage to composites can result from consumption of nutrition content of material and, thereby, reducing mechanical properties and creating discoloration. Other effect like production of extracellular metabolites and pigments, like stain the surface of the material with colored spots which varying from green to red to black also appears. In the latter case, they are not necessarily physically damaging the composite or cause its degradation, but they spoil the product and make it look rather unaesthetic.

Typically for WPC, the word resistance is not clearly defined. In other words, microbial degradation of WPC is whether deterioration of the material, while mold growing at the surface does not mean actual deterioration but both of molds and fungi introduce some changes to the materials properties or visual factors which are not desirable. The composite material in the case of mold growth is still intact, as well as the original material. Mold can be removed by pressure washing from the surface of a composite material. Klyosov (2007) classified microbial effects on wood-plastic composites as follow:

- Spots on the surface of deck boards caused by mold which does not degrade the material and remains structurally untouched. Mold feeds itself by dust, airborne particles such as pollen, etc ;
- Mold assist with other fungi which insignificantly consume some ingredients of the composite formulation, using them as nutrients, vitamins, etc ;
- Specifically and rapidly attack of fungi on wood/cellulose fiber which in turn causes diminishing of mechanical properties of the composites.

The latest is the most important that will be focused in current study.

Fungal attack

It has been well indicated that the presence of molds can be taken as a signal of a potential fungal decay. Wood decay fungi can attach to the surface, and then secrete a whole family of cellulolytic enzymes which will eventually hydrolyze cellulose fiber to glucose and then glucose is consumed by the fungus. The fungus grows, proliferates into pores and other voids of the composite material, and makes more enzymes to attack cellulose, until a significant part of the cellulose is digested and utilized by the fungus. This obviously diminishes the mechanical properties of the composite material. Not only surface of the composite material can be largely covered by the fungi, but also actual “mushrooms” grown on the cellulose can appear (Klyosov 2007).

Evidence for the presence of fungal decay and discoloration on WPC decking materials in service was first presented by Morris and Cooper (1998). For fungal growth on wood and WPC, there are some necessary factors: fungi are aerobic microorganisms that need oxygen for their growth. In case of temperature they are particularly active from about 30°C to about 40°C. They need water for their activities, and are active at 85% air humidity and higher (Basidiomycetes wood decay fungi, like Coniophora and Coriolus need only 20 to 22% of moisture content in the wood, but Molds need a higher humidity) and they prefer slightly acidic conditions, and are typically disseminated by spores (except for soft rots which are inferior fungi and do not produce spore, only mycelium). Because WPC absorb less moisture and do so more slowly than solid wood, they have better fungal resistance and dimensional stability when exposed to moisture. Although unfilled plastics alone have little moisture absorption, good resistance to fungal attack, and dimensional stability when exposed to moisture, it expands when heated. Adding wood

decreases thermal expansion of plastic, however increase the moisture absorption and biodegradation. Thus, it becomes susceptible to fungal attack.

Involving factors on WPC fungal resistance

In general, the durability performance of wood or natural fiber-reinforced thermoplastic composites depends on the material composition (Falk et al. 2000; Abu-Sharkh and Hamid 2004; Stark and Matuana 2006), exposure conditions (Schut 2005; Stark and Matuana 2006), and processing methods (Stark et al. 2004; Stark 2006). In fact, the most effective factor is the ratio of wood/polymer. Higher content of wood and moisture content make microbial degradation faster. In this regard, Rowell et al (2000) showed that the presence of cellulose whiskers increased the rate of degradation of rubber in soil (Rowell et al. 2000). Similar research showed composites containing a 70 wood /30 HDPE blend were more susceptible to fungal attack, whereas two different 50 wood /50 HDPE composites experienced little or no attack in the same experimental conditions (Mankowski and Morrell 2000). In this regards, it was shown that wood/polypropylene composites with 30, 40, 50, 60, and 70% wood content (with fiber dimension of 20 mesh ponderosa pine particles), lost weight under brown-rot fungus, *Gloeophyllum trabeum*, attack, for 12 weeks in the following order: 0.2, 2.4, 3.6, 4.4, and 9.7%, respectively, while control pine sample lost 17.2% of its weight.

Moreover, inherent characteristics of the wood filler can affect the properties of wood plastic composites especially durability of the products (Kim et al. 2008). The use of durable wood species could result in the improvement of durability performance of WPC products. Results of such study showed that WPC made with Eastern Red Cedar and Osage Orange (both very stable durable timbers) had low moisture sorption characteristics, lower levels of fungal decay, and increased resistance to mold compared with composites made from other species (Kim et al. 2008). Investigating the WPC made with extracted wood flour demonstrated that extracted for different wood flour resulted in lower mechanical properties, higher moisture sorption, thickness swelling and also higher levels of fungal decay in comparison with unextracted WPC with the exception of pine WPC (Kim et al. 2009) because it contains naturally very few (almost none) extractives. Besides that, studying microbial degradation of 50% wood/ 50% plastic in WPC by brown-rot and white-rot fungi (*G. trabeum* and *T. versicolor*, respectively), showed that the decay was more pronounced as the wood particle size increased (Verhey and Laks 2002).

Also manufacture methods can affect the sensibility of fungal decay. Indeed, extruded composite material samples are much more sensitive to soil block test compared to compression-molded and injection-molded samples. This can be due to the polymer rich surface produced through compression-molded and injection-molded. After 12 weeks, the respective samples lost 6, 2, and 3% of their weight, but the same samples which have been boiled showed loss of 23, 2.5, and 0.5% of their weight, respectively (Clemons and Ibach 2002).

Increasing WPC fungal resistance

When wood plastic composites (WPC) first emerged on the market, they were touted as impervious to biological attack because the plastic was presumed to completely encapsulate the wood particles, thereby protecting them from both moisture and fungal attack. However, an array of subsequent studies have clearly illustrated that the wood in many WPC remains susceptible to degradation (Khavkine et al. 2000; Laks et al. 2000; Mankowski and Morrell 2000; Silva et al. 2001; Verhey et al. 2001; Pendleton et al. 2002; Silva Guzman 2003; Ibach et al. 2005; Lopez et al. 2005; Schirp and Wolcott 2005; Schauwecker et al. 2006; Fabiyi et al. 2009). Although improvements have been made in product formulations designed to increase durability, it is clear that these materials are not completely immune to deterioration.

There is a wide variety of biocides used by WPC producers. Some manufacturers use some additives such as zinc borate to improve fungal resistance for composites with high wood

contents. However, some of those biocides are totally ineffective in end-use situations or effective but only toward certain microbial species. Being leach out of the composite surface, or on the contrary, being barely water-soluble and locked-in in the composite are two main reasons for decrease the efficiency of these materials (Klyosov 2007).

For slowing down or even eliminating microbial growth in WPC, two options exist, one is the use of minerals as fillers in a relatively high amount (20–60%) to shield physically, protecting cellulose fibers from cellulolytic enzymes diffusing into the matrix and the other is slightly alkaline pH (7.5–9) environment which can be the result of calcium carbonate (Klyosov 2007).

To sum up, we can say that it is true that the plastic component of a WPC has the potential to envelope the dry wood particles and thus keeps the moisture away from it for the while. But eventually, water will penetrates and bio-degradation will happen (Larsson-Brelid et al. 2006) by different means (see section2.5).

Termites attack

Several insect species such as termites, beetles, and ants can damage wood or wood containing materials. By far the most important insect group, worldwide causing destruction of wood, are termites, especially, soil inhabiting and dry wood termites (Stephan and Plarre 2008). WPC are commonly resistant to termites. Although wood fibers are accessible on the surface of WPC and also form a continuing chains across WPC materials in the high percentage of wood content (more than 20 %) termites cannot get into the plastic materials. They just can slightly trim cellulose fiber at the WPC surface (Klyosov 2007). As a result, weight loss of WPC materials by termites is negligible, if any exist. This behavior is due to the largely resistance of plastic to insect attack. However, it is possible that WPCs be mined or grazed by social insects such as carpenter ants or termites, or inadvertently by adult beetles for creating galleries for rearing. While insects might be capable of obtaining some nutrition from the wood particles, substantial insect attack of WPC is rare (Morrell et al. 2009). Because of high density of most WPC, it is unlikely that social insects such as carpenter ants would attack WPC, since they tend to seek softer materials (Hansen and Klotz 2005). As confirmed by one termite field testing of WPC, “No” termite activity on any of the WPC test blocks was observed throughout a 27-month period of test. Whereas seven out of ten aspen specimens which were used as control were severely attacked by termites (Schirp et al. 2008). However, previously another study reporting termite activity after 3 years in-ground exposure in Mississippi revealed different founding (Ibach and Clemons 2004). In this report, after the first and second year of in-ground exposure, there was no reported termite attack on 50% wood flour/50%HDPE composites. After the third year, nibbles of up to 3% cross-section were reported. Thus, it can be concluded that maybe other factors contribute to make the product sensitive to termites. This is what we also tried to investigate in this research.

2.4.2. ABIOTIC DEGRADATION

Weathering

Weathering is the general term used to define the slow degradation of materials exposed outdoors. Weathering is mostly caused by the UV radiation portion of sunlight. The degradation mechanism depends on the type of material, but the cause is a combination of factors found in nature: moisture, sunlight, heat/cold, chemicals, abrasion by windblown materials, and biological agents. All natural and man-made materials undergo degradation by the weathering process (Williams 2005).

The UV and visible solar radiation that reaches the earth's surface is limited to the range between 295–800 nm. Wavelengths from 800 to about 3000 are infrared radiation. The radiation from 295–3000 nm comprises distinct ranges that affect weathering: UV radiation, visible light, and infrared radiation (IR) (Table 2). The photon energy is inversely proportional to the wavelength of the radiation. The energy of the photon will become important when we consider the photochemical reactions that this radiation can initiate.

Table 2- Percent of Total Spectral Irradiance for UV, Visible, and IR Radiation.

Radiation	Wavelength Range	% of Total Irradiance
UV radiation	295-400 nm	6.8
Visible light	400-800 nm	55.4
Infrared radiation	800-3000 nm	37.8

In order for a photochemical reaction to occur, sufficient energy to disrupt a chemical bond (bond dissociation energy) must be absorbed by some chemical moiety in the system. The absorbed energy may not result in a degrading chemical reaction, but the absorption is an essential condition. The bond dissociation energies and corresponding wavelengths having the necessary energy for breaking these bonds for several chemical moieties are listed Table 3. The energy for UV radiation at a wavelength of 295nm which constitute approximately 7% of radiation reach earth (Table 2) is about 97Kcal/mole and for 400nm is about 72Kcal/mole. Several of the chemical moieties have bond dissociation energies well above the energy of terrestrial UV radiation and therefore cannot be affected by natural UV radiation. The bond dissociation energy must be below 97kcal/mole for the chemical reaction to occur.

Table 3- Bond Dissociation Energies and Radiation Wavelength^a

Bond	Bond Dissociation Energy (Kcal/mol)	Wavelength (nm)
C-C (Aromatic)	124	231
C-H (Aromatic)	103	278
C-H (Methane)	102	280
O-H (Methanol)	100	286
C-O (Ethanol)	92	311
C-O (Methanol)	89	321
CH ₃ COO-C (Methyl ester)	86	333
C-C (Ethane)	84	340
C-Cl (Methyl chloride)	82	349
C-COCH ₃ (Acetone)	79	362
C-O (Methyl ether)	76	376
CH ₃ -SH (Thiol)	73	391
C-Br (Methyl bromide)	67	427
N-N (Hydrazine)	57	502
C-I (Methyl iodide)	53	540

^a Bond energies abstracted from Table 2 (Ranby and Rabek 1975).

Most researches on weathering are conducted in accelerated UV weathering (QUV) or xenon-arc weathering device, because long-term observation of the weathering of material (for instance WPC) outdoors is not sufficient to identify all the phenomena of interest (Wei-hong et al. 2010). Artificial weathering is shown to be a valid means of representing natural weathering and can provide the basis for the systematic investigation of the mechanisms of photo-degradation (Derbyshire et al. 1995). In this apparatus all the factors can be controlled. In such study, temperature must remains under control because elevated temperature (higher than 60°C) accelerates both ultraviolet and oxidative degradations (Zahirul Islam et al. 2011).

In these kinds of accelerated weathering devices wavelength producing from the light resource is very important. In all of early studies, the light source had UV wavelengths down to 254 nm which has energy of approximately 135 Kcal/mole. This energy is higher than the most energetic photons found at the Earth's surface and can mislead in the researches. It is difficult to relate these higher energies to the exact chemical moiety important in the degradation (Williams 2005). So, using xenon lamp with proper filter solves this problem and gives mostly the similar wavelength that can be found on natural weathering.

Wood weathering

By comparing the energy available from the photons in the UV range of the spectrum (Table 3), it is apparent that there is sufficient energy to break bonds in the chemicals that comprise wood. However, in order for a bond to break, according to the first law of photochemistry (Grotthus-Draper Principle), energy must be absorbed by some component of the wood. Additionally, a particular molecule in the wood can absorb only one quantum of radiation (Stark-Einstein Principle) (McKellar and Allen 1979). The absorbed energy puts the molecule in a higher energy (excited) state that can be dissipated through a number of paths. The most benign would be a return to the ground state through dissipation of heat. Other alternatives would involve chemical reactions.

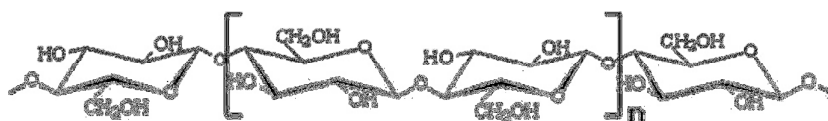
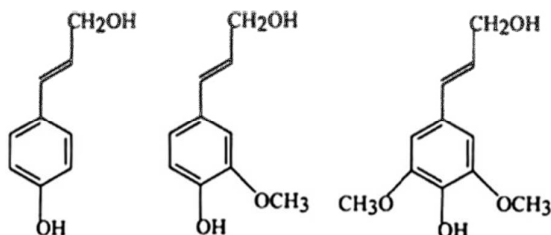
Weathering of wood is surface degradation that is initiated primarily by solar radiation, but other factors are also important and increase this effect. The color of wood is affected very rapidly by outdoor exposure. Generally, all woods in outdoor environments initially change toward a yellow to brown color due to photo-oxidation of lignin and wood extractives (Feist 1983) and then grey due to leaching of the degraded product (Feist and Hon 1984). This discoloration and yellowing of wood surfaces result from the loss of methoxyl content of lignin, photo-dissociation of carbon-carbon bonds and formation of carbonyl-based chromophoric groups such as carbonyls, carboxylic acids, quinones, and hydroperoxy radicals

The wetting and drying of wood through precipitation, diurnal and seasonal changes in relative humidity (RH), abrasion by windblown particulates, temperature changes, atmospheric pollution, oxygen, and human activities such as walking on decks, cleaning surfaces with cleaners and brighteners, sanding, and power washing all contribute to the degradation of wood surfaces which have their own influence on wood (Table 4). Nevertheless, factors mostly affect the weathering of wood are sunlight (UV light, visible light), moisture (rain, dew, water vapor), heat, and acid rain (sulfur dioxide). However, it is primarily the ultraviolet (UV) portion of the solar spectrum that initiates the process we refer to as weathering. As mentioned before, weathering is a surface phenomenon; which we can refer to as the physical (surface roughening, checking, cracking) (Hon et al. 1986; Cui et al. 2004) and the chemical (surface phenomenon, sequence of free radical reactions, breakdown of lignin, color changes)(Chang et al. 1982) degradation that happens in wood when exposed to the natural elements and in some cases acid rain which is different from what we call biodegradation (Brooks 2000). Degradation rates vary with wood species (Pastore et al. 2004; Pandey 2005). In several softwoods, UV rays do not penetrate deeply (<75 μm) and visible light penetrates up to 200 μm (Fengel and Wegener 1989). However, the depth of penetration depends on the color of the original wood and the color change during exposure.

Table 4 - Relative Effect of Various Energy Forms on Wood (Brooks 2000)

Energy Form	Relative Effect	Degree of Effect
Thermal-intense	fire	severe
Thermal-slight	darkening	slight
Light-UV and visible	large color changes, chemical degradation	severe
Mechanical	wear and tear, wind erosion, surface roughening and defiberization	slight to severe
Chemical	surface roughening, defiberization, selective leaching, color changes and strength loss	severe

Wood is a composite material consisting mainly of three major polymers: cellulose, hemicelluloses and lignin (Figure 6 and Figure 7), as well as extractives in percentages depending on the wood species. On the contrary to the other components of the fibers which have amorphous structures, the cellulose has mainly a crystalline structure beside the amorphous region. The cellulose chains are joined together into micro fibrils which are arranged into several layers.

**Figure 6- Chemical structure of cellulose.****Figure 7- Monomer constitutive of lignin (coumarylic, coniferic and synaplyic alcohol).**

Considering the chemical composition of wood, lignin is the key structure in wood photo-degradation, because only lignin absorbs in the UV-visible spectral domain (Ayadi et al. 2003; George et al. 2005; Mitsui and Tsuchikawa 2005). It means that lignin is more subjected to degradation among other constituents of the wood (Béarnais-Barbry 2001; Ayadi et al. 2003; Lundquist et al. 2003; George et al. 2005; Mitsui and Tsuchikawa 2005; Ruggiero et al. 2005). The mechanism of lignin photo-degradation is complex, involving different pathways giving the formation of radical species at the wood surface during irradiation. Free radicals and singlet oxygen are important in discoloration and deterioration reactions of wood surfaces. There have been many studies to investigate the mechanism of wood weathering, and it has been clearly shown that the absorption of UV photons results in the formation of free radicals, and that through the action of oxygen and water, the hydroperoxide is formed (Figure 8). Both the free radical and hydroperoxide can initiate series of chain scission reactions to degrade the polymeric components of wood. Despite many studies spanning several decades, the mechanism is still not well defined and can only be represented in a general way.

Research on weathering mechanisms and free radicals formation in wood was as old as 1966, when Kalnins proposed a free-radical initiation, the necessity of oxygen for weathering and

noted the decrease in lignin content (Kalnins 1966). He characterized the IR spectrum of the wood surface following irradiation and the post-irradiation reactions. He also evaluated the effect of extractives, and analyzed surface and inside cellulose and lignin contents of nine wood species. His work established a basis for subsequent studies by others. Although his results showed many of the important aspects of weathering, the light sources he used did not represent the UV light at the Earth's surface. About 85% of the energy of the lamp he used was at wavelengths below 295nm. The UV degradation process being initiated by the free radicals' formation, and presumably beginning with oxidation of phenolic hydroxyl, was suggested for the first time shortly later (Hon 1981). Chang et al. (1982), showed that the reaction with oxygen to form a hydroperoxide was an integral part of the photo degradation process. The investigation of the hydroperoxides continued, and in 1992, Hon and Feist reported differences in the hydroperoxide formation at two different UV radiation distributions (>254nm or >300nm) and found the reliance of differences in hydroperoxide formation to wood species and the cross section (tangential or radial). They attributed these differences to the difference of the wood components and lignin concentration for the various species and grain angles (Hon and Feist 1992).

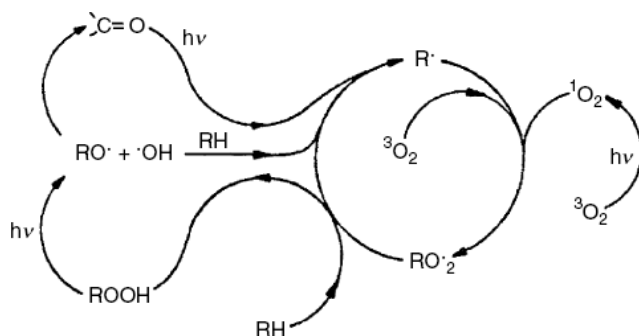


Figure 8- Mechanism of wood photo-degradation (Feist and Hon 1984).

Thus degradation process results in a decrease in methoxyl and lignin contents. It also results in an increase in acidity and carboxyl concentration of the wood substance (Hon 1979). These attitudes are attributed to the chromophoric groups. Hon and Glasser [1979] classified the potential chromophoric groups as follows: (i) chromophoric functional groups which include phenolic hydroxyl groups, double bonds, and carbonyl groups; (ii) chromophoric systems are quinones, quinone methides, and biphenyls, (iii) leucochromophoric systems are methylenequinones, phenanthrenequinones, phenylnaphthalenediones, and bimethylenequinones and (iv) intermediates, which are free radicals.

Then, as shown in Figure 8, the interactions of the free radicals with oxygen molecules form hydroperoxides followed by production of chromophoric groups, as carbonyl and carboxyl groups, also lead to chain cleavage and yellowing. One of the main radicals in wood is a long life guaiacoxyl radical, which undergoes transformation into quinoid structures (Figure 9) and is the origin of the yellowing of wood (Ayadi et al. 2003; George et al. 2005; Mitsui and Tsuchikawa 2005).

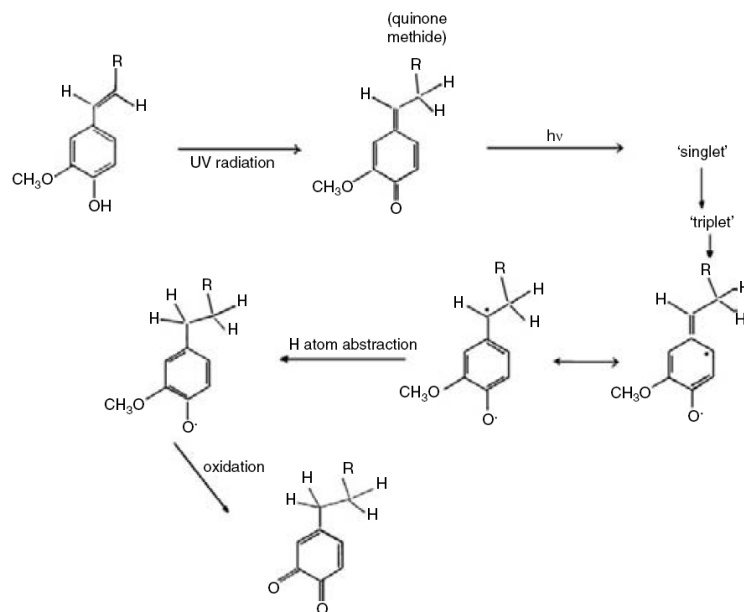


Figure 9- Lignin photo-oxidation mechanism (Anderson et al. 1991).

UV radiation at wavelengths shorter than 295nm are absorbed by the Earth's ozone layer and do not reach the surface (Williams 2005). The wavelength below 295nm can cause degradation that cannot be found in normal UV exposure and cause the different procedures of forming hydroperoxide, so as a result, it can cause a conflict between data from natural weathering and accelerated weathering (Hon and Feist 1992; Barta et al. 1998).

The UV radiation has sufficient energy to chemically degrade wood structural components and sufficient energy to cause bond dissociation of lignin moieties having α -carbonyl, biphenyl, or ring-conjugated double bond structures. For wood photo-degradation, the UV region (<380 nm) is the most effective wavelength region (Feist and Hon 1984). In fact, lignin is easily degraded by light with a wavelength below 350 nm (Brooks 2000), and causes photobleaching or whitening and decrease in methoxyl content of lignin (Table 5). Phenoxy radicals are readily produced from phenolic hydroxy groups and photo-dissociated of carbon-carbon bonds adjacent to α -carbonyl groups (Brooks 2000), while carbon-carbon bonds are so resistance and need high energy to be broken. It is because the high resistance to photo-dissociation compounds bearing benzoyl alcohol groups when photosensitizers are present becomes susceptible to photo-dissociation. α -carbonyl groups function act as photosensitizers in the photo-degradation of lignin (Brooks 2000).

Table 5- Chemical Composition of Aspen wood before and after accelerated weathering (Brooks 2000).

Component	Exposed Wood (%)	Unexposed Wood (%)
Klason Lignin	1.9	20.5
Acid-soluble Lignin	3.1	5.6
Glucose	82.2	49.8
Xylose	10.1	23.3
Mannose	1.6	4.2

Several other authors identified the main degradation process of lignin by the demethoxylation of the guaiacyl or syringyl ring. In this process phenoxy radicals, which are the key intermediates, are formed through different pathways. Existing phenols might be photo oxidized into quinones and muconic acids. The abstraction of phenol hydrogen by excited α -carbonyl or

singlet oxygen is considered as the explanation. Direct oxidation of phenols absorbing near UV light or homolysis of the β -O-4 bond in aryl glycerol-b-aryl ethers can then occur. Scission of chemical bonds can also take place leading to a production of radicals. This process is also claimed to be responsible for yellowing of wood (Mitsui and Tsuchikawa 2005).

In macroscopic scale surface checking in samples was quantified after 12, 24 and 36 weeks of exposure, while the chemical and micro-structural changes occurring immediately at weathered wood surfaces (Evans et al. 2008). In addition to the checks, in long time other processes also occur. The wood may develop slow erosion and a raised grain. Density of wood plays an important role in its weathering effects. More dense is the wood, the less it weathers and shows less visual effects (Sudiyani et al. 1999). Modification of wood surface has been used to hinder these kind of effect of photo-degradation (Evans et al. 1992). Effects of weathering have also been concerned for changes in different properties of wood composite products (plywood panels) (Cremonini and Pizzi 1999; Garay 2009) and it has been tried to control the effect of weathering on wood components by melamine layer or different coating. However, still changes and degradation could be observed.

The effect of weathering is not visual from the beginning. Thus, not having enough knowledge on the effects of weathering can lead to catastrophic failure of wood products. The degradation starts immediately after the wood is exposed to sunlight and the surface of the wood will degrade. During short exposure period (one to two weeks), however, the surface of the wood will not show any evidence for degradation, but damages have already occurred. First visual effect of weathering is the color changes, then the surface fibers loosen and erode, but these visual processes are rather slow and takes time to happen. It can take more than 100 years of weathering to decrease the thickness of a board by 5–6 mm. In the absence of biological attacks, the weathering of wood can give a beautiful bright gray patina (Williams 2005). If boards contain compression or juvenile wood, cross-grain cracking may also develop more. The boards may warp and cup, particularly in decking applications (Williams 2005).

It has been noted that the visible portion of sunlight also causes changes in wood surface, but except for minimal damage at the short wavelengths of visible light, the changes do not involve degradation of the wood structure. However, the extractives chemicals that gives wood its color such as: organic compounds of various types that may contain halogens, sulfur, and nitrogen can undergo photo-degradation reactions with lower energies than lignin and carbohydrates. So in addition to the UV radiation, visible light has sufficient energy to degrade extractives. They fade much the same as the dyes in textiles. In addition, rain will leach the water-soluble chemicals away from the wood surface.

Weathering of HDPE and based composites

Since polymers are organic materials, they undergo undesirable chemical changes during their lifetime (Fabiya 2007). Polyethylene (PE) is a widely used material for outdoor applications, so its lifetime is determined by various environmental factors. In outdoor applications of polymer, many simultaneous factors determine the degradation such as ultra-violet (UV) radiation, other solar radiation, temperature and thermal cycling, humidity, environmental pollutants, abrasion, rain, wind, and etc. Of all these factors UV is the most important cause of degradation on PEs (Hamid and Prichard 1991; Husein 2007).

HDPE consists of only C-C and C-H bonds and does not absorb light in the wavelength region longer than 190 nm (Grigoriadou et al. 2011). It is while it has been claimed that the most damaging region of wavelengths for polymer is between 280nm and 315nm (Torikai et al. 1995). This happens because polyolefins have some impurities, formed during their synthesis, like carbonyl, peroxide, hydroxyl, hydroxyperoxide, unsaturated groups, etc., which absorb the light at higher wavelength and lead to the generation of free radicals. These impurities act as

initiators for photo-degradation of HDPE and it is well known that this process can be accelerated by metal ions which can be found in catalyst residues or in applied additives (Grigoriadou et al. 2011). Several chemical reactions, accompanied by irradiation with sunlight, take place because of the presence of chromophoric groups in the polymer and the consequent ability of the polymer to absorb UV light. The UV degradation in PEs is due to combined effects of photolysis and oxidative reactions. The UV decomposition of HDPE, without stabilizers, is so fast that the lifetime of a product could be less than one year.

The mechanisms and rheological investigation of the influence of molecular structure on natural and accelerated UV degradation of polyethylene were reviewed by Ibbelwaleed (2007). UV exposure causes cross linking and dissociation of HDPE molecular chains, which at the end caused embrittlement of HDPE (Li 2000). In other words, the absorbed UV light breaks, or cleaves, the weak chemical bonds or molecular chains and this leads to shorter chains, which in turn causes the plastic material to become more brittle. In other words, during UV irradiation, macromolecular chain scission is taking place that reduces the molecular weight of the polyethylene (Angulo-Sanchez et al. 1994). However, beyond chain scission, cross linking reactions are also taking place simultaneously (Torikai et al. 1990). Cross linking accompanied by stiffening (Lewis 2004) may compete against chain scission and at the end resultant loss in molecular weight (Hamid 1998). This was also proved by Carrasco et al. (2001) who have reported an initial increase (6% in 60 days) in tensile strength, followed by a decrease (30% over the next 60 days). This was due to the structural and molecular reorganization which dominated during the first period of irradiation, whereas the chemical changes become dominant afterwards.

Researches on weathering of polyolefin materials carried out by many researchers, mostly focused on investigating properties of the polymer including melt flow, molecular weight, viscosity, and mechanical strength (Pospisil and Nespurek 1995). Many studies have shown that degradation of polymer initiates by UV radiation followed by different complex paths, starting with free radical chain initiation, propagation, chain branching and termination (Geetha et al. 1987; Gijisman and Sampers 1997; Hamid and Hussain 2000). Therefore, the degradation and stabilization of polyethylene have attracted many researchers' attentions (Raab et al. 1982; Gijisman and Sampers 1997; Tidjani 2000; Corrales et al. 2002; Mendes et al. 2003; Pock et al. 2004; Ojeda et al. 2011; Zahirul Islam et al. 2011). The degradation of HDPE, compared to LLDPE, also has been the target of many investigations (Allen et al. 2000; Gulmine et al. 2003; Zahirul Islam et al. 2011). Degradation of exposed LLDPE and HDPE geomembranes and how the structure of HDPE is important in this process were reviewed in detail (Zahirul Islam et al. 2011). Accelerated aging test for thin sheets of LLDPE and HDPE Pellets under different temperature and UV irradiation was investigated; these research resulted in evaluation of carbonyl index and density, indicate that stabilized HDPE is more resistant to photo-oxidative aging than stabilized LLDPE (Gulmine et al. 2003). It can be due to the fact that, the degradation of HDPE and PP by UV light includes surface oxidation because of the less degree of molecular branching of HDPE compare to PP, the oxidation rate is less (Wypych 1995). Therefore PP oxidizes more readily than HDPE. For the HDPE sample with zero branches the degradation is very slow and dominated by cross-linking. However, studies on rheological data suggest that the natural exposure of the linear HDPE shows low levels of cross-linking as indicated by the increase in viscosity. Accelerated weathering experiments within 250 and 500h resulted in similar or higher degrees of cross-linking in HDPE (Ibbelwaleed 2007).

In general, we can say that during degradation, polar groups are generated in the polyethylene films, as well as chain scission and cross-linking causing an increase in crystallinity, density and hardness and surface cracking at the later stages of degradation (Gulmine et al. 2003). The following HDPE properties are depending on its crystallinity: strength, modulus, density, shrinkage, creep resistance, wear resistance, and hardness. Initially lower crystallinity often offers better processability and impact resistance (Klyosov 2007). The oxidation of amorphous

area (such as outdoor exposure), partially in crystalline PE, is leads to a noticeable increase of its brittleness due to an increased fraction of the crystalline regions.

Changes in hardness of aged polymers suggest that the aging process leads to a closer packing of the material in the macroscopic scale, resulting in harder and denser products. This packing can be attributed to modifications in the amorphous regions which are more labile to oxidation with subsequent chain scission. The result is shorter molecules with an increased mobility so that secondary crystallization processes can take place. The polar groups, introduced by oxidation, can also interact through intermolecular dipolar forces or hydrogen bonds, and thus can undergo further crystallization processes as well (Gulmine et al. 2003). Therefore, increases in density and hardness with aging indicated an increase in the polymers' crystallinity and/or the occurrence of cross-linking reactions.

Weathering of Wood/Plastic Composites

Weathering of WPC can be divided under two fields. First is oxidation which caused crumbling. Second is photo-oxidation which cause color change in product due to UV irradiation and increase with water spray and temperature.

Oxidation and crumbling

Board crumbling caused by oxidation is unpleasant, and some WPC materials happened to be vulnerable to that. In fact crumbling of the WPC board is the occurrence of tiny and then developing cracks on the surface. Due to this phenomenon the surface of WPC becomes dustier and softer, and become easily to scratch (Klyosov 2007). Lack of antioxidant, decreased density, presence of metals (in pigments, lubricants, and other additives), moisture content, and unsettled stress in boards are the factors that accelerate the WPC oxidation. However, Li (2000) showed that oxidative degradation was not significant at low temperature (37 °C), but can demonstrate an impact at higher temperature than 67 °C (Li 2000). So in accelerated weathering where the temperature is fixed at 60°C we do not expect this phenomenon. Nevertheless, after accelerated weathering also small cracks (also known as crazing) were observed by SEM at the surface of weathered HDPE and PP based WPC (Fabiya 2007). It has been suggested that this crazing of WPC may be due to differential contraction (results from wetting and drying cycles) between the surface and interior sections during xenon-arc and outside weathering (Stark 2001). Surface cracks occurred at 400 h of accelerating weathering, and their frequency along with the size increased upon extended weathering. Oxidation of WPC and crumbling caused production of the OIT (Oxidative Induction Time) parameter into characterization of WPC products which is an evaluation of WPC lifetime in real situation (Klyosov 2007).

Photo-oxidation and fading

Like all materials, placement of WPC in exterior environments subjects them to weathering because the two major components of WPC, wood and synthetic polymer, are both susceptible to weathering. As we discussed for wood, the initial obvious effects of weathering are loss in aesthetic values such as general appearance including color, surface checks, cracks and/or splits. Under extreme conditions, wood may also warp or twist. Wood color may vary from light (almost bleached) to grey, reddish brown to yellow. While, it has been shown that the WPC lighten in color during weathering (Falk et al. 2000; Lundin 2001; Matuana et al. 2001; Stark and Matuana 2003; Stark and Matuana 2004; Stark et al. 2004; Bajwa and Bruce 2005; Muasher and Sain 2006; Stark 2006) and a white chalky layer appears on the surface of composite after weathering (Rowell et al. 2000). This layer was easily scraped off and was used as indicator to show changes in material weight and thickness. The amount or rate of lightening can depend on manufacturing method (Stark 2006), weathering variables, and photostabilizers added in WPC (Stark and Mueller 2008). For instance, injection-molded composites lightened more slowly

upon weathering than extruded composites, caused by the hydrophobic character of the HDPE-rich layer that formed on the surface of the composite during injection molding. This delayed some changes to the composite during weathering (Stark and Matuana 2004; Stark et al. 2004). In the same regard, Stark et al. (2004) investigated the effect of different manufacturing methods on weathering. They compared the weathering of injection-molded, extruded, and extruded then planed 50% wood/50% HDPE specimens. They showed that the manufacturing method affected the surface composition. Planed specimens had a higher wood component at the surface than the injection-molded or extruded specimens and had higher degradation during the first 1000 hours of xenon arc weathering with water spray compared to other samples. These researchs highlight the effects of fiber part in degradation process. In this regards, Rowell et al. (2000) who evaluated the effects of fiber content in an aspen/polyethylene composites (with fiber loading of 0, 30% or 60% w/w) showed that with the increase of fiber content, the weight loss increased, although after 2000 hours, and when the degraded surface was scraped from the surface, the weight loss was greater for the polyethylene with no wood fiber (Rowell et al. 2000).

In WPC, it seems that the polyethylene degradation products are not washed from the surface during weathering as the wood degradation products are. This is the reason why WPC become whiter after weathering. Moreover, it has been shown that the photo-degradation is much greater in the presence of water, and water facilitates deeper light penetration into previously inaccessible cellulose microfibrils via swelling (Hon and Chang 1986). The water spray both accelerates oxidation reactions (Hon et al. 1986) and removes natural wood extractives responsible for the coloration and clearly results in composites lightening (Stark and Matuana 2004). To understand the cause of the color characteristics in WPC made of solid wood (maple wood) and neat HDPE bars, they were separately exposed to UV radiation and water condensation (Matuana et al. 2011). It has been shown that, while UV radiation had a small influence on the discoloration of HDPE films; it significantly impacted the surface of solid wood confirming that wood components made major contribution to the color changes of WPC. Nevertheless, in other studies it has been shown that both rice hulls and wood flour increase the stability of composite materials to oxidative degradation. So, it can be said that an increasing amount of cellulose filler in WPC on one hand increases fading, and on the other hand increases stability of the material to oxidation (Ndiaye et al. 2008). In the same study, it has clearly showed that the presence of wood in polymer composites does not change the photo-oxidation pathway of the host polymer. Yet, wood absorbs in the UV- Visible domain and can contribute to the degradation initiation through the creation of radicals (Ndiaye et al. 2008). Although, it has been proved that the degradation of WPC is mainly attributed to high susceptibility of both wood fibers and polymer matrix (Lu et al. 2000), adding wood to polymer increase plastics photo-degradation. Elsewhere, it was reported that the wood in wood/polyvinyl chloride (wood/PVC) composites act as an effective chromophore and wood/PVC degraded faster than PVC (Matuana and Kamdem 2002).

In general, weathering causes changes in WPC appearance. For many WPC consumers the surface appearance is often a reason for deciding for or against a product. So the subject of WPC weathering becomes a great concern. As long as WPC are used mostly in automotive (dashboards or screen-doors of the vehicles) and construction industry (interior floor coverings, profiled for doors and windows, ornamental panels, external shutters, pavements, garage or entrance doors, and so on) which stipulate routine exposure to solar radiations, their use can be limited (Ndiaye et al. 2008). Moreover, in WPC this phenomenon is not really a surface change like wood. Changes in WPC go deeper because of the activity of free radicals. For depth of degradation, it has been shown that after 2000 hours of UV and water exposure surface of WPC samples become white and this whitening continues throughout the 10mm of specimen (Stark and Rowlands 2003). But in another study, it has been claimed that it is just restricted to the outer 0.5 mm of the surface (Rowell et al. 2000).

Looking closer to this matter for better understanding the process of weathering and reduce its effects, we should note all factors that cause these changes. The primary factor which exerts the greatest effect on weathering is the UV portion (295– 400 nm) of the solar radiation. As mentioned before it primarily affects lignin. On other hand, moisture, especially rain impacts the weathering process through removal of degraded chemical components (Filson et al. 2009). The degree of fiber degradation and erosion, leaving cracks and pits increase upon extended weathering (Fabiya et al. 2009). Gnatowski (2010) attempted to establish the relationship between laboratory exposure of samples of WPC to accelerated weathering (fluorescent lamp apparatus) and exposure in exterior conditions in different climatic zones based on the carbonyl index measurements which is the main products of photo-oxidation of polymers, to understand the most efficient factor on weathering. Short term exposure indicated that 4 months of summer exposure in Vancouver was the equivalent of approximately 400 hours of accelerated weathering using 340 nm lamps with irradiance 0.77 W/m²/nm and 8 hours of light (60°C) followed by 4 hours of condensation (50°C) cycle. A similar comparison showed that 4 months exposure in the cloudy Hawaiian winter in Hilo was equivalent to only about 200 hours of accelerated weathering and 4 months exposure in sunny California was equal to approximately 650 hours laboratory exposure (Gnatowski 2010). Therefore, major factors which constituted environment condition can vary between geographic places and change the resistance and effects of weathering on the WPC.

Wood plastic composites are less susceptible to moisture cycles than wood composites (Stark and Matuana 2006), but they are sensitive to photo and thermal degradations. During weathering of wood/HDPE composites, thermal degradation of the polyethylene component is an important factor and can be described by first order kinetics with an activation energy of 23.2 kJ/mol (Li 2000). However in accelerated weathering, temperature is fixed to avoid the thermal degradation. Although, it has been shown that WPC are less susceptible to moisture cycles than wood composites, wetting and drying of the wood components during weathering process causes the HDPE to crack which causes loss in mechanical properties. These effects cause more damage than photo-oxidation on WPC properties (Li 2000). So, most studies are trying to reduce this mechanical and chemical failure by different means. A variety of technologies are available for protecting WPC against photo-degradation.

2.5. Protection of WPC against degradation

As we mentioned, the WPC have been traditionally sold as low maintenance materials. As a result, much of the research on WPC has been dedicated to improving the mechanical performance while the protection of WPC from biodegradation and weathering has been less considered (Hristov and Vasileva 2003). In 2005, the 8th International Conference on WPC was held in Madison United States and there have underscored the need to improve the durability and resistance of WPC against degradation and weathering (Klyosov 2007).

Adding photo-stabilizers to the plastic is the most common strategy for protecting WPC from weathering (Matuana et al. 2001; Stark and Matuana 2003; Stark and Matuana 2006; Taib et al. 2010). Common types of photo-stabilizers include ultraviolet absorbers (UVAs) that protect the matrix by preferentially absorbing UV light, and hindered amine light stabilizers (HALS) that protect the matrix by interfering with the free-radical degradation mechanism. Both materials have been shown to offer some protection to WPC (Stark and Matuana 2003; Muasher and Sain 2006). Thus, many works in this field have been done to evaluate the efficiency of these materials. Stark and Matuana (2002) examined various formulations of chemicals in wood-flour/HDPE composites and HDPE. They exposed samples to 2000 hours of xenon arc weathering and studied the mechanical loss (Stark and Matuana 2002). They reported that hindered amine light stabilizers (HALS) did improve color stability and mechanical properties of

WPC to some extent. They showed that the wood/HDPE composites maintained flexural modulus of elasticity (MOE) until about 2000 hours of weathering, whereas the HDPE showed decreased MOE after 1000 hours. Before that it was claimed that rutile titanium dioxide was an effective UV stabilizer for wood/PVC composites (Matuana et al. 2001). Besides additives, many others methods exist which have been applied by different researcher to reduce the effect of weathering: like chemical treatments of fibers (Feist and Hon 1984; Patil et al. 2000; Beg and Pickering 2008; Stark and Mueller 2008) or surface covering (Stark and Matuana 2007; Matuana et al. 2011). For instance, Fabiyi et al. (2007) searched for a relationship between the chemical (wood content, carbonyl and vinyl concentrations) and color changes. From the relationships they found, they assumed that if wood is modified by using appropriate methods and chemicals, wood lignin degradation and surface oxidation could be minimized and this in return may lower total color change and lightness of WPC production (Fabiya 2007). The simplest method to protect WPC from weathering is to apply a protective coating (Gupta 2006).

2.6. Applied treatments

In current study it has been tried to use all 3 different methods (pigments as additive, delignification as chemical modification and coating as surface protection) of WPC protection to evaluate the effect of each treatments on different aspect of WPC properties and how they can protect this product alone or in combination of each other's. Hereafter, some similar works which has been done until now on same subject will be presented.

2.6.1. *USAGE OF DELIGNIFIED FIBERS IN WPC*

For exterior applications of WPC, color will change due to the photo-degradation, mostly attributed to wood which is more susceptible to photo-degradation than polymers (Fabiya 2007). The discoloration of the wood filler is due to losses in lignin and other extractives, and the generation of chromophore groups (such as carboxylic acids, carbonyls, and quinones) in the filler (Chang et al. 1982; Hon et al. 1986; Adhikary and Pang 2009). Lignin has been reported to be a good UV radiation absorber and therefore, the energy, which is transferred in the range between 200 and 400nm, initiates degradation processes (Fengel and Wegener 1989). This is because the location of most wood chromophores is in lignin (Müller et al. 2003). Hence, lignin which is a photosensitive material, accounts for 80-95% of light absorption of wood, is primarily responsible for the absorption of UV radiation by wood in first step and shows early effects of degradation caused by weathering in second step (Feist and Hon 1984). Although lignin was reduced in weathered specimens, cellulose was largely unaffected (Filson et al. 2009). As long as lignin is the most temperature-sensitive fraction of wooden materials, and is responsible for discoloration in wood, theoretically reduction of this component in cellulosic fibers could be used in improve WPC photo-stability property. Since now, most of the study focused on mixture on bleached delignified cellulose (lignin content ≈ 0) with wood flour to reduce lignin content (Chaochanchaikul et al. 2012) or used cotton as pure cellulose as reinforcement in HDPE. All these study show good results. However, bleaching is expensive and is extra process in pulping, but until now the effect of non-bleached delignified samples has not been considered.

Huge amount of wood fibers are commonly used for the production of pulp for paper and board products. The wood pulps used for papermaking are produced by chemical (alkaline or acidic) or mechanical treatment, or by combining these types of treatments to separate the fibers and to partially or completely remove lignin. Depending on the fiber separation process, the chemical composition, fiber dimensions, fiber shape, fiber strength, flexibility, and ability to adhere to other fibers or matrix material differ widely between different types of wood fibers (Neagu et al. 2006). In composites these properties are not as important as pulp since stress is transferred through the matrix. So the part of this material which cannot be used in paper production and was rejected as fine fibers can be used in WPC production. But still the surface properties of

these fibers can have influence on bonds between components in WPC which cause change in properties.

At the moment, delignified cellulose is used as commercial WPC filler in only one form (Klyosov 2007). This fiber is delignified by virtue of chemical treatment of wood pulp for papermaking applications. This composition has practically unavoidable impact on processing and properties of the resulting composite product. Klyosov (2007) explained the advantage and disadvantage of different component of wood on WPC properties in his book. He noted that the cellulose provides positive effect on mechanical and other properties of the composite material (such as decrease in coefficient of thermal expansion, etc.); however, lignin generally makes the product weaker, easily burns in the course of processing and releases CO₂ and other gaseous products, making the product density lower, and greatly accelerates fading of the WPC after outdoor exposure. Also wood extractives (terpenes, pinenes, tannins, carbonyl compounds, etc.) produce volatile organic compounds (VOC), making the product density lower. Hemicelluloses easily decompose at plastic melt temperatures, particularly at sharp changes of pressure, and form acetic acid, thereby causing significant corrosion of the equipment. Thus, pure cellulose fiber which has a relatively low density, such as 1.0–1.1 g/cm³ is more desirable. However, being penetrated with lignin and hemicelluloses, its density reaches 1.3–1.5 g/cm³ (Klyosov 2007). For normal fibers, pulping process is needed to obtain pure cellulose fiber, and this is not possible without bleaching of fibers, although it's never reach zero and always some amount of lignin remains in fibers.

In pulping process, the kappa number is used as a measurement for the lignin content of the pulp. Lignin is responsible for the brown coloration of paper, and can be removed by bleaching. It is also responsible for yellowing effect in papers. Lignin is also known to act as a matrix between fibrils in the cell wall, and its removal by bleaching can reduce stress transfer ability between the fibrils, which can lead to a reduction in the fiber stiffness (Neagu et al. 2006). Therefore, holocellulose-based WPC may be preferred for applications where color stability is of high priority (Fabiyyi et al. 2009), not when the high stiffness is required. This is the point of view of a wood scientist. Nevertheless, from a plastic manufacturer point of view, wood pulp fibers can be a useful reinforcement for increasing stiffness of plastic.

Neagu et al. (2006) found out that there is an optimum in fiber stiffness as a function of lignin content. It was also found that industrially pulped hardwood fibers have higher stiffness than the corresponding softwood fibers. These results indicate that mild defibration process should be used, that does not damage the cell wall structure so that the inherent high stiffness of the native fibers can be retained. Also, they showed that the industrially produced fibers obtained by the chemical pulping processes produce fibers that are more suitable as reinforcement than the fibers that are separated by mechanical pulping. This suggests that a gentle defibration method should be used, e.g., chemical defibration, such as the kraft process, and the process should be tuned to preserve the inherent stiffness of the cell wall.

Optimized delignification methods

The commercial pulping processes like kraft and sulphite technologies produce high quality pulp in case of mechanical properties, not high quality in case of lightness. Nevertheless, they cause high fraction in lignin and hemicelluloses (which include 50–55% of the dry weight of wood and straw) so that they can just be employed in low added value applications such as producing energy (Vila et al. 2003). Also, traditional pulping processes need bleaching in chlorine based sequences which without appropriate chemical recovery system cannot be tolerated anymore.

Organosolv pulping, based on the utilization of organic solvents as delignification agents, provides an interesting alternative to the current commercial technologies, since they lead to a solid phase enriched in cellulose and to liquors containing hemicellulose-degradation products

and lignin-degradation products free from sulphur (Xu et al. 2006). Alternative pulping processes with non-conventional chemicals, such as organic solvents, e.g., monoethanolamine (MEA), might be suited for an environmentally sound process with a closed mill system. Pulping process of wheat straw with MEA as the main delignifying agent was compared to soda and soda/anthraquinone (AQ) pulps. Results showed that MEA forms in combination with water and AQ a very selective pulping system providing effective delignification and maintaining extremely high yields (Xu et al. 2006). MEA is an organic chemical compound that is both a primary amine and a primary alcohol. Like other amines, MEA acts as a weak base/alkali. Nevertheless, MEA presents disadvantages: a toxic nature, flammable, corrosive, colorless liquid with a mild odor of ammonia.

2.6.2. COATING OF WOOD PLASTIC COMPOSITES

All researches demonstrated that degradation in exterior environments occurs in the form of color change, mechanical property loss, and loss in weight. Some of the current research demonstrates that controlling moisture absorption by the composite is key to controlling the degradation that occurs during weathering and fungal attack (Clemons and Ibach 2004; Stark 2006).

Coating is the one of the methods widely used in the wood industry, which provides protection against environmental damage such as weathering, biodegradation, and mechanical abrasion. Many researcher tried to improve the surface quality and prevent effects of weathering on the wood through coating (Roux and Wozniak 1988). For protection against photo-degradation, opaque pigmented coatings block the UV/visible light but cover the aesthetics of wood. Conversely, semi-transparent and clear coatings maintain the natural appearance of wood, but the UV/visible light transparency of the coating results in the photo-degradation of wood substrate and the result in failure of the coating adhesion due to the photo-degraded substrate (Chang and Chou 1999; Chang and Chou 2000; George et al. 2005; Chou et al. 2008). For instance, investigation of the photo-discoloration of UV-curable acrylic coatings and the underlying wood revealed that coating wood specimens with non-photo-stabilized UV-curable acrylic clear films such as aromatic urethane, aliphatic urethane, epoxy and silicone, fails to protect wood underneath the films against discoloration (Chang and Chou 1999). Both the coating films and wood specimens underneath these films experienced severe discoloration after exposure to UVA lamps at 60 °C for 12 h. Thus, photo-degradation of the interfacial layer led to flaking and peeling of the coating.

Different modifications have been applied to improve the efficiency of clear coating. The effect of photo-stabilized aliphatic or aromatic urethane-modified acrylic clear coatings have been studied on the photo-discoloration of coated wood (Chang and Chou 2000). This method was used as a mean to reduce the intensity of UV light reaching the interfacial layer without changing the natural color of coatings and wood beneath it. Incorporation of benzophenone and hydroxyphenyl benzotriazole into coating films resulted in evident screening effect on UV irradiation. They inhibited the photo-discoloration of wood coated with both aliphatic and aromatic urethane-modified acrylics (19-24 h exposure). Nevertheless not all the additives can be effective. The addition of HALS failed to reduce the discoloration of wood coated with aromatic urethane-modified acrylate containing UVA. Therefore, the efficiency of coating highly depends on its structure and its additives. In general, an aliphatic polyurethane has many used as a clear coating to prevent the weathering effects than aromatic urethane (Dawson et al. 2004). In addition with improvement in technology, nanoparticles are introduced as a novel type of low-refractive-index additives for the formation of transparent polymer powder coatings (Dietmar Holzmann et al. 2009). Besides of all technologies and additives, pretreatment of surface beneath coating can also help its efficiency. For instance, chemical methods can improve the effect of coating. In one study delignification of the wooden boards surfaces has been done before applied clear coatings to try to retard the possible photo-degradation (Dawson et al.

2008). The surface delignification was conducted chemically with a per-acetic acid treatment created a partial delignification to a depth of 2–3 mm, and, a pre-weathering treatment, which resulted in a 100 μm deep delignification zone. The coatings applied to the exposed surface of the pre-treated boards were either polyurethane or acrylic varnish. The clear-coated boards were exposed to exterior and accelerated weathering regimes for 3 years and 3000h of UV light, respectively. Pre-treated coated boards did not darken and yellowed on exposure but untreated coated boards did. Despite of decrease in photo-degradation processes on coated board surfaces, pre-treatment of coated surface has not showed significant improvement in the performance of coating over those of coated untreated control boards. Nevertheless, experience of coating application always shows promising results (Waldron and Moyer 2009)

In case of WPC, in general, while wood can be readily coated because of its polar and porous surface, difficulty arises in coating the plastic composite at the surface of WPCs due to the low surface energy of plastic. Thus, the pre-treatment of surface is the necessary step. Coating also involves solvent evaporation, which often causes environmental concerns. For wood mostly waterborne coatings are used, but solvent based coatings are applied for polymers (Gupta 2006). Furthermore, the drying stage of coating requires additional time, reducing the efficiency of the assembly line in factories. Thus new methods were developed to efficiently cover the disadvantage of coating on WPC. One of these methods is the use of co-extruder. Reason for applying this method is that the adding stabilizer or pigment into the entire composites to improve their resistance to photo-degradation is not necessary because weathering primarily occurs at the surface of a material. Also in terms of cost, it is not economically reasonable. Therefore in co-extruding, two layers were produced, on which additives are just applied on the surface layer (Matuana et al. 2011). In this method, transparent cap layer can be used to allow the beauty of the natural fiber color to show through, resulting in a higher valued, durable product. Used co-extruding method which gave WPC samples a HDPE clear cap layer enhanced resistance to water sorption initially and improves durability (Stark and Matuana 2007). The co-extruded composites and corresponding WPC without a plastic coating were tested for moisture absorption and weathering performance. During weathering, this cap layer cracked, and some delamination occurred (Stark and Matuana 2007; Stark and Matuana 2007). In addition this layer did not provide protection against changes in mechanical performance. However, composites capped with high-density polyethylene exhibited some resistance to color change. Stabilizing the cap layer provided even further protection which has already showed some good effects. For instance, in related study the nanoTiO₂ and the photo-stabilizer package was used to improve the photo-stability and showed some improvements (Stark and Matuana 2009). Also Matuana et al. (2011) examined the role of a clear HDPE cap layer coextruded onto HDPE/wood-flour composites. Co-extrusion has been also used to measure the increase of samples weight and thickness during the water soaking. It has been shown that after 10 days the increase in weight and thickness was much higher for the control samples than for those coated with a co-extruded HDPE or PP layer.

Thus we can say that another advantage of coating or cap layer is to improve the moisture resistance of WPC, thereby improving durability. This can be obtained by coating the WPC surface using polyurethane as a transparent layer. For wood clear-coating as mentioned is not recommended for use in exterior conditions since irradiation with visible and UV radiations darkens them and leads to delamination and subsequent coating failure (Dawson et al. 2008). However, for WPC there are no studies available. Recent research has suggested that adhesion of coatings to WPC can be improved by selected surface pre-treatment (Gupta 2006). Measuring the wettability of the WPC surface with contact angle showed $95\pm 5^\circ$ to $102\pm 6^\circ$ ranges which is more closer to the pure plastics (Morra et al. 1990) than to wood (75° and 46°) (Ziegler et al. 2004). This indicates that WPC have wetting characteristics similar to neat polyolefins.

Common pre-treatments on plastics include flame, cold-plasma, corona, acid etching, UV, electron beam, ion-beam, excimer laser and other reactive gas treatments (Gupta 2006). The

general system which is used often in polymer coatings involve three parts: 1) primer (thickness 25 μm) acts as an adhesion promoter, eliminates surface defect, reduces porosity and improves surface quality (Ryntz 1998); 2) basecoat applied to cover the primer 3) topcoat which is a color or clear coat for protecting the substrate from UV degradation, chemical resistance, chip mark and scratch resistances, etc (Ryntz 1998). The primer adhesion strength to WPC (168-309 N/m) which was measured by Gupta in 2006 was interim to neat polyolefins (48-126 N/m) and wood (524 N/m) (Gupta 2006). He used eight different formulations of WPC to analysis their surface properties, as well as evaluate the adhesion of a standard coating and its dependence on formulations. The study revealed the heterogeneous and low energy of the WPC surface. Furthermore, he showed that the adhesion of the primer on WPC depended on the amount of surface wood content and surface roughness.

Manufacturing method of WPCs can have a tremendous influence on surface quality, thereby influencing moisture absorption and adhesiveness. Few studies have been conducted on surface characteristics of WPC. However, it has been well shown that the injection molded and extruded composites have skin-core morphology with the high fibers content orientated perpendicular to flow direction in the core layer and less fiber content which are parallel to flow in the skin layers (Clemons et al. 1999). Injection-molded surfaces were smoother and had a plastic-rich layer that inhibited moisture penetration but also reduce the adhesiveness of the surface. In contrary, extruded surface absorbed four times as much moisture as injection-molded (Clemons and Ibach 2004) but still because of high quantity of polymer and lubricant content in surface reduce the adhesiveness (Gupta 2006). Akhtarkhavari et al (2004) found different surface fiber content, contact angle and paint adhesion properties within the two composites manufactured by cold molded and hot molded (Akhtarkhavari et al. 2004). Cold molded composites with high surface fiber content, shows low contact angle and consequently high paint adhesion followed by a better coating durability. In the same study, the effect of aging on corona treated WPC was investigated and a 20% reduction in surface tension was found within seven days of aging. A similar study was conducted, and other researchers observed an increase in surface energy with increasing fiber content in WPC formulation (Yang et al. 2005). The planed WPC composites like bulk material have a much higher wood content and showed greater primer adhesion to the extruded surface. Of course, sanding the surface of a WPC prior to coating application could be very easily implemented on an online extrusion line. Thus it is a good way to increase the surface wood content for better adhesiveness.

Weathering causes greater accessibility to hydroxyl groups which lead to greater uptake of water, and hence swelling, during the water spray step of the ageing cycle (Colom et al. 2003). This behavior causes loss in mechanical properties. Therefore, if moisture absorption and swelling decrease due to coat, maybe the effect of weathering in mechanical loss is reduced.

2.6.3. PIGMENT APPLICATION IN WPC

The most extensively used additives in WPC are pigments. Outdoors pigments are not color-stable and special treatment is required to protect their color against fading in WPC which is intended for hot dry climates. Some believe that pigments act as an anti-oxidant or play the role of a physical barrier against photo-degradation. For instance, some researches proved that adding photo-stabilizers and pigments will provide protection against discoloration caused by UV radiation (Du et al. 2010; Zhang et al. 2010). Stark and Matuana (2003) also studied the effects of an ultraviolet light absorber (UVA), a colorant, and two HALS on the photo-stabilization of HDPE-based WPC composites using a factorial design. They showed that UVA absorbed some UV radiation and the colorant was able to block the penetration of UV radiation to mask the bleaching of wood fiber. The UVA and the colorant significantly lowered the lightness upon weathering. Conversely, the two HALS did not show significant effects on lightness.

Investigation of photo-aging and stabilization of rigid PVC/Wood-Fiber composites using rutile titaniumdioxide as pigment shows light stability of these composites is quite improved with the addition of titanium dioxide rutile photoactive pigment during formulation (Matuana et al. 2001). However, coloring WPC can follow different ways with different materials. In one study, there has been shown that the effect of pigments depends on the nature of coloring. For instance, during weathering the composites containing fibers stained by using an oil-based stain lightened less than those containing natural wood fibers. Composites containing dyed fibers with water-based dye lightened more than those containing natural fibers (Stark and Mueller 2008). Nevertheless, adding pigment to the HDPE component of the composites containing natural fibers or dyed ones resulted in more color stability, while adding pigment to the HDPE component of the composites containing stained fibers only slightly improved color stability. These results showed that coloring wood flour with an oil-based stain can be a promising method to improve the color stability of WPC during weathering.

In another study action of pigments in WPC as light-blockers limiting the penetration of UV light into the matrix has been noticed: the effects of three different color inorganic pigments on the durability against photo-degradation of WF/HDPE, which were added at 2%w/w, were investigated (Du et al. 2010). Samples were weathered in QUV aging equipment for 1500 h. All samples showed significant fading and color changes in exposed areas. The results indicated that surface oxidation occurred immediately within 250h of exposure for all samples; the surface of the control composites was oxidized to a greater extent than that of the dyed composite. This suggests that adding pigments to the Wood/HDPE composites results in less weather-related damage. The optimal dosage of 2.28% pigment in the composites was suggested (Zhang et al. 2010).

Nowadays weatherable, inorganic oxide pigments are typically used to color WPC. The improved master-batches are undergoing accelerated weather testing and outdoor exposure testing in commercially produced deck boards, with promising initial results. Single-component forms of inorganic pigments are mainly produced with red, yellow, orange, and black colors. Their composition corresponds to that of the minerals hematite, goethite, lepidocrocite, and magnetite. Brown pigments usually consist of mixtures of red and/or yellow and/or black (Buxbaum and Pfaff 2005).

Although these informations are useful, but the effect of pigment on mechanical properties and their performance on weathering effects is never been studied.

2.7. Methods to evaluate weathering of WPC

In order to evaluate the effects of weathering and treatments impact on aging, different methods for WPC qualification can be envisaged which some of the common methods and some of the suggested ones will be presented in this section.

Functional groups such as carboxyl, amine, aldehyde, ketone, ester, halide, thionyl, and etc. which are present in an organic compound can be used as a good ways to determine the composition of that material. There are several spectroscopic techniques used for characterizing functional groups such as: UV-Visible, Nuclear Magnetic Resonance (NMR), and Mass Spectrometry. Infrared spectroscopy is one of these fundamental techniques.

2.7.1. FTIR SPECTROSCOPY

This technique is based on molecules vibration: bond stretching and bending (Figure 10). These stretches and bends are symmetric and asymmetric. Also bending vibrations can be either in-plane or out-of-plane vibrations. When the frequency of incoming infrared radiation matches the

frequency of the vibrations, energy is absorbed by the vibrating bonds (Silverstein et al. 1991; Urban 1993). This causes the bonds to stretch and bend a bit more. In other words, the absorption of energy increases the amplitude of the vibration but does not change its frequency. This change in amplitude can be seen in an IR spectrum as a peak at the frequency of the chemical bond that absorbed the energy. Depending upon their vicinity from the neighboring group, the position of bond vibration varies in the spectrum.

Thus, FTIR spectroscopy is a simple non-destructive method that can be used in case of WPC to assess chemical functionality of materials, such as carbonyl groups and vinyl groups (Stark and Matuana 2004; Fabiyi et al. 2006). Also it is a very good method to follow the chemical changes occurred on the surface of materials. The spectra obtained by FTIR revealed that there are bands that are formed or disappeared, while some increased or decreased on WPC surface upon longer exposure time to accelerated weathering.

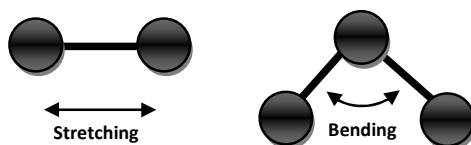


Figure 10- bond stretching and bending of Molecules

Different phase of material can be used for obtaining this kind of spectra. However, for some samples it is impossible to perform analysis in the usual absorbance mode. These samples cannot transmit light for example opaque films or surfaces of solid samples. So the Attenuated total reflection (ATR) mode of IR spectroscopy solved this problem. ATR accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (Figure 11). In this method an optically dense crystal with a high refractive index is used which an infrared beam is directly goes through it at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal to reach the sample which is in contact with the crystal. This evanescent wave protrudes only a few microns ($0.5\mu - 5\mu$) beyond the crystal surface and into the sample. In regions of the infrared spectrum where the sample absorbs energy, the evanescent wave will be attenuated or altered. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.

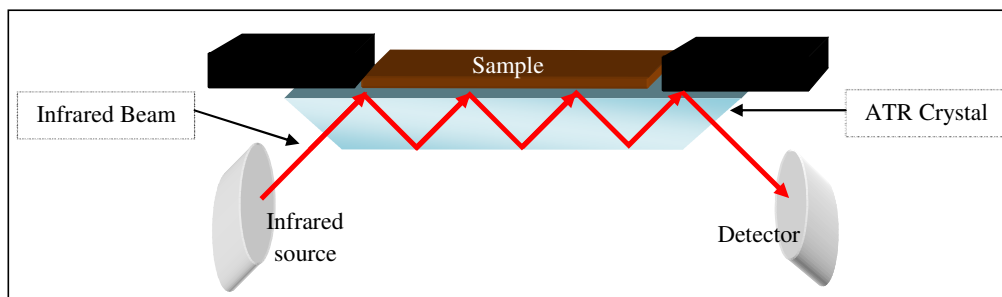


Figure 11- An attenuated total reflection (ATR-FTIR) system.

Typically, ATR crystals have refractive index values between 2.38 and 4.01 at 2000 cm^{-1} . It is assumed that the majority of solids and liquids have much lower refractive indices.

According to references, for WPC assignment of absorption bands of IR spectrum for wood part and polymer part listed in Table 6.

Table 6- Assignment of absorption bands of IR spectrum (Matuana et al. 2011).

<i>Wave number (cm⁻¹)</i>	<i>Assignment</i>
WOOD PARTICLES	
3354	-OH stretching in hydroxyl groups originating mainly from cellulose
2903	CH stretching in -CH ₂ - group
1729-1737	C=O stretching (ester carbonyl)
1714-1717	C=O stretching (acid carbonyl)
1591	Aromatic ring stretching (lignin)
1029	C-O stretch in cellulose and deformation in the primary alcohols
HDPE	
2915	CH ₂ stretching of CH ₂ , CH ₃ (asym.)
2847	CH ₂ stretching (sym.)
1713	C=O stretching (acid carbonyl)
1472	CH ₂ deformation (scissor vibration), crystalline
1462	CH ₂ deformation (scissor vibration), amorphous
1176	C-O stretch (ester)
730	CH ₂ rocking vibration, crystalline
718	CH ₂ rocking vibration, amorphous

There are many researchers using ATR-FTIR for studying chemical reactions and changes on the surface of solid wood (Matuana et al. 2001) and wood plastic composites (Torikai and Hasegawa 1999; Lu et al. 2000; Kim et al. 2004; Marcovich et al. 2005; Bodîrlă et al. 2009), since with this method chemicals can be studied on films and solid materials. This is a good method because the peaks that appear in the spectra can be assigned to functional groups present at the composite surface and its absorbance peaks indicates the chemical bonds rather than atoms. Also, it can be used as a mean to qualitatively and quantitatively investigate the mechanism of inner-polymer interaction through hydrogen bonding (Bodîrlă et al. 2009).

The change in spectra obtain by this method can be related to change in amount of chemicals on the surfaces. This technique, also, has been used often for characterizing the different components in wood. For instance, it was claimed that the spectrum of the un-weathered wood composite sample showed a dramatic increase in the absorption band intensity at 1731cm⁻¹ and 1594 cm⁻¹ (Matuana et al. 2001). These bands are characteristic of the main components of wood. Thus the very intense and sharp band appearing at 1731 cm⁻¹ has been claimed to be represent cellulose due to the stretching vibration of carbonyl groups (C=O). The two absorption bands at 1594 cm⁻¹ and 1459 cm⁻¹ are indicative of the presence of lignin, an aromatic compound, and are attributed to the C=C vibrations of the benzene ring. The absorption bands at 1150 cm⁻¹ and 1058 cm⁻¹ are assigned to the ether linkages (C-O-C) from lignin or hemicelluloses.

In addition, changes caused by weathering or treatments efficiency can be followed by this method. Weathering has the biggest influence on chemical changes. Therefore, periodic FTIR surface analysis was often used in researches to follow these chemical changes. The change appears in intensity or presence or absence of different peaks. For instance, FTIR surface analysis showed perceptible lignin loss in a short time as little as four hours and substantial lignin loss after six days in weathered wood (Evans et al. 1996).

Wood spectra obtain from this method have a strong peak at 1023cm⁻¹ as a result of C-O stretching in cellulose and C-O deformation in lignin (Faix 1992; Pandey 1999), which disappeared upon longer exposure to accelerated weathering. Also the absorption at 1730-1740 cm⁻¹ increased in intensity during the early exposure to accelerated weathering and then decreased, and the 1514 cm⁻¹ also showed decrease. In the laboratory case it has been shown that carbonyl absorption cause these two peaks (1720 and 1735 cm⁻¹) in wood exposed to UV radiation (Matuana et al. 2001) and a decrease in absorption at 1265 and 1510 cm⁻¹ (Hon 1983;

Hon and Chang 1984). The carbonyl absorption was attributed to the oxidation of cellulose and lignin. The decreased carbonyl absorption and lack of absorption at 1265 and 1510 cm^{-1} was attributed to leaching of the degraded chemicals from surface by rain as the exposure progressed. In other words, the decrease in the absorption at 1265 and 1510 cm^{-1} was attributed to loss of lignin (Anderson et al. 1991). In addition, Evans (1988) according to FTIR spectra attributed weight loss of wood specimens during weathering to lignin degradation, not to leaching of water-soluble extractives (Evans and Banks 1988).

The effects of other characteristics which affect the weathering process have been extensively studied by this method. These studies exemplify the importance of the surface composition on weathering and the importance of water in the process (Matuana and Kamdem 2002).

Similarly in case of WPC, it has been reported a rapid increase in the intensity at 1650 cm^{-1} early in the exposure period, followed by a rapid decrease in intensity of this peak which attributed to the formation of quinones and quinone methides in first step and in the next step to the leaching of these chemicals by water (Fabiya et al. 2008).

The spectral structure at 1015 and 1050 cm^{-1} and 3080-3500 cm^{-1} regions were assigned to C-O and OH groups, respectively in wood (combination of cellulose, hemicelluloses and lignin) (Faix 1992) also appear in WPC spectroscopy and has been shown that they will decrease upon extended weathering for all WPC made from different wood species (Figure 12) (Fabiya 2007). The spectra of HDPE/poplar WPC before and after weathering are compared in Figure 12 which is showing these reductions.

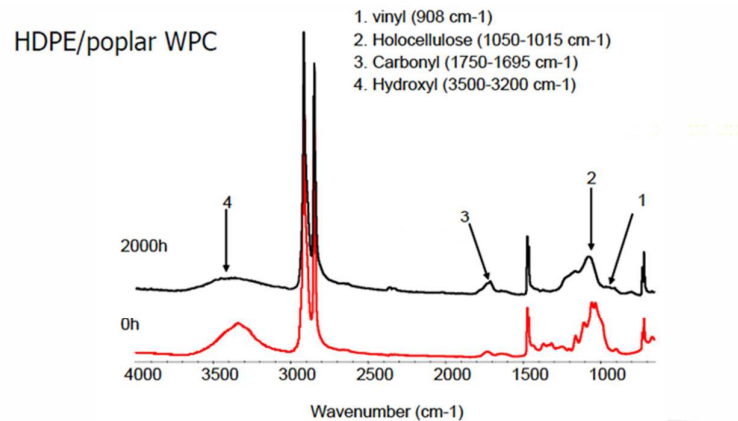


Figure 12- The comparison of the HDPE/poplar composite spectra before and after weathering (Fabiya et al. 2009).

In early references the band at 1508-1512 cm^{-1} was just assigned to lignin (Faix 1992) which disappeared upon longer exposure. All these data again indicates that, lignin degrades on the weathered WPC surface. The band at 1630-1660 cm^{-1} , assigned to the vinyl groups (Tidjani 2000), increased upon WPC weathering. More importantly, the bands between 1680 and 1800 cm^{-1} were assigned to the carbonyl functional groups (Mayo 2003). This carbonyl region has been divided to: carboxylic acids (1725 - 1715 cm^{-1}) and esters (1735-1720 cm^{-1}) (Faix 1992; Tidjani 2000; Mayo 2003). The extent of oxidation and other functional group changes also have been successively analyzed by FTIR spectroscopy (Matuana et al. 2001; Colom et al. 2003; Fabiya et al. 2006). Thus, oxidation at the degraded surface can be detected throughout weathering (Colom et al. 2000; Matuana et al. 2001; Stark and Matuana 2004; Muasher and Sain 2006).

In the case of co-extruded samples, this method also has been applied successfully. FTIR spectra of HDPE matrices before and after cyclic UV/water spray exposures were used to investigated the effect of a clear HDPE cap layer on ultraviolet weathering of coextruded HDPE/wood-flour composites (Figure 13) (Matuana et al. 2011). Distinct absorption peaks of HDPE appears

around 2915, 2847, 1472, 1176, 730, and 718 cm^{-1} . The appearance of strong peak at 1713 cm^{-1} and 1176 cm^{-1} on the surface of HDPE clearly indicates the evidence of photo-degradation of the polymer used in both core and cap layers. Peaks associated with wood are clearly seen around 3354 (broad peak), 2903, 1737, 1591, and 1029 cm^{-1} . After weathering the main spectral changes are seen at around 3300-3354 cm^{-1} , 1714-1738 cm^{-1} , and 1029-1033 cm^{-1} frequency ranges, which are characteristics to wood components. Unlike coextruded composite surface, a significant decrease in the intensity of peaks at 3300-3354 cm^{-1} (OH in cellulose) and 1029-1033 cm^{-1} occurred on the surface of uncapped composites even after only 192h exposure and these peaks almost disappeared as the weathering exposure time increased indicating fiber removal.

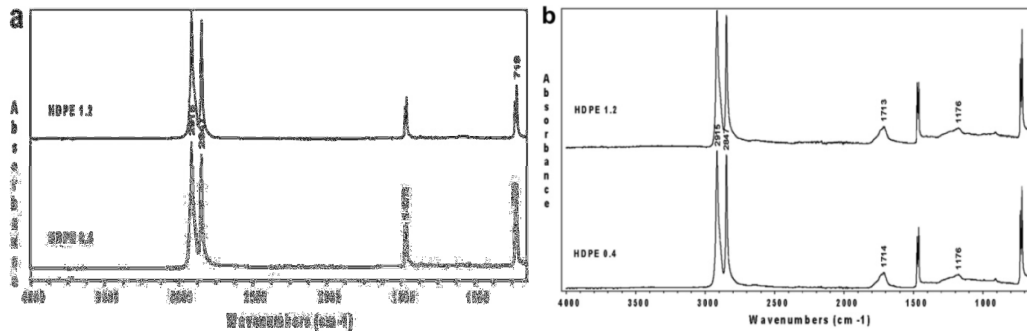


Figure 13 - FTIR spectra of HDPE1.2 (for cap layer) and HDPE0.4 (polymer matrix for uncapped WPC and core layer of coextruded WPC). (a) before and (b) after exposure to 1952 h UV (Matuana et al. 2011).

FTIR was also used to determine the change in crystallinity of HDPE before and after weathering. Some researchers have calculated crystallinity using the doublet peaks at 730 cm^{-1} and 720 cm^{-1} (Stark and Matuana 2004; Muasher and Sain 2006). The peaks at 1474 cm^{-1} and 730 cm^{-1} correspond to the polyethylene crystalline content, and the peaks at 1464 cm^{-1} and 720 cm^{-1} represent the amorphous content.

Other methods beside FTIR can be used to give some extra information about the surface components of material, for instance color of the surface.

2.7.2. CIE LAB COLORIMETRY

Discoloration is the initial visual effect of weathering. Because of that it has been used in most of the case studies of weathering of wood or WPC. During weathering, color of WPC fade and become lighten (Falk et al. 2000; Lundin 2001; Matuana et al. 2001; Stark and Matuana 2003; Stark and Matuana 2004; Stark et al. 2004; Bajwa and Bruce 2005; Muasher and Sain 2006; Stark 2006) and if it is exposed to UV irradiation for long period, a white chalky layer will appear on its surface. The extremity of these changes can be studied as a severity of weathering and will be evaluated as total color changes (ΔE) and lightening (ΔL^*) after weathering often by CIE $L^*a^*b^*$ method.

The CIELAB or CIE $L^*a^*b^*$ color scale is a standard, three dimensional, approximately uniform color scale which the color values can be easily compared with. In this scale, the differences between points plotted in the color space correspond to visual differences between the colors plotted (Figure 14).

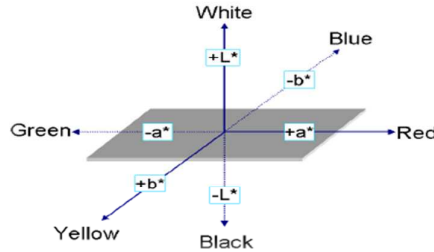


Figure 14-Diagram of CIE Lab color space in 2D and 3D (<http://learn.colorotate.org/color-models.html>).

The CIELAB color space is organized in cube form. It measures the lightness of the sample (L^*) and color coordinates: redness (a^*) in the green-red axis and yellowness (b^*) in the blue-yellow axis. L^* value ranges between 0 and 100 (black and white, respectively) which maximum value (100) represents a perfect reflecting diffuser. Therefore higher value indicates that the color of sample is lighter than others.

The a^* and b^* , both represent the index for color of the samples. The color coordinates a^* and b^* range from -150 to +150. From these indexes total color change (ΔE) measured for each samples.

ΔE always increased with increasing exposure time (Colom et al. 2003; Fabiyi et al. 2009). In weathered samples a^* or b^* also changed due to the chemical changes and photo-degradation. Therefore, the contribution of L^* coordinate may not be significant to ΔE (Fabiyi 2007). Thus, in such studies ΔL and ΔE measured and studied separately.

2.7.3. CONTACT ANGLE TEST

Contact angle test is representing the ability of surface to become wet. This test is mostly use for evaluation the coating or wettability capacity of the surface. Matuana et al (2001), showed that weathered rigid PVC/Wood fiber composites exhibited lower contact angle values (increased wettability) it means that it wettability increase more than the un-weathered ones regardless of the amount of wood fibers (Matuana et al. 2001). The increased wettability of the artificially weathered samples implied changes in their surface chemical compositions. Measurement detail will be explained more in section 4.3.2.

2.7.4. ROUGHNESS

The roughness average or " R_a ", is the most commonly used parameter for expressing measurements of surface contour, the other roughness parameter " R_q " representing the quality of the fine irregularities on a machined surface. The R_a value represents the arithmetic average of the height of the roughness irregularities above the mean line along the sampling length. Measurement of these values, normally presented in microinches or microns in the metric system, will be discussed in details in section 4.3.3.. In WPC improper encapsulation of wood particles by the matrix could account for the rougher surface of uncapped WPC (Matuana et al. 2011). Weathering caused increase in roughness (Tolvaj and Faix 1995). This increase due to surface degradation is believed to be associated with removal of degraded lignin components which leads to the exposure of the wood filler at the composite surface (Hon et al. 1986; Adhikary and Pang 2009). Thus after weathering it can be used as a indicator of surface quality and degree of fiber removal from the surface. Although these parameters are universally accepted as a means of expressing surface roughness, sometimes they can be somewhat misleading. It is possible that two surfaces having widely different profiles could have same R_a , but perform quite differently. Therefore, they should be used with caution.

2.7.5. MECHANICAL TESTS

Mechanical properties also change due to the weathering. Three points bending (Flexural properties) is the common test for measuring the MOE of the materials. In this part the work that has been done mechanical properties by means of evaluating flexural properties (as a classical method) and indentation (as a new suggested methods) is presented.

Flexural properties

Flexural properties are important in wood and wood products design. For many structural designs the bending strength and stiffness are important properties. For example for applications like decking or bookshelves it is important to know the deflection of the products. In addition, the most evident consequence of photochemical degradation is the deterioration of mechanical properties in response to the mechanical loading. Changes in mechanical properties of WPC after weathering can be due to a combination of changes, such as composite surface oxidation, matrix crystallinity changes, and interfacial degradation caused by moisture absorption (Matuana et al. 2001).

On the contrary, Lundin et al. (2002) showed no loss in strength or stiffness for weathered wood/PVC specimens, while the unfilled PVC lost almost 50% of its strength after only 400 hours of weathering; this was attributed to the improved load bearing properties and stress transfer of the wood flour. However, microstructural observations revealed a decrease in interfacial bonding between the wood flour and polymer matrix caused by increased in exposure time of weathering (Adhikary and Pang 2009). Also, more wood components will be washed away from the surface of WPC because of UV radiation and water spray, therefore, it is normal to expect from this product to experience a larger loss in flexural modulus of elasticity and strength (Stark 2006) which can be follow by change in ductility. It has been shown that, during the initial stages of weathering, the crystallinity of the polymer surface of injection-molded wood fiber/HDPE composites increases (Stark and Matuana 2004). In other study it has been confirmed that the HDPE in weathered WPC experienced an increase in crystallinity during xenon-arc weathering (Stark and Matuana 2004). This change in crystallinity can affect the ductility of the material. In some reports, the increase in crystallinity was attributed to PE chain scission of polymer chain during photo-degradation. Further degradation may be initiated by the free radicals and shorter chain molecules generated during weathering. This chain scission reduces the density of entanglements in the amorphous phase thereby allowing lower molecular weight PE molecules to crystallize again due to higher mobility (Jabarin and Lofgren 1994). Thus the reduction of molecular weight which increased the polymer chain mobility, leading to a higher degree of crystallinity, causes loss of ductility (embrittlement) and a consequent loss of the elongation properties. Brittleness is the opposite term of ductility. It is reported that the addition of wood flour (WF) with a particle size of 147 μ m can significantly increase the brittleness of LLDPE/WF composites (Marcovich et al. 2001). Like ductility, this property of WPC also can be affected by UV irradiation.

Another reason for mechanical loss of WPC during weathering, beside chemical changes, is water absorption. Although, it has been shown that WPC are less susceptible to moisture cycles than wood composites, wetting and drying of the wood components during weathering process cause the HDPE to crack which is one of the reason of the loss in mechanical properties after weathering. These effects cause more damage than photo-oxidation on WPC properties (Li 2000). Bending tests of kanaf-filled HDPE following 2000 hours of xenon arc weathering with cycles of water spray showed significant decreases in bending strength and stiffness (24% and 42%, respectively) (Lundin et al. 2002). Wood flour-filled HDPE showed similar results; strength and stiffness decreased 20% and 33% respectively.

Indentation test

Instrumented indentation is a convenient method for determining the mechanical properties of solids (Foerster et al. 2007) and thin films (Volinsky and Gerberich 2003). Analysis of the unloading load–displacement response, which is assumed to be elastic behavior, allows obtaining hardness and elastic modulus (Oliver and Pharr 1992). For polymer, it was noted that macro-indentation tests may provide a good material characterization of unfilled polymers and showed that Flat punch indentation tests are useful to extract local mechanical performances of polymers (Guglielmotti et al. 2008). The advantage of macro indentation to micro indentation is that the macro-scale allows reducing measurement errors due to surface defects and irregularities, and preserving the local nature of the indentation. Indentation loading curve is a useful tool for homogenous elastic-plastic material qualification (Menčík 2011).

Many researchers applied macro- and micro-indentation for measuring elasto-visco-plastic behavior on the surface of any kind of composites (Lucignano and Quadrini 2009). Also macro-indentation test was used to measure the effect of local filler content in the polyester matrix. The Flat punch indentation tests were performed on composite slices to evaluate the effect of the graded filler content. Indentation load and unload phases were extracted from the experimental curves, and correlated one to the others (Lucignano and Quadrini 2009). Result of such study showed that measuring the elastic modulus is possible by extracting it from the loading phase of the indentation curve using a numerical model (Lucignano and Quadrini 2009). It has been noted that the un-loading stage is necessary to extract elastic properties from an instrumented indentation test but it has its disadvantages. A complex experimental set-up is necessary for extract elastic properties from an instrumented indentation test and at the end poor test reliability is often obtained. For researchers the loading stage was sufficient because of ability of the numerical model in the simulation of the involved physical phenomena. However, due to the fact that the loading phase in thermoplastic materials has no clear initial linear stage the same concept cannot be applied. However, it can be innovative to know if this indentation test can be used for studying the effects of weathering on mechanical properties changes in WPC.

These mentioned tests are useful for evaluation of weathering process (Photodegradation) in WPC. In case of biodegradation of WPC the test are limited. In next part more information presented. Although biological resistance and moisture sorption are related in some degradations, such as fungal attack, here they are discussed separately.

2.7.6. BIOLOGICAL RESISTANCE TEST

A multitude of methods are available to test the fungal degradation of wood and plastics; however, there is no laboratory standard available for specifically testing the fungal durability of WPC (Schirp et al. 2008).

In case of WPC resistance test, laboratory data demonstrate general regularities of microbial degradation, such as effect of temperature, nutrients, pH, and effect of antimicrobial agents. Each one of these factors can be very different in the field and be more severe in cooperation other factors. Research showed that mold can growth on wood thermoplastics composite in outdoor tests which is not considered in laboratory test. It is the same for weathering, the outside weathered WPC samples lightened initially (first 8 months) then became darker as mildew or mold and dirt started to deposit on the surface (Fabiya 2007). Because of these misleads most of the results from ASTM standards laboratory tests show WPC as resistant to bio-degradation. But the truth is until we have fibers in WPC the risk of bio-degradation never vanishes.

Another factor that complicates the biological resistance test of WPC is that water absorption in WPC takes time. Thus, short periods of time cannot reveal the difference between laboratory test and real life. An examination for laboratory and soil block have been conducted on very thin samples of composite boards containing 60% wood flour and 40% of PP, smeared with potato

dextrose agar or malt extract agar (microbial growth media). Different types of fungi (brown-rot fungi, *Gloeophyllum trabeum* and *Poria placenta*, and white-rot fungus, *Coriolus versicolor*) were employed for 12 weeks' incubation. Concurrently, similar samples were employed in the soil block test (ASTM D 1413). Sample boards exposed to agar showed as much as 40–50% weight loss and those exposed to soil lost 40–45% weight. In the both cases, a linear correlation between moisture content and weight loss were obtained (Silva Guzman et al. 2005). For WPC ASTM standard laboratory tests using isolated brown- and white-rot fungi showed a very small weight loss during a 12-week test. These tests, however, are not reliable since the test specimens are not absorbing water to elevate the moisture content up to the level where fungi are able to attack, and since water absorption takes times, and duration of this test are short, then they will not show the real values of degradability.

AWPA (the American Wood-Preservers' Association) conducted a research on polyethylene-wood composite materials with wood content ranging from 50 to 70% (w/w) by soil block test method. Their results showed weight losses as a result of microbial degradation of white-rot organism, *Coriolus versicolor* up to 18% for 16 weeks, and up to 7% in 12 weeks with brown-rot organism, *Gloeophyllum trabeum*. They suggested, since the wood content was the only part that degraded by fungus and it contained just 50% of their samples, the weight loss for the wood component could be doubled to 36 and 14%, respectively (Klyosov 2007).

In a durability test, moisture and fungal are act simultaneously. Thus, there is not clear that changes after test are mostly caused by which. For understanding that Schirp and Wolcott (2005) employed white-rot fungus, *Trametes versicolor*, and the brown-rot fungus, *Gloeophyllum trabeum* to clarify the contributions of moisture and wood decay fungi to WPC damage. They tried to find which one of losses in weight or stiffness in WPC formulations, caused by decay fungi, is more sensitive as an indicator of fungal decay. The results showed that stiffness of WPC was affected more severely by moisture absorption than by fungal colonization. Also, strength of WPC was not affected by decay fungi but significantly reduced by moisture absorption for a formulation containing 70% wood filler (Schirp and Wolcott 2005). Thus, in these kinds of researches, mostly weigh loss is considered.

Light and scanning electron microscopy showed that in all of the WPC samples that exhibited weight losses, the degradation was most severe on the surface that was in direct contact with the decay organism at the beginning of the test. By means of scanning electron microscopy, the presence of voids between the wood and plastic in the composites were revealed that were colonized by fungi, for the composites exposed to fungi and the fungal hyphae were also prevalent in the voids deeper in the composite, particularly with 70 wood /30 HDPE material.

Also Plastic is largely resistant to insect attack. However, after weathering WPC surface become uneven and can increase the risk of termites attack

2.7.7. MOISTURE ABSORPTION

WPC absorb moisture very slow. For accelerating the absorption WPC species often are immersed in water or boiling water (Clemons and Ibach 2002). However, different methods have been presented to evaluate effect of moisture absorption. Several authors have focused on the water uptake of different WPC materials (Clemons and Ibach 2004; Wang and Morrell 2004). This moisture absorption can lead to a degradation of mechanical properties since the wood particles swell. Repeated cycles of wood swelling and shrinking are causing the interfacial break down of composite and the appearance of microcracks on the plastic. Also, internal fracture of wood particles happened due to restrained swelling and caused mechanical loss. For instance, soaking an injection-molded WPC containing 40% wood flour for 2000h induced a 9% moisture increase and 39 % decrease in flexural modulus and 22 % decrease in strength (Stark 2001). Manufacturing method can have a tremendous influence on surface quality of the WPC, thereby

influencing moisture absorption. Injection-molded surfaces were smoother than extruded materials, and had a plastic-rich layer that inhibited moisture penetration compared to extruded WPC that absorbed four times as much moisture as injection-molded composites in a two-week water soak (Clemons and Ibach 2004). Comparing different manufacture methods determined that in two-week soaking or cyclic boiling-drying extruded composites absorbed the highest moisture, compression-molded composites absorbed less, and injection-molded composites absorbed the least (Clemons and Ibach 2004). Manufacturing stresses may also play a role in moisture uptake. For example, uneven stresses produced during manufacturing may result in crack development near the WPC surface that accelerates moisture uptake (Morrell et al. 2009). Results from subjecting WPC to 90% relative humidity (RH), humidity cycles and soaking in liquid water for an extended period of time showed that even after 200 days, all of the composites continued to gain weight and equilibrium moisture content was not reached. Also, the maximum weight gain due to water soaking was approximately 11% in the specimens with the highest percentage of wood fiber (Rowell 2005). Fuentes et al (2007) measured the water absorption and thickness swelling for different bagasse/HDPE boards with various bagasse contents. The lowest moisture absorption corresponded to the boards with a high (60%) plastic content (Fuentes Talavera et al. 2007). Thus, from all these results we can conclude that WPC will absorb moisture eventually.

3.Material

In this study we used bagasse as reinforcement of HDPE and applied delignification as chemical modification to reduce lignin content in order to obtain more photo-stabilized WPC product (less color change and less mechanical loss). Also efficiency of coating has been studied beside delignification on pigmented samples and non-pigmented ones. The evaluation of samples is carried on by classic and not usually applied methods. Samples were made by extrusion, sanded, coated and cut to desirable dimension.

WPC manufacture method were repeated twice (two sets), each time control samples were produced. The extruder used in this study was at industrial scale. Furthermore, as referred in Table 8, to facilitate the coding, we used postfix "0" to samples without any treatments, "c" to coated, "p" to pigmented, and "cp" to samples contains pigment and also covered with clear coat.

After preparation of samples, non-destructive tests have been done on samples. Then, half of samples were placed in a QUV device and the other half remained un-weathered and went through different destructive and non-destructive tests. After weathering the same tests were repeated for weathered samples. Scheme of tests applied on each sample is shown in Figure 15. The repetition of each test is mentioned in annex A.

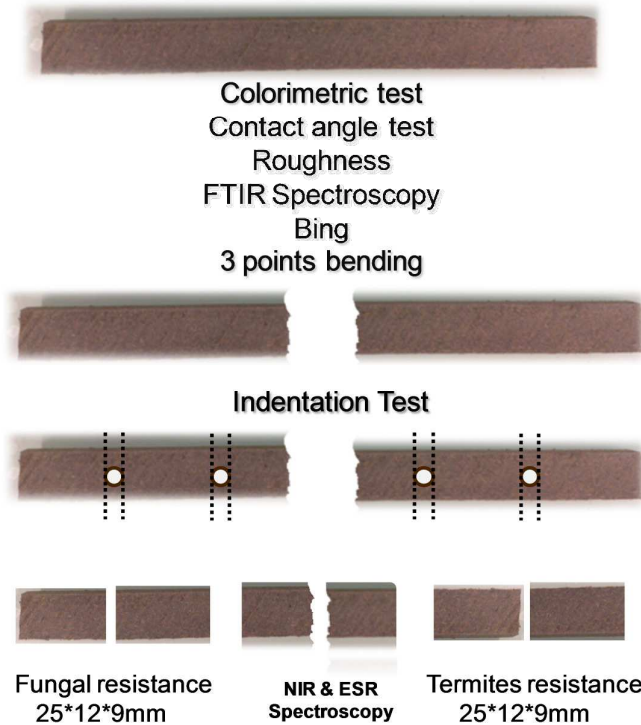


Figure 15- Scheme of the tests carried on un-weathered and weathered samples.

3.1. Preparation of fibers

Sugar cane (*Saccharum officinarum* L.) bagasse was collected at a wood plastic factory DEZCHOOB in south of Iran in powder shape (with fiber dimension equal to 20 mesh). Bagasse powder was oven-dried at $100\pm 3^{\circ}\text{C}$ for 24 h before processing. The collected bagasse was divided into 2 sets: the bagasse attain from factory without any treatment as a control (sample

code A, Table 8), and the other set went through a pulping process for delignification (for more information of coding refer to Table 8). We used organosolve pulping process as a mean of gentle delignification method having less impact on cellulose and hemicelluloses. Two solvents have been used for delignification in organosolve pulping process with the same experimental conditions (130°C for 1 h): ethanol and monoethanolamin (MEA) (both supplied by Iran Petrochemi Co.). MEA was chosen as solvent because it acts more selectively towards lignin (Claus et al. 2005). We tried to obtain two different levels of lignin content (9% and 5%). However, with the method used we could not obtain 5% of lignin content with the ethanol solvent. Thus, we have only 1 level of delignification for ethanol and 2 for MEA.

Delignification system was conducted in digester with fix temperature of 130°C for 1h. A group of bagasse (sample code B, Table 8) went through organosolve pulping process with ethanol at 70% and 4g NaOH, for 100g bagasse. Pulp with a kappa number of 67 was obtained at a total yield of 85% based on o.d. bagasse. However, to obtain different levels of lignin content, we also used different ratio of water and MEA as cook liquor:

-5% MEA – 95% water led to a bagasse with 9% lignin content and a Kappa number of 65 (sample code B', Table 8).

- 50% MEA- 50% water led to a bagasse with 5% lignin (sample code C', Table 8).

Before and after delignification, bagasse was sieved through 20, 40 and 60 mesh. The percentage of weight which remains on each sieve was measured and it has been tried to use the same percentage remain on the sieve for different groups. Therefore, further changes in mechanical properties can be directly attributed to the chemistry of the fibers, not to the change of fibers size and dimensions.

3.2. Raw materials of the composite

After delignification bagasse was rinsed with water and dried for at least 24h at 100±3°C. The sieved dried bagasse was mixed with High Density Polyethylene (HDPE) to compose samples. The characteristics of HDPE, supplied from Iranian Petro-chime Co (WE6040), are presented in Table 7.

Table 7- General Characteristics of High Density Polyethylene

<i>Characteristic</i>	<i>Test Method</i>	<i>Unit</i>	<i>Value</i>
Max Flew Index (180/6)	ASTM 1238	g/10mm	0.45±0.05
Density at 25°C	ASTM D792	g/cm ³	0.951
Crystalline Melting Point	DSC	°C	139
Bulk Density	No method	g/cm ³	0.40
Powder Size (Avg.)	-	µm	<210
Wax Content	-	%	<2
Color	-	-	White

Table 8 summarizes the formulation of blend compositions and necessary additives (lubricant, coupling agent) used for each group of this investigation and their codes. In this table the values of bagasse/plastic composites, lignin content, methods of delignification, usage of pigments, and coating on the surface are shown. The following experimental parameters were constant in this study: manufacture method, filler/plastic ratio and percentage of additives.

Biodegradability in PE films has a pronounced effect only if it contains 30% or more of cellulose-based fibers (Behjat et al. 2009). Therefore, we used 50% w/w fibers to ensure a visible contribution of the fiber addition to the durability of the final product.

As shown in Table 8, 3% of W/W of master batch brown pigments (Grade 7110, Ilam Fara Shimi Co.) were used for half of the A and B sets. This pigment contains 44.5% LDPE base polymer, 7% wax, 8% additives, 1.5% antioxidant, 1% stabilizer, and 38% mixture of mineral pigments.

Table 8- Combination of variables used in the manufacture of bagasse/plastic composite boards. (Zero (0) and C, P, CP are the abbreviations for non-treated, coated, pigmented and coating pigmented samples, respectively)

Samples Code	HDPE	Coupling agent	lubricant	Bagasse fibers	Lignin content of fibers	Substance for Delignification	Pigment in Master Bach	Clear Coating
A0	49%	2%	1%	49%	18-22%	-	0	-
Ac	49%	2%	1%	49%	18-22%	-	0	Applied
Ap	47.5%	2%	1%	47.5%	18-22%	-	3%	-
Acp	47.5%	2%	1%	47.5%	18-22%	-	3%	Applied
B0	49%	2%	1%	49%	9%	Ethanol	0	-
Bc	49%	2%	1%	49%	9%	Ethanol	0	Applied
Bp	47.5%	2%	1%	47.5%	9%	Ethanol	3%	-
Bcp	47.5%	2%	1%	47.5%	9%	Ethanol	3%	Applied
A'0	49%	2%	1%	49%	18-22%	-	0	-
B'0	49%	2%	1%	49%	9%	MEA	0	-
C'0	49%	2%	1%	49%	<5%	MEA	0	-

For coating samples, chlorinated polyolefins (CPOs) were used as a primer between the WPC sanded surfaces and subsequent coatings which was polyurethane (supply by Iran petrochemi CO.).

3.3. Manufacture of WPC profiles

The mixtures of each group were rotated in a Valtorta-Brescia pre-mixer device at 300 rpm and 115°C for 5 min before processing to obtain the homogenous mixture and also to remove the remaining moisture of fibers (Figure 16a). After pre-mixing, the components were passed through heated barrels and mixed again by rotating in a conical twin screw extruder (Conical screw 2 m, output capacity 80 to 100 kg/hr, QC Future Plastic Machinery CO., LTD) (Figure 16b) with an I-shaped die (industrial profile extruder). The final shape of the composite is given by this die attached to the end of the barrels (Figure 16c). The temperature of the die is controlled by water flow. Processing conditions are shown in Table 9.

Table 9- Compounding conditions for the base WPC material the cap layers.

Zone	Barrel 1	Barrel 2	Barrel 3	Barrel 4	Join core	Melt temp. (°C)	Screw speed (RPM)	Melt pressure (BAR)	Feeder1 speed (RPM)
Temperature	185	190	180	180	180	180	7.5	127-130	3

After die WPC profiles were immediately cooled in a water pool (Figure 16d) and cut to the smaller length.

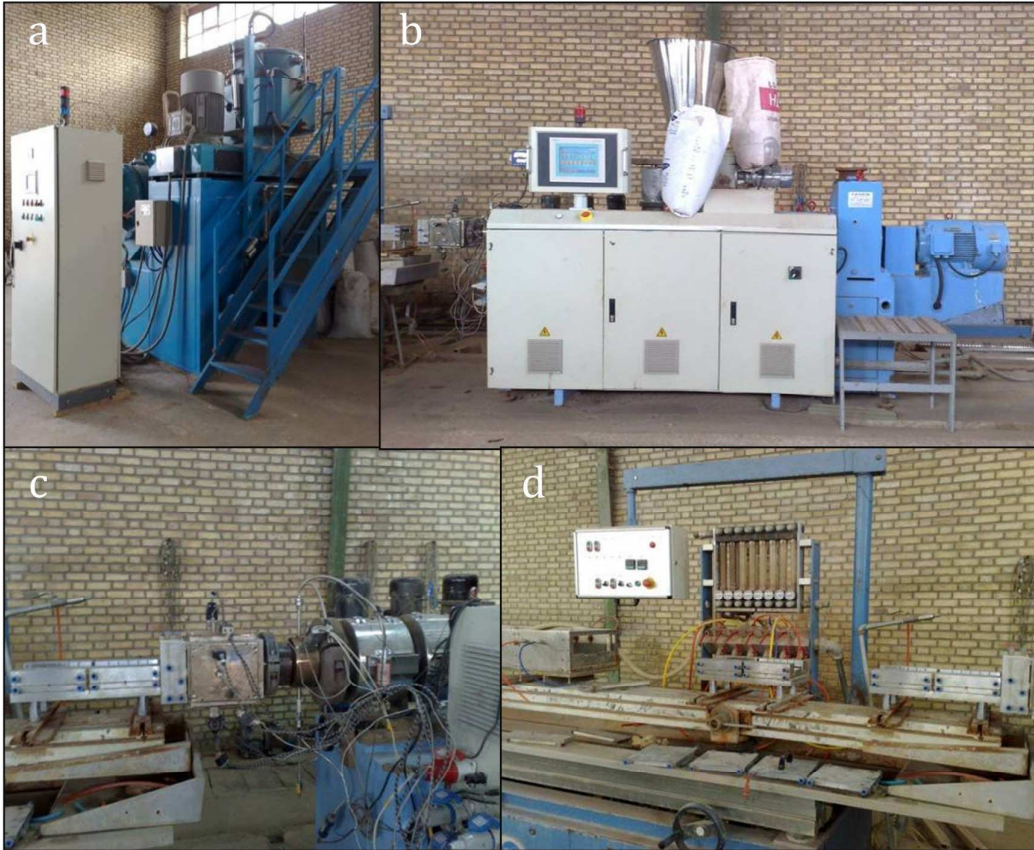


Figure 16- These pictures represent different parts of industrial extruder used for this study: a) Pre-mixer b) Feeder and Control Monitor of extruder; c) End part of extruder barrel and Die; d) Die and opened calibrator (Water pool).

3.4. Preparation of test samples

After air drying, the sides of profiles were cut (Figure 17b) and half of samples were sanded to remove the polymer-rich surface with 120 grain paper (Figure 17c) and conditioned at $20\pm 2^{\circ}\text{C}$ and $75\pm 5\%$ relative humidity (RH) until constant weight is reached (prior to coating). Sanding action were conducted for two reason: first for improving the capacity of adhesiveness of surface since it resulted in more fiber exposed to the surface; and second because we tried to be more practical since nowadays it is performed by most factories (it is an industrial process in most cases). In WPC manufactures, sanding plates with different patterns are added to production line, to provide a wood-like character to final product.

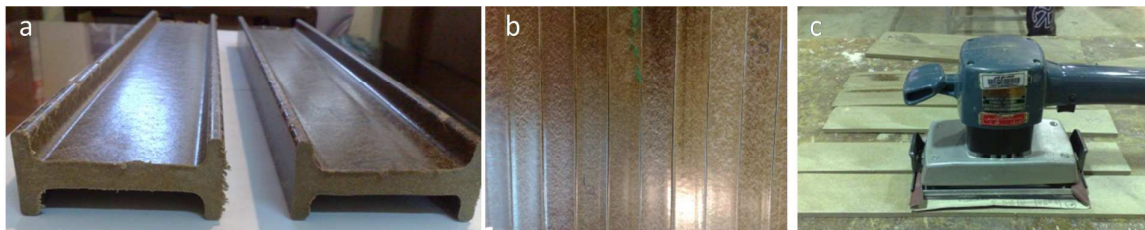


Figure 17- Prepration of samples: a) Profil of samples; b) after cutting the sides; c) sanding

As a pre-test, also coating with primer applied on the non-sanded surface to study the efficiency of sanding. After coating, samples again are cut into 150x12x8 mm (length, width, and thickness) specimens for further tests.

3.5. Coating application

In this study polyurethane was applied to the sanded and non-sanded surface of half of A and B sets as a clear coating by means of spraying. For this purpose, samples were conditioned at $20 \pm 2^\circ\text{C}$ and $75 \pm 5\%$ RH until constant weight was reached prior to coating. Non-destructive tests have been conducted on the samples which have been considered for coating so the effect of coating on samples can be evaluated. Chlorinated polyolefins (CPO) were used as a primer between the WPC surface and a coating (aliphatic Polyurethane). Before applying the primer and coating, samples surface was cleaned by wet cotton (with ethanol) to remove all dirt or remaining fibers on the surface. Then, the samples remained in the conditioning room until they dried. A thin layer was added to the surface by spraying these materials respectively. CPO primer was sprayed on the surface of the samples to form a thin layer with thickness of approximately $100\mu\text{m}$. Thick CPO films often result in poor adhesion properties, so it has been tried to obtain a uniform thin layer by spraying the material on the samples surface by fine nozzle. Aliphatic polyurethane was also sprayed immediately after CPO primer was dried, which was within 2-3 min. Samples then stayed in clean conditioned room ($20 \pm 2^\circ\text{C}$ and $75 \pm 5\%$ RH) for two months.

4. Procedures and methods

4.1. Aging procedure (weathering)

Accelerated artificial UV weathering tests were conducted in a QUV weather-ometer according to EN4892-2, as recommended in test methods for characterization of WPC (CEN/TS 15534-1), for 1440 hrs in Critt Bois Epinal, France.

EN ISO 4892-2 specifies methods of test for sample exposure to light sources xenon arc, in the presence of moisture, to reproduce the effects of aging that occur when materials are exposed at real environments end-use, in the day light (Method A) and daylight filtered through window glass (Method B). The specimens are exposed to suitable light sources under controlled conditions (temperature, humidity and/or wetting). EN ISO 4892-1 provides general guidelines for the application of the method described in EN ISO 4892-2 and describes general performance requirements for devices of exposure of plastics to laboratory light sources. For use outdoor uses, Method A of EN ISO 4892-2 is used with the following test conditions:

- Temperature of the Black Stallion: $(60 \pm 3)^\circ \text{C}$;
- Cycle of vaporization;
 - Duration of spraying: 18 min;
 - Exposure to dry interval between two sprays: 102 min;
- Relative humidity: $(65 \pm 5)\%$.

All properties of the composites were measured/observed before and after weathering.

4.2. Chemical tests

Near Infra-Red Spectroscopy (NIR), Electron Spin Resonance Spectroscopy (ESR) and FTIR spectroscopy have been conducted in this study but none of the results was as useful as FTIR results for studying the effect of weathering.

4.2.1. FTIR SPECTROSCOPY

Spectra on fibers

FTIR spectra from EQUINOX 55 (Bruker) spectroscopy have been obtained from non-delignified and delignified fibers which were embedded in KBr pellets. The data were recorded in the absorption mode in the range $4000\text{--}400\text{ cm}^{-1}$ with an accumulation of 32 scans. Two different ratios from IR spectra have been measured. First the IR ratio A_{1370}/A_{670} which is the ratio of the area of the IR peaks between $1300\text{ and }1400\text{ cm}^{-1}$ to the area of the IR peak at 670 cm^{-1} . This ratio shows the cellulose I/cellulose II ratio in fibers. The IR ratios H_{1429}/H_{897} is ratio between different peak heights, $1429\text{ and }897\text{ cm}^{-1}$, representing the crystalline packing of the chains (Akerholm et al. 2004). Also peak at $710\text{ and }750\text{ cm}^{-1}$ were studied for understanding the change in cellulose crystallinity (Gümüşkaya et al. 2003).

Spectra on WPC

For chemical analysis of WPC samples a Vertex 80 Spectrum with attenuated total reflectance (ATR) acquired was used in aim of understanding chemical changes occur on the surface of weathered samples and efficiency of delignification to reduce the photo-degradation. The Fourier transform infrared spectroscopy (FTIR) scans were obtained at a resolution of 4 cm⁻¹ from 4000 to 600 cm⁻¹. The FTIR spectra of the surfaces of both weathered and non-weathered materials were obtained. Spectra obtained from this method were used in 2 different ways. First is a qualitative observation. The changes in peaks intensity can represent the existence or change in the amount of different bond due to the materials. Second is quantifying the spectra data, from net peak absorbance obtained after the baseline correction. This method mostly used for studying the chemicals changes due to weathering. Following the approach described by Stark and Matuana, For quantifying data, the peak intensities of absorption bands (I) at 1030, 1715, and 2915 cm⁻¹ were used to calculate both wood index (WI) and carbonyl index (CI) using the following equations (Stark and Matuana 2004; Stark and Matuana 2004; Stark and Matuana 2007):

$$\text{Wood index (WI)} = \frac{I_{1030}}{I_{2915}} * 100 \quad \text{Equation 1}$$

$$\text{Carbonyl index (CI)} = \frac{I_{1715}}{I_{2915}} * 100 \quad \text{Equation 2}$$

where I represents peak intensity. Peak intensity was normalized using the peak at 2912 cm⁻¹, which corresponds to alkane C-H stretching vibrations of methylene groups (-CH₂) (Stark and Matuana 2007). These indexes were applied in order to determine the effect of weathering on wood polymers (lignin, cellulose, and hemicelluloses) and compare the changes between weathered index and un-weathered index.

Hydroxyl index (HI) was also calculated as the ratio of the area (absorbance) of the band at 3500 to 3080 cm⁻¹ and the antisymmetric C-H stretching band of methylene groups (2917 to 1912 cm⁻¹). HI determines the amount of OH and changes in intensity of peaks related to bagasse flour. OH/CH index was computed based on area under peak instead of peak intensity for measuring the amount of cellulosic hydroxyl groups present of WPC surface (Gupta 2006). The variation in OH/CH ratio for the composite formulations is explained by the differences in amount of wood component in surface of WPC, because HDPE do not possess hydroxyl groups.

In addition, lignin index (LI) was taken as the ratio of the area (absorbance) of the band at 1512 to 1508 cm⁻¹ and the antisymmetric C-H stretching band of methylene groups (2917 to 1912 cm⁻¹) (Gupta 2006; Fabiyi and McDonald 2010).

$$\text{Lignin index (LI)} = \frac{A_{15012-1508}}{A_{2917-1912}} \quad \text{Equation 3}$$

$$\text{Hydroxyl index (HI)} = \frac{A_{3500-3080}}{A_{2917-1912}} \quad \text{Equation 4}$$

where A is the area beneath the bonds. Thus, the wood index, lignin index and hydroxyl index were used as representative factors of wood part remaining on surface after weathering (Stark and Matuana 2004). Therefore, using these indexes we can follow the wood degradation and also surface oxidation through Carbonyl Index. Also, Lignin Index (LI, eq. 5) allows monitoring and semi quantify the lignin content during weathering. Also, by looking at the spectra after implement, it is possible to draw out some qualitative data.

For quantitative measurement from FTIR and comparing different spectra it is necessary to normalize the peaks. Mostly the peak that doesn't change a lot between different spectra chose for normalizing FTIR spectra. The antisymmetric C-H stretching band of methylene groups was chosen in studies as a reference because it changed minimally during weathering (Fabiyyi et al. 2008; Fabiyyi and McDonald 2010).

4.3. Surface quality

4.3.1. COLOR ANALYSIS (COLORIMETRY)

Color change was measured using a Datacolor spectrophotometer based on the CIELab color system according to the procedure outlined in ASTM D2244. In CIELAB color space the lightness of the sample (L^*) and color coordinates: redness (a^*) in the green-red axis and yellowness (b^*) in the blue-yellow axis were measured.

The a^* and b^* , both represent the index for color of the samples and mostly have same trend. That means if a^* increases b^* will also increase. Thus, these two can be summarized in one index which called metric Chroma and it can be calculated as follow:

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad \text{Equation 5}$$

Color indexes were measured on more than 20 replicates for each group, following different stages of the experience: right after samples were extruded and sanded (before weathering), after QUV exposure, and after fungal resistance test. Color change is expressed through differences of color indexes,

$$\delta L^* = L^* - L_i^* ; \quad \delta a^* = a^* - a_i^* ; \quad \delta b^* = b^* - b_i^* \quad \text{Equation 6}$$

where i indicates the initial value (the initial values were measured before weathering or fungal attack and the final values after weathering or fungal attack).

a^* is defined as the red/green coordinate, for a^* when the difference between two samples or before and after weathering become $+\Delta a^*$ it signifies a more reddish color or color shift toward red, and if it becomes $-\Delta a^*$ it means that color shift toward green). It is the same for the yellow/blue coordinate, b^* ($+\Delta b^*$ toward yellow, $-\Delta b^*$ toward blue). From these algebraic increments, the so-called "total color change" ΔE , a positive quantity corresponding to a distance in the (L^*, a^*, b^*) space, according to ASTM D 2244 can be computed:

$$\Delta E = \sqrt{\delta L^2 + \delta a^2 + \delta b^2} \quad \text{Equation 7}$$

4.3.2. CONTACT ANGLE TEST

Contact angle (θ) tests were conducted with a Thermo Cahn DCA (Dynamic Contact Angle, Model No: DCA 300) as a quantitative measure of the wetting of samples' surfaces. It was measured and defined by fitting a mathematical expression to the shape of the drop and by calculating the slope of the tangent to the drop at the liquid-solid-vapor (LSV) interface line (according to ASTM D7334) as shown below (Figure 18) base on young's equation.

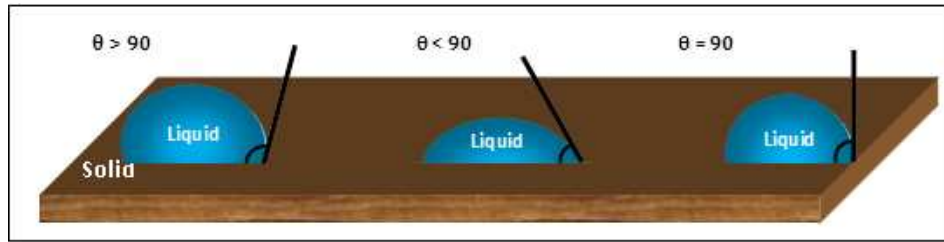


Figure 18- schematic diagram of the contact angle, θ angle between the solid-liquid interfaces.

This test is mostly important for evaluating the coating, thus it conducted only on coated samples and their non-coated pairs, before and after weathering to evaluate the efficiency of coating on wettability of the WPC surface.

4.3.3. ROUGHNESS

Roughness parameters are determined by measuring the height, width, and shape of the peaks and valleys produced on surface (Figure 19). By means of these measurements, 3 parameters of surface roughness, average roughness (R_a), root means square roughness (R_q), and average distance between highest peak and lowest valley (R_z) were measured automatically with a Surftest SJ-201 Series 178-Portable Surface Roughness Tester device (Mitutoyo). This device is a user-friendly surface roughness measurement instrument designed as a handheld tool that can be carried on-site. This test was conducted for: sanded, non-sanded, coated, uncoated, and weathered, non-weathered samples.

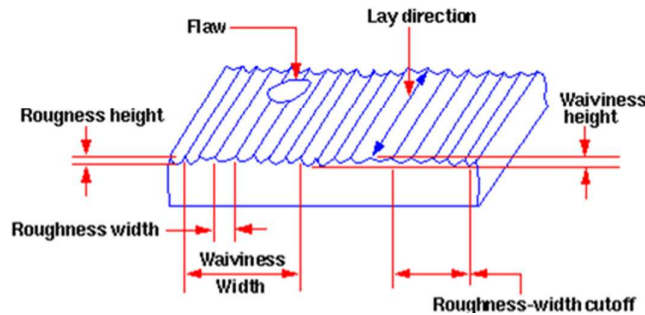


Figure 19- Surface characteristics (Courtesy, ANSI B46.1-1962).

The value of R_q which represents the root mean square of the peak heights, is more sensitive to occurrence of occasional high and low points on surface than R_a .

$$R_a = \frac{y_1 + y_2 + y_3 + \dots + y_n}{n} \quad \text{Equation 8}$$

$$R_q = \sqrt{\frac{y_1^2 + y_2^2 + y_3^2 + \dots + y_n^2}{n}} \quad \text{Equation 9}$$

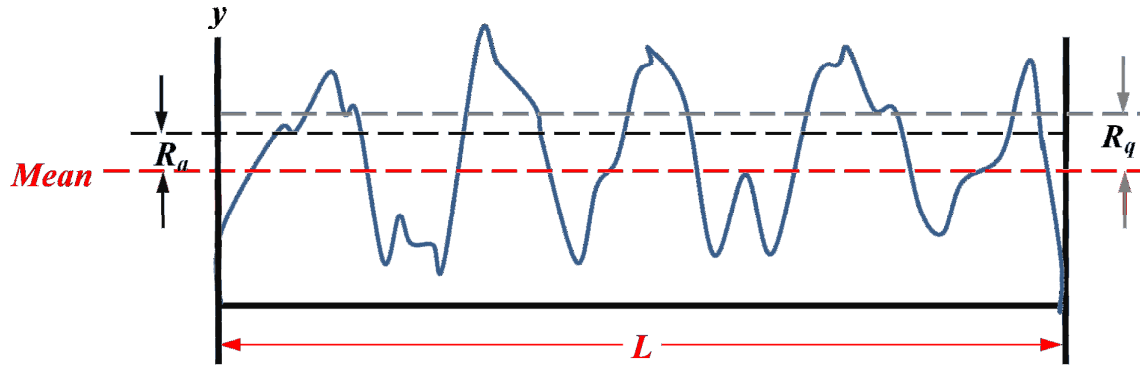


Figure 20 - Surface roughness measurement.

4.4. Mechanical tests

In this study, we concentrated on finding the most reliable variables which can reveal the effect of weathering. Also, we try to study the effect of treatments on the mechanical changes caused by weathering and sometimes we defined a correction factor for one or more properties. The last aim of this study was to see if Non-Destructive Test (NDT) like vibration can be a reliable method to measure the weathering effect and if it can be used to predict the static properties. For all these targets, we used 3 different tests: three points bending, indentation and vibration tests. All of these three tests will be described one by one afterward. It should be noted that for the mechanical samples the weight, volume (mass) and density of all mechanical samples have been measured.

4.4.1. THREE POINTS BENDING

The three points bending flexural test consists in applying force on the samples and measure it and its displacement to the material, provides values for the flexural stress (σ), flexural strain (ϵ) and the flexural stress-strain relationship response of the material. For this purpose (MTS) device is used with a 10kN load cell and a crosshead speed of 2mm/min. The specimen's dimensions are $130 \times 12.7 \times 9 \text{ mm}^3$ (L, W, T), because of the small length of samples the inverse three points bending has been used (Figure 21). Each material was tested for at least 3 replicates in which the weathered face of the sample was subjected to the tensile stresses.

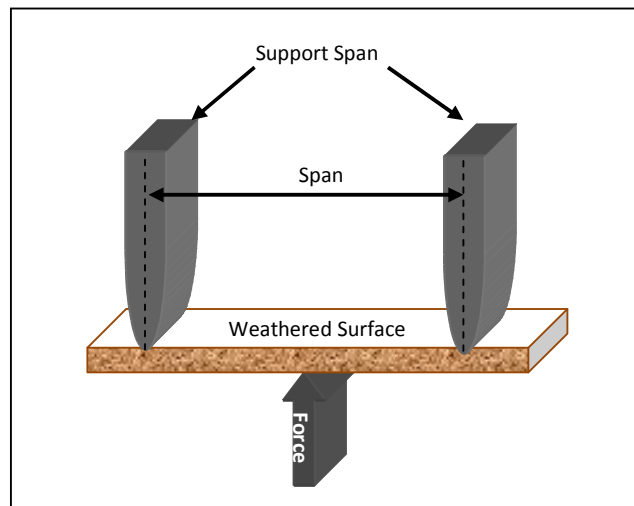


Figure 21- Position of the samples under the load.

Beside maximum stress and strain, other mechanical properties which can be calculated from the stress-strain relationship of a standard bending test are modulus of rupture (MOR), modulus of elasticity (E), and work to maximum load (W).

The MOR is the ultimate bending strength of a material. Thus, MOR describes the load required to cause a beam to fail. The E quantifies this behavior and shows the material's elastic resistance to deformation under load. The E can be measured from the slope of the linear portion of the stress-strain relationship from zero to the part that linear relationship is finished which called proportional limit. In this study E was calculated as if the stress distribution across beam is linear. It means that the E can be calculated from the stress-strain curve as the change in stress causing a corresponding change in strain. Stiffness ($E \cdot I$), often by mistake, is thought as the same as E . However, E is depending on just a material property, while stiffness depends both on the material and the size of the beam.. Work to Maximum Load (W), is the amount of work needed to actually fracture or fail a material. In fact, it is an amount of energy which is required to fracture the material and it has similarity with toughness. W is calculated as the area under the stress-strain curve from zero to the ultimate strength of the material (Figure 23). These are classical parameters commonly calculated for evaluation of material mechanical properties. However, as confirmed by literatures the ductility of WPC is changed after accelerated weathering. Ductility is more commonly defined as the ability of a material to deform easily upon the application of a tensile force, or as the ability of a material to withstand plastic deformation without rupture. Ductility also defines as bendability and crushability. When the material shows large deformation before fracture it is called a ductile material. On the contrary, a material without ductility is often called brittle. If two materials have the same strength and hardness, the one that has the higher ductility is more desirable. Ductility of material changes due to different factors. For instance, in most of the materials an increase in temperature will increase ductility.

In order to evaluate this alteration a reliable criteria should be produced. In case of wood, ductility can be measured from stress-strain relationship via different formula (Eq. 10 and 11) where linear proportion of elasticity behavior can be recognized (Figure 22).

$$D'' = \frac{W_t}{W_e} - 1 \quad \text{Equation 10}$$

$$D''' = \frac{D_{max}}{D_{yield}} \quad \text{Equation 11}$$

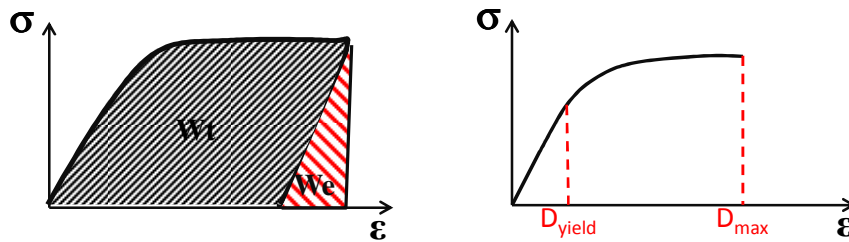


Figure 22- Classic methods for calculation ductility.

However, in our tests the linear part was not that easily separated from the non linear part, so that such indexes were not calculated. Instead we introduced indexes, mostly related to the shape of the stress-strain curve of our composites where elasto-plastic deformation emerges. Afterwards, we tried to evaluate our Ductility indexes in relation to other mechanical indexes to see which one shows more related changes to mechanical behavior. In this regard, two indexes for ductility (D and D') have been introduced (Figure 23) obtained from Eq. 13 and 14.

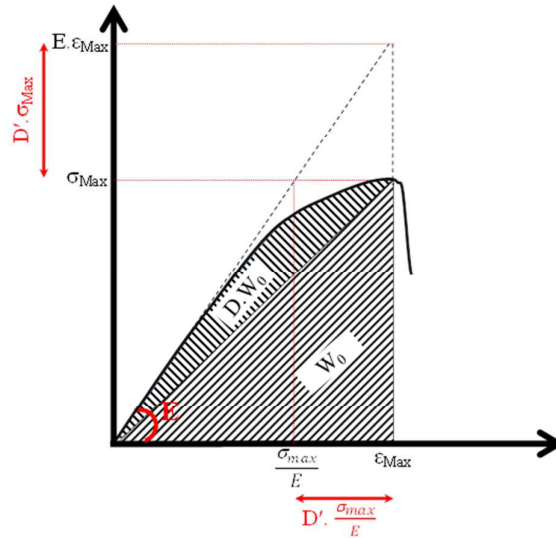


Figure 23- Examples of the relationship between a typical stress-strain diagram and some mechanical properties obtain from it.

$$W = \int \sigma \cdot d\varepsilon \quad \text{Equation 12}$$

$$D = \frac{W}{W_0} - 1 \quad \text{Equation 13}$$

$$D' = \frac{E \times \varepsilon_{\max}}{\sigma_{\max}} - 1 \quad \text{Equation 14}$$

These two values of ductility have different meaning. The first one (D) is mostly calculated from W_0 and W . W_0 , calculated as $\sigma_{\max} \cdot \varepsilon_{\max} / 2$, would be observed if we had perfect fragile material (complete linear relation between strain and stress) and W is the area beneath the curve of strain-stress from zero to maximum stress value. If $W = W_0$ ($D = 0$) it means that the material is fragile and if $W > W_0$ ($D > 0$) it is ductile.

The second index of ductility (D') comes from the relation of strain, stress max and elasticity modulus. Thus, change in D' is related to the change in E . It means that if the E changes with the same ε_{\max} , σ_{\max} , W_0 , W and D , we can have different D' (Figure 24). In case of a perfectly fragile material, we would have $D' = 0$, in case of elasto-plastic behaviour $D' > 0$.

Figure 24 shows how D and D' can describe different shapes of non-linear stress-strain curves. In Figure 24a the same D' is obtained for different values of D , in Figure 24b different D' values are obtained for the same D .

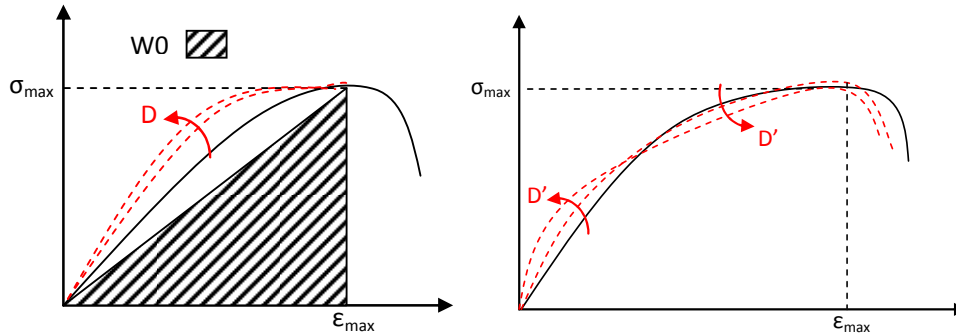


Figure 24- Schematics of strain-stress relationship curve and its relation with ductility (D and D') and how ductility can be changed in relation to other variables.

In this study the samples are tested by 3 points bending at ambient conditions of 20 ± 2 °C and 65 ± 5 % relative humidity with an MTS machine. As mentioned before, weathered surfaces are exposed to tension stress and the bottom surfaces to compression stress. The maximum flexural stress (σ_{max}), maximum flexural strain (ϵ_{max}), E , W , D and D' are recorded for each test.

4.4.2. VIBRATION TEST

Vibrational analysis is a simple and efficient way of characterizing the elastic properties of a material. In the field of wood science, natural vibration analysis is used to measure the longitudinal and the shear modulus of elasticity of prismatic beams. Also internal friction also called damping ($\tan\delta$) from decrease of frequency can be measured by this method.

In this study the vibration test was carried on weathered and un-weathered samples by the device which is based on the study of the vibrations properties and works with software called BING at CIRAD, France. This method is based on the specific modulus obtained from ratio of the modulus of elasticity to the density of the material and is equal to the square of speed and corresponds to the propagation speed of a signal in the material. This relationship indicates the existing connection between mechanical properties and vibratory behavior (Aramaki et al. 2007). Spectral analysis of longitudinal or transversal natural vibrations permits to identify the natural frequencies of a beam from its response to an excitation pulse, applied to one end to simultaneously seek all vibration modes. The first mode called fundamental mode always has the higher frequencies. From analyzing the recorded acoustic signal by using this fundamental simple mode developed by Bernoulli or by using more elaborate model developed by Timoshenko, the mechanical properties of the tested sample can be measured. Both models of Bernoulli and Timoshenko are based on the assumption of a homogeneous material. The difference is that Bernoulli's model does not take into account the shear between the beam's straight sections, in other words beam's sections stay perpendicular to the beam's neutral line. While the Timoshenko's model takes into account a shear angle that reflects that straight sections are not perpendicular to the neutral line (Aramaki et al. 2007). For WPC we used both methods. However, since the shear modulus is very low in WPC, we applied Bernoulli's model.

In the Bing device the samples are placed on the two elastic supports. These supports let the samples have free vibration by a simple impact on one end (Figure 25). For this purpose a pendulum, consisting of a nylon cord (30 cm long) and a metal ball (diameter 14mm, mass 12g), was set in motion to trigger a vibration in the longitudinal direction of the specimen by hitting the end. At the other end, a microphone records the vibrations and transmits them via an anti-aliasing filter (low-pass) and an acquisition card to the digitized signal, processed by Fast Fourier Transform (FFT) to interpret the information in the frequency domain. The mathematical processing of selected frequencies (calculation and linear regression) is software-made from the geometrical characteristics and the weight of the sample (Brancheriau et al. 2006).

The determination error was less than 0.1% for the fundamental frequency and 4.3% for the damping coefficient of the first mode.

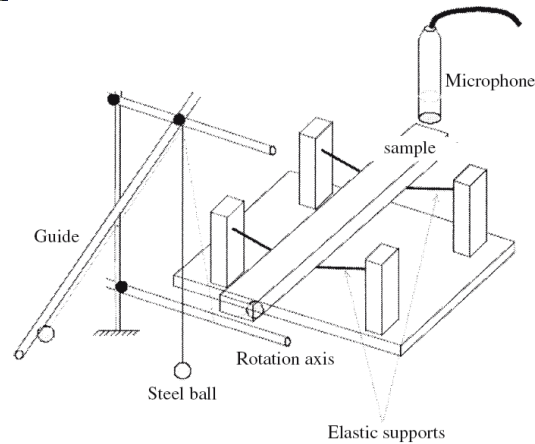
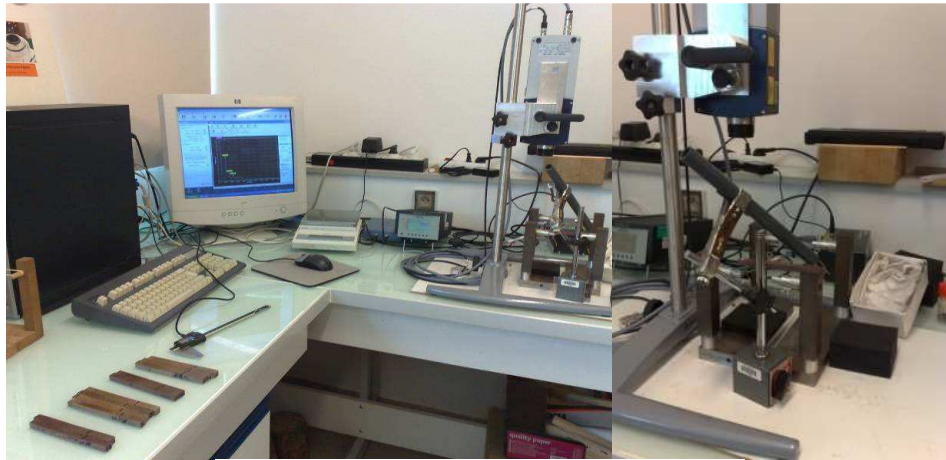


Figure 25- Experimental setup for BING dynamic tests (Brancheriau et al. 2006).

The excitation spectrum is given by the Fourier transform of the impact force, so that the shorter the impact, the broader the spectrum excitation. The temporal signals are characterized by a short onset and a fast decrease, with durations generally not more than 1s. Their spectra are composed of emergent resonances that do not overlap much (Figure 20). As shown by the time frequency representation, the damping of these spectral components is frequency dependent, Thus, the damping is proportional to the square of the frequency. The high frequency components being more heavily damped than the low frequency ones (Aramaki et al. 2007).

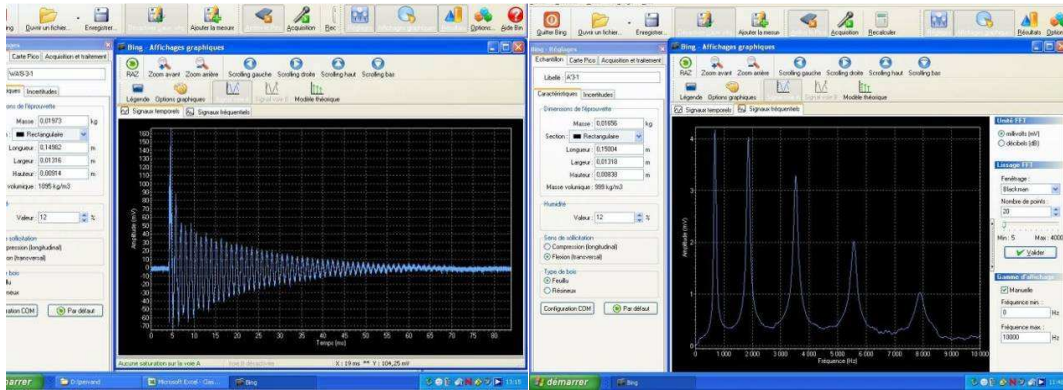


Figure 26- Software of Bing software. The spectral representing the time-frequency relation of a typical sound obtained experimentally.

In this study flexural vibration tests with sampling frequency of 312500 Hz carried on more than 3 repetitions. All tested samples are stabilized in a climatic chamber (20°C, 65% RH). Transversal modulus of elasticity (perpendicular to the axis direction of the sample) is analyzed. As mentioned before record signals are primarily determined by the frequency of the first vibrational mode.

4.4.3. INDENTATION TEST

Indentation is a method, based on force and displacement, for measuring the hardness of materials. In fact, the hardness of a material is its resistance to deformation, indentation, scratching, and to abrasion. In this device the hardness measured by penetration a sharp object called indenter to the surface. In this study macro-indentation test is used by means of a flat punch indenter (on an MTS machine) (Figure 27). The flat punch had a diameter of 2mm and the composites samples thickness is 9mm. The loading stage was carried out by using a pre-load of 100N, and test rate of 0.1mm/min until a maximum penetration depth of 3mm. Meanwhile, the unloading carried on from 0.5mm thickness. It means that the loading continues until the indenter reach 0.5mm and then indenter start to go up until the force on the surface reach approximately zero, then again indenter after short pause starts to go down. The pre-load value was optimized to reduce the initial non-linearity of the curve which is due to the absence of a perfect parallelism between sample and indenter surface. The part after this part of the loading stage is approximately linear. By increasing the penetration depth, the indentation curve approaches a plateau which corresponds to a significant material flow (Figure 27).

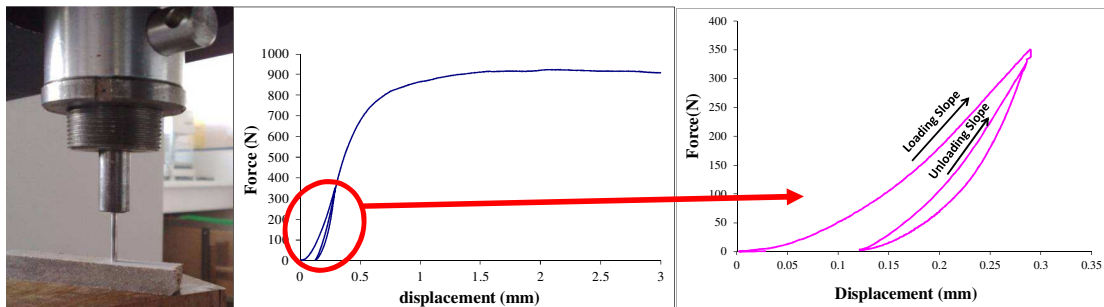


Figure 27- Diagram of relation between force and displacement of indenter into depth of 3 mm of the samples surface.

During an indentation test the response of a polymeric material is initially elastic for the small part. When the stresses exceed the elastic limit, plastic flow occurs and a permanent deformation arises. At this stage, the plastic yield stress and the elastic modulus govern the elasto-plastic response to indentation. So the slope of loading part of curve with macro flat

punch indentation contains the elastic modulus inside it and we couldn't measure elasticity apart from plastic behavior. However, we can try to find effect of weathering on the total change in elasto-plastic response. Therefore, two slopes were measured in this study one from the first loading part (K_L) and second from the unloading part (K_U) which mostly in literature represent the E of the viscoelastic material (Figure 27). Also maximum force (F_{max}) and energy at rupture point (W_{ind}) are obtained by this device.

4.4.4. STATISTICAL ANALYSIS

Loss in mechanical properties caused by weathering has been well proved and can limit the performance of WPC in structural applications. However, measuring of this MOE loss in WPC board requires flexural test which is destructive. Acoustic vibrations measuring system is mostly used with the aim of evaluating the mechanical properties and investigation of defects in a non-destructive way (NDT). In this study, it has been tried to compare the results from three points bending test to results obtained from vibration as NDT test and to indentation test as semi-destructive test, in order to see the efficiency in NDT to evaluate the effect of weathering on mechanical properties of WPC. Another reason is to present the best index in non-destructive test which is best reflecting the weathering effects on mechanical properties.

For analyzing the mechanical data 2 different software are used: Statistica and SPSS. Statistica is used for conducting the Principal Components Analysis (PCA) and SPSS used for measuring correlation and variance analysis (ANOVA).

PCA is a way of identifying patterns in data, and expressing the data in such a way as to highlight their similarities and differences. In simple word it is a simplified representation of the matrix of correlation. We used that to visually explain the relationship and correlation between variables. PCA is a powerful tool for analyzing data without much loss of information. Thus, we used correlation and PCA for analyzing the variables, while ANOVA was used for analyzing the effect of treatments on WPC properties. To make this analyzes less complicated, analysis are conducted only on group A'0, B'0 and C'0 to have the effect of lignin content level and weathering as two independent factors.

ANOVA analysis on all groups will help us to look closer to details and focus more on effects of weathering and delignification on each variable. Thus we conduct ANOVA by means of SPSS for all mechanical variables and also color indexes. In this analyze weathering and each treatments (lignin content, pigmentation, and coating) have been considered as the principal factors and A'0 group and un-weathered samples considered as controls. P values related to weathering, level of lignin content and other treatments, as well as the interaction between these factors and weathering have been quantified by the magnitude of these effects comparing with controls..

4.5. Biological tests

4.5.1. FUNGAL RESISTANCE TEST

Biodegradation towards Basidiomycete fungi was evaluated using an agar-plate test method. Samples of dimensions 25*12*9 mm (length, width, thickness) were dried at 103°C, weighted, gamma ray sterilized, and exposed to cubic decay fungi (*Coniophora puteana*, strain BAM Ebw. 15). For control, 30*10*5 mm (L,R,T) pine sapwood (*Pinus sylvestris*) samples were used. 1 control and 2 samples were placed in each of the malt-agar plates (40 g malt/L, 20 g agar/L) (Figure 28). After 12 weeks at 22°C, 65% RH, samples were removed, cleaned and dried at 103°C. The surface was qualitatively assessed, and the weight loss (WL), moisture content at the end of fungal test (MC) as well as color (L^* , a^* , b^*) were measured.



Figure 28- Agar-block test plates for WPC samples and controls in beginning of the test.

Pine sapwood (50*25*15 mm, L, R, T) were also used as virulence controls, in the same conditions.



Figure 29- Agar-block test plates for WPC samples and control after 1 month.

4.5.2. *TERMITES RESISTANCE*

Resistance towards termites (*Reticulitermes flavipes, ex santonensis*) was also evaluated according to the guidelines of EN117. Samples of dimensions 25*12*9mm (length, width, thickness) were exposed to 250 termite workers, 5 nymphs and 5 soldiers for 8 weeks (27°C, 70% RH). Pine sapwood samples (50*25*15 mm, L,R,T) were used as controls. At the end of the test, the survival rate of termites, the weight loss of the samples and their moisture content at the end of the tests were calculated. Visual rating according to EN 117 was not selected as criterion.

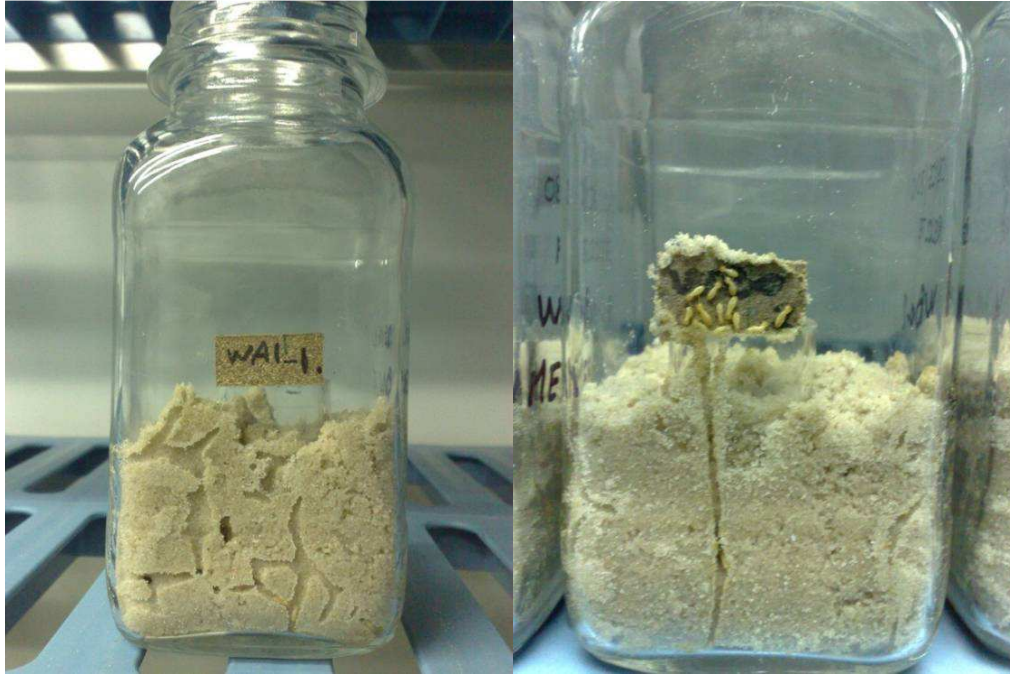


Figure 30- Termite test plate in beginning of the test and two weeks after test started.

4.5.3. MOISTURE ABSORPTION

WPC materials will absorb variable amounts of moisture. However, most absorption will be at the surface which can cause further more biodegradation. Later absorption by WPC materials may lead to a number of unpleasant events. Therefore, in this study we also measure the moisture absorption of our different groups.

In this study clear coating was applied just on one surface of the samples. Therefore soaking them into the water might not show the efficiency of the coating or give us the expected results. The important data for our study was the amount of moisture which samples absorbed before and after weathering and during fungal media exposure. Thus, we used contact angle test for weathered and non-weathered samples and for samples exposed to fungi we measured moisture content and dimension stability before and after exposure, which was measured as follows.

For moisture absorption before fungal test, samples were conditioned at $20 \pm 2^\circ\text{C}$ and $75 \pm 5\%$ relative humidity for two months and after this period the weight and dimensions, length, width and thickness of each specimen was measured. Then dried for 24h in $103 \pm 2^\circ\text{C}$ and EMC of all samples were measured. Each value obtained represented the average of at least twelve samples. Moisture content was calculated according to the following equation:

$$\text{Moisture Content (MC)} = \left(\frac{M_W}{M_D} - 1 \right) \times 100 \quad \text{Equation 15}$$

Where MC is the Moisture Content in percentage, and M_W and M_D are the sample weights before and after drying. After fungal test (12 weeks), the same measurements were carried out on the samples. The values of the swelling were calculated from dimension changes occur from moisture up take during fungal exposed. Shrinkage was calculated from wet and dry dimensions of samples exposed to fungi.

$$\text{Swelling (SW)} = \left(\frac{V_w}{V_D} - 1 \right) \times 100 \quad \text{Equation 16}$$

Where V_W is the initial volume of the sample after remove from fungal test plates and V_D is the volume of the dried samples after fungal test.

$$\text{Shrinkage (SH)} = \left(1 - \frac{V_{D1}}{V_{D2}}\right) \times 100 \quad \text{Equation 17}$$

Where V_{D1} is the volume of the dry sample before expose to fungal test plates and V_{D2} is the volume of the dried samples after fungal exposure.

The following parts are presenting “results and discussion” for each aspect of this study. In these sections we strive to present the results through a more comprehensive approach. Initially, we will explain the chemical changes for the reader to obtain the general idea about the basic information on each group and how their nature changes through weathering. Afterward, the effect of different treatments and how they change the process of weathering on different aspect of WPCs properties will be discussed, individually in each chapter.

All the mean and standard deviation of quantitative results obtained for each part which will be discussed in different chapter are presented at the end in Annex A in three different tables. Also results of ANOVA which has been used to assess the significance of the effect of different treatment and weathering and their interaction on color and mechanical parameters presented in two different tables in Annex B.

5. Analysis of chemical properties

5.1. Chemistry of fibers (before board production)

Since we used organosolve pulping on bagasse fibers in our study, we tried to find the changes that occurred due to delignification methods we have used, because most of WPC properties result from fibers characteristics. Comparison of chemical changes due to different solvents and levels of delignification on bagasse fibers are shown in Figure 31. In this figure, we can see that the process of the chemical changes caused by organosolve pulping with ethanol (B) and MEA (B' and C') is quite different. Mostly, the peak related to OH vibration in 3300 cm^{-1} shows high increase in B'0 and C'0 fibers, while it is decrease for B0. It is the same for peak related to C-O vibration in 1030 cm^{-1} wavenumber. This can be due to the more separation of cellulose from lignin which increases the opportunity of higher hydroxyl bond and recrystallization of cellulose.

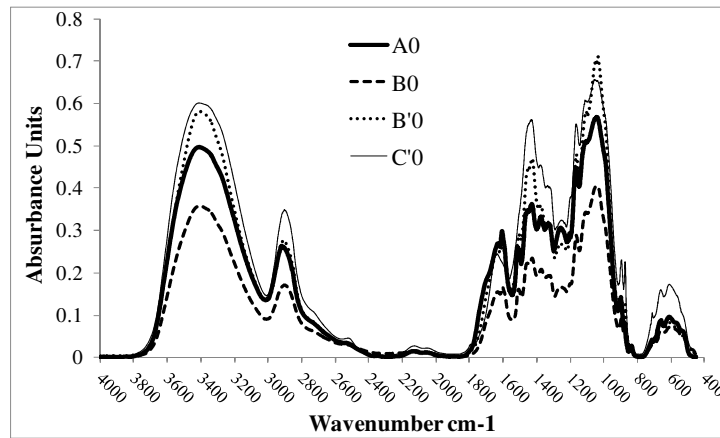


Figure 31- FTIR spectroscopy of bagasse fiber in form of: Control (A0), delignified by ethanol until 9% lignin content (B0), delignified by MEA until 9% lignin content (B'0) and delignified by MEA until 5% lignin content (C'0).

Thus, the crystallinity of cellulose in delignified fibers has been studied. The allomorph composition has been found to be species specific and may change during pulping process (Gümüşkaya et al. 2003). This matter is important, because the hydrogen-bonding pattern is different for the different cellulose allomorphs and therefore, the mechanical properties ought to be different (He et al. 2007). Thus, the peaks in the range of 710 and 750 cm^{-1} representing I_{β} and I_{α} structures of cellulose, respectively, have been studied (Figure 32). The peak relevant to I_{β} shows an increase in B'0 and C'0 compared to control. This increase is significantly higher in C'0, however for B0 this peak does not exist anymore. No specific peak for crystallized portion of I_{α} has been detected which is normal since this peak mostly appears in dynamic FTIR (Akerholm et al. 2004). However, increase in intensity peak of I_{β} in MEA delignified fibers during extraction of lignin means more I_{α} structure convert to I_{β} during delignification process. It is also confirmed by literature that crystalline structure of cellulose in cotton linters was more affected and become higher (degree of crystallite and crystallite size) in organosolve pulping than in soda and sulfate pulping. This has been attributed to the temperature and pressure in cooking digester which can have a major effect on crystalline structure of cellulose in cotton linters during cooking (Kırcı et al. 1994; Evans et al. 1995; Gümüşkaya et al. 2003) and it was established that triclinic structure of cellulose converted to cellulose I_{β} at $160\text{ }^{\circ}\text{C}$. In current study we fixed the parameters of the digester (time, temperature, pressure) for all sets of fiber, and the temperature was fixed to $130\text{ }^{\circ}\text{C}$. Still, we can see that there is some effect of solvent on the crystallite of cellulose (increase in intensity peak of I_{β}). The monoclinic I_{β} is most thermodynamically stable form of crystallinity of

cellulose since it is not only the most dense, but also invariably tends to be final product in the heat-annealing of all celluloses (Sassi et al. 2000). In case of pulping process with ethanol amine like MEA, researches have proved that during organosolve process the amount of carbohydrates remain stable (Shah et al. 1991) which confirms our results for MEA delignified fibers. It means that in this case cellulose remain untouched and we can explain the increase in peaks in 1039 and 3000 cm^{-1} region by higher crystallinity and new hydrogen bonds in B'O and C'O groups. Then, from this results it can be expected that due to thermal degradation through extrusion manufacture of samples and further accelerated degradation, less changes happen to cellulose component of MEA delignified samples than other samples.

Although fibers of B0 group were delignified with organosolve pulping process using ethanol, the related peaks for I_{α} and I_{β} do not appear in these samples. References showed that ethanol protects carbohydrates against reactions during the cooking processes and recrystallization of amorphous cellulose (Kirci et al. 1994; Evans et al. 1995). These results comply with the results from delignified samples with MEA solvent, but not with alkaline ethanol. Maybe because of the alkaline media, the crystalline chains of the cellulose go through high breakage. Thus, this causes a decrease in the absorbance peak related to the crystallized portion of I_{β} during delignification process with ethanol sample. Thus, in process with ethanol, cellulose is highly affected by chemicals. Decrease in peak of C=O stretch vibration within carbohydrates for B0 group confirm this conclusion. Thus, we obviously can prove by these results that MEA has better effect on cellulose part.

Figure 32- The peak related to cellulose crystallization region and frequency of the aromatic structure vibration.

Moreover, the three different ratios from IR spectra also have been used to study the crystallinity of cellulose (Figure 33

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