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Effect of acetylation and additive on the tensile properties of wood fiber–high-density polyethylene composite

Talel Ben Mbarek[1,2], Laurent Robert[3], Habib Sammouda[4], Bertrand Charrier[2], Jean-José Orteu[3] and Françoise Hugot[5]

Abstract

The wood plastic composites studied in this work are composed of high-density polyethylene matrix and *Pinus pinaster* wood fibers. Despite some interesting intrinsic properties, this wood plastic composite has limited mechanical properties because of the incompatibility between the polar hydrophilic fibers and the non-polar hydrophobic matrix. In this study, the effects of maleic anhydride-modified polyethylene additive, of carbon chains grafted by acetylation and of wood fiber contents on the tensile mechanical properties of the wood plastic composite were studied. Tensile tests were carried out using digital image correlation as an intrusiveness and robust method for strain measurements. Results showed first that the addition of wood fibers made the wood plastic composite stiffer but less flexible. Acetylation improved the interfacial adhesion properties: the Young modulus was increased and a lower strain at failure was reported. The coupling agent also increased the compatibility but mainly in the case where there was no grafted chain. With regard to the carbon chains, the number of grafts improved the elastic properties while their length did not appear to have any influence. Finally, a scanning electron microscope was used to characterize the post-mortem morphology of the fracture surfaces, the results of which supported the observations obtained from the tensile mechanical properties.

Keywords

Wood plastic composite, polyethylene, coupling agent, grafted chains, tensile test, mechanical properties, elastic properties, digital image correlation, micrography, scanning electron microscope

Introduction

Currently, the production of wood plastic composites (WPC) made of thermoplastic matrix and wood fillers such as fibers or flour is obviously increasing in the world.[1] WPC market reaches about 1 million tons annually in North America and some 10,000 tons in Europe.[2 4] In the United States, the request is expected to increase by 10% per annum. This kind of composite material presents many advantages: good performance, low cost, low maintenance, good break resistance, high aesthetical quality such as color and touch and low toxicity. For these reasons, such materials are very attractive. However, poor compatibility between hydrophilic wood fibers and hydrophobic polymer matrices induces low resistance to moisture, a tendency of aggregate during the processing and low

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thermal stability. This is one of the major disadvantages because it often leads to a non-uniform dispersion of fibers within the matrix.

Many studies have been proposed to improve the affinity and adhesion between fibers and thermoplastic matrices. The chemical "coupling" or "compatibilizing" agents are widely used as a solution to strengthen composites containing fillers and fiber reinforcements.[4] In small quantities, these polymer substances are able to treat a surface and make a bond with other surfaces, wood and thermoplastics for example. Also, as another solution, some chemical treatments can be used to modify the properties of plants fibers. Some compounds are known to promote adhesion by chemically coupling the adhesive to the material, such as sodium hydroxide, silane, acetic acid, acrylic acid, isocyanates, potassium permanganate and peroxide. Liu et al.[5] have modified wood–polyethylene (PE) composites through treatment with plasma under different discharge powers to enhance their adhesion properties. The changes in the surface properties of the composites were studied by contact angle, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscope (SEM), atomic force microscope (AFM) and X-ray photoelectron spectroscopy (XPS). FTIR study showed that the polar groups such as hydroxyl, carbonyl and carboxyl were formed on the surface of the treated composites. SEM and AFM results showed that the roughness of plasma-treated samples increased. The XPS analysis indicated that a lot of carboxyl groups were formed. It was shown that these polar groups were beneficial to the adhesion of composites and the shear bonding strength test showed that the adhesion properties of wood–PE composites improved effectively after plasma treatment. Jiang and Kamdem[6] have investigated contact angles and surface energy of wood, as well as interfacial shear strength between wood and polyvinyl chloride (PVC), by modifying the wood surfaces with a copper ethanolamine solution. In their study, it was reported that an increase in surface energy of wood after treatments promoted wetting of PVC on wood surfaces. This treatment allowed the formation of a stronger wood–PVC interphase, which improved the adhesion between wood and PVC, yielding products with enhanced mechanical properties. Keener et al.[7] have studied the effect of maleated coupling agents on agrofiber–polypropylene (PP) by selecting the appropriate balance of molecular weight and maleic anhydride content. For wood–PE WPC, it was shown that new PE couplers could double the tensile strength and triple the impact properties, compared with non-coupled wood–PE blends. To improve the toughness of wood fiber–PP composites and the interfacial compatibility between fibers and PP, Dang et al.[8] used maleic anhydride-grafted polypropylene (PP-g-MAH) and maleic anhydride-grafted styrene-ethylene-butadiene-styrene copolymers (SEBS-g-MAH) as modifiers. It was reported that the mechanical properties of the composites were significantly improved because of the good interfacial bonding between wood fibers and PP when PP-g-MAH and SEBS-g-MAH were added. Gosselin and Rodrigue[9] studied the effect of maleic anhydride polypropylene (MAPP) coupling agent on injection molding of WPC based on post-consumer high-density polyethylene (HDPE)–PP blends and birch wood fibers. The morphological analysis showed that the skin thickness changed with MAPP content (0–10 wt% of wood content). Adhikary et al.[10] examined the properties of wood–plastic composites made using either recycled or virgin HDPE with wood flour as filler. It was shown that 3–5 wt% MAPP added in the formulations had significantly improved both the stability and mechanical properties, by improving the interfacial bonding observed from microstructure analysis of the fractured surfaces. Cui et al.[11] also used MAPP coupling agent together with three types of surface treatments to improve the interfacial adhesion between the wood fiber and the recycled HDPE. Wood fibers surface treatments, included an alkaline method, a silane method and an alkaline followed by silane method, were evaluated using FTIR technique. It was shown that WPC material with wood fiber treated by the alkaline followed by silane treatment method together with the MAPP coupling agent induced the best mechanical properties.

In addition, few studies used new methods such as non-contact optical method to analyze the mechanical properties and the effect of coupling agent and wood treatment of WPC. Godara et al.[12] studied the influence of additives on the mechanical behavior and on the strain localization in wood-reinforced PP composites during tensile tests using digital image correlation (DIC). It was found that the addition of MAPP coupling agent proved to be more efficient than acetylation by increasing overall mechanical performances such as stiffness and strength and had induced global microstructural homogeneity. In a previous article,[13] the influence of wood contents and coupling agent on mechanical properties of wood-fiber–HDPE composites was studied by providing full-field measurements by stereo-correlation (3D-DIC). This technique allowed us to characterize the macroscopic elastic properties of the WPCs and made it possible to observe strain spatial distributions. It was shown that the degree of the strain heterogeneity increased both with wood contents and strain levels, as did the damage and thus led the loss of mechanical properties.

In this article, the analysis of the mechanical behavior of WPC based on HDPE and *Pinus pinaster*

sawdust was conducted by using tensile tests and microstructural observations by SEM. The effects of: (a) wood fiber acetylation that led to the various lengths and numbers of carbon chains being grafted to the fibers, (b) maleic anhydride polyethylene (MAPE) additive as coupling agent and (c) wood percentages on the mechanical properties and failure morphologies were investigated.

Materials and experimental method

WPC materials

In this study, the polymeric matrix of the WPC was a HDPE of co-polymer grade with a narrow molecular weight distribution (trade name Rigidex® HD5218EA from BP Solvay®) and with a melt flow index of 18 g/10 min (190°C, 2.16 kg). Additive coupling used as compatibilizer was a MAPE (Orevac® 18307 from Arkema®) with a melt flow index of 2.5 g/10 min (190°C, 2.16 kg). When it was used, MAPE was added at a level of 3% wt.

The size characteristics of the wood fiber sawdusts of *P. pinaster* were determined using an optical scanning device. A MorFi LB-01 fiber analyzer, produced by Techpap (France) was used to determine the size distribution of the wood fibers (see Table 1). The very small elements of length lower than 30 μm, called fines, represented about 76% of the total mass of all analyzed elements. Without considering fines, the mean size was 220 μm, the mean thickness was 30 μm and the mean curvature was 4.5%.

Treatment of wood fibers

Before the acetylation, the wood fibers are subject to an extraction process to eliminate the extractable substances from wood (terpenes, lignanes, stilbenes, and so forth) as these substances can disrupt the grafting reaction by acetylation of lignocellulose.[14] Prior to use, using an oven tunnel rotary, the fibers were vacuum dried until moisture content was <0.5%. These fibers were then treated with a solution of pure acetic acid with one drop of sulfuric acid for 1 h at room temperature and then washed with distilled water until a pH of 9 was reached. The fibers were then placed in an oven at 104°C for 24 h. The density of different wood fibers used varied from 1.45 to 1.49 g/cm^3.[15 17] The esterified fibers were then re-dried under vacuum and weighed to determine weight percentage gain.[15] Two percentages of wood fibers were considered in this work: 10% and 30%. The denomination of the grafted WPC was done by the addition of the number of carbons constituting the grafted chains, followed by the gain of mass of the wood fiber after the reaction of acetylation. For example, WPC with 30% of wood fibers and grafted by chains of three carbons (–O–CO–CH_2–CH_3) with a gain of mass of the wood fibers of 10% were named WPC3Cgm10-30, simplified to M_1-30. For the grafted specimens, mainly one family of gain of mass of the wood fibers was considered in this study: 10%. The different formulations of grafted WPC are shown in Table 2. Besides the 12 formulations with grafted chains, 6 for 10% wood and 6 for 30% wood (see Table 2), were added 2 standard formulations without grafted chains and containing 30% of wood fibers: they were referenced to as aWPC30 and WPC30, respectively, with or without 3% MAPE additive.

Table 1. Size distribution of wood fibers.

Size (μm)	Mass ratio (%)
<30	76
30 150	9.7
150 250	6.5
250 300	1.5
300 450	2.5
450 680	1.3
680 1030	1.2
>1550	1.3

Processing of WPC samples

After wood fiber drying, premixed wood–HDPE pellets were obtained by extrusion process in a single screw extruder. Then $4 \times 10\,mm^2$ cross-section tensile specimens were produced by injection molding. Parameters were set at: 200°C (injection temperature), 160°C (zone 1), 170°C (zone 2), 180°C (zone 3), mold temperature from 50°C to 70°C, injection pressure at 100 bar, injection speed at 47 mm/s, speed of screw at 60 r/min, holding time at 6 s and cooling time at 25 s.

Experimental methods

Tensile tests were based on the standard guide for evaluating mechanical properties of WPC products (ASTM D 7031-04). They were carried out onto a set of three specimens for each test using a universal testing machine device (INSTRON 5800 R) with a crosshead displacement velocity equal to 2 mm/min. Prior to testing, all specimens were conditioned at a temperature of 20°C. Tensile specimen has the following dimensions:

Table 2. Formulations of treated fibers. True values of wood fiber gain of mass, determined by reverse-phase chromatography in laboratory conditions at the Laboratoire de Rhéologie du Bois de Bordeaux (LRBB, Cestas, France), are also indicated.

Chemical reaction on wood	Symbol	Nomenclature	Gain of mass (%)
Wood O CO CH_3	M_0	2Cgm10	12.5
Wood O CO CH_2 CH_3	M_1	3Cgm10	11
Wood O CO $(CH_2)_2$ CH_3	M_2	4Cgm10	10
Wood O CO $(CH_2)_8$ CH_3	M_3	10Cgm10	12
Wood O CO $(CH_2)_{16}$ CH_3	M_4	18Cgm10	12.6
Wood O CO CH_2 CH_3 + MAPE	M_5	3Cgm10MAPE	12.8

MAPE: maleic anhydride polyethylene.

10 mm width, 4 mm thickness and 150 mm length. Strain measurements have been performed using the DIC technique, as described subsequently.

It is known that due to the non-linear behavior of WPC, mechanical properties such as modulus of elasticity (MOE) are difficult to obtain. In their study, Hugot and Cazaurang[18] have concluded that the tangent MOE was more appropriate to calculate tensile MOE. In this study, the non-linear strain–stress relationship was modeled in the range where the stress remains monotonous by the Maxwell–Bingham model

$$\sigma \quad a(1 - \exp(-b\varepsilon)) \tag{1}$$

where a and b are material parameters. A least-square fitting was carried out between the experimental curve and the Maxwell–Bingham model in order to identify the sought parameters. The MOE was then calculated as the first derivative for zero strain of the fitted model of equation (1), i.e. MOE $\quad a \times b$.

In a previous study,[13] DIC has been used for characterizing the mechanical behavior of wood fibers–HDPE composites and for analyzing the spatial strain distributions. It has been shown that this technique, in addition to providing full-field measurements, can give confident average strain measurements very close to those obtained by mechanical extensometers, with the advantages that vision-based measurement is contactless and, in our concern for highly heterogeneous materials, not dependent on the position of the sensor. Details on the DIC technique can be found in the study of Sutton et al.[19] In this study, 3D-DIC, also known as stereo-correlation, was used instead of 2D-DIC because it has been shown in the study of Ben Mbarek et al.[13] that during the tensile tests and due to the injection process, 3D shape and out-of-plane displacements of the specimens must be taken into account for an accurate planar strain measurement. It is recalled that the 3D-DIC method, which is based on stereovision (two cameras) and DIC for matching the image-points, allows to obtain the 3D displacement field. The 2D surface strain tensor is post-processed by differentiation. In the experiments, the stereo-rig was composed of two 8-bit QICAM® (QImaging) CCD cameras with 1360×1036 pixels resolution, equipped with Nikon 50 mm aperture 11 lenses. Calibration and image processing were carried out with the assistance of the Vic-3D® commercial software.[20] For improving the measurement, a random black-and-white speckle pattern was spray painted on the surface of the specimens. The DIC parameters were as follow: region of interest, $60 \times 10\,\text{mm}^2$; magnification factor, 16.5 pixels/mm; subset size, 19×19 pixels and strain spatial resolution or optical gauge size, $1.5 \times 1.5\,\text{mm}^2$. It has been shown in another study[21] that strain standard uncertainty can be estimated to be about 10^{-4} in similar experimental conditions and better that 10^{-5} for averaged strain, calculated in this work as the arithmetic mean of all the strain values in the region of interest.

For the morphological studies, the fracture surface of the sample was sputter-coated with gold deposit before examination to have a better observation with an Environmental Electron Scanning Microscope (ESEM) FEI/Philips FEG XL30.

Results and discussion

Mechanical properties of the samples

The root cause of the various observed morphological and chemical local behavior is due to the interaction between the polymer matrix and the surface of the wood fibers during the injection processing. These features can also be analyzed at the macroscopic level by evaluating the mechanical properties of the composite material. In this section, the effects of the carbon chains grafted and of the addition of MAPE on the

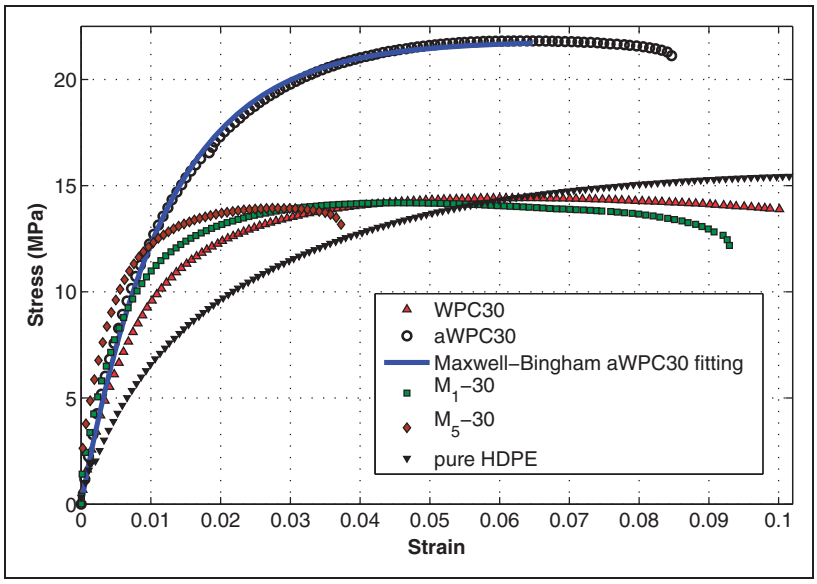

Figure 1. Tensile stress strain curves of HDPE wood fibers composite.
WPC: wood plastic composites; HDPE: high-density polyethylene.

Table 3. Modulus of elasticity (MOE), maximal stress σ_{Max}, modulus of rupture (MOR) in tensile and strain at failure for the 30% wood content WPC formulations. Values in parentheses are the standard deviations from all experiments.

	Pure HDPE	WPC30	aWPC30	M_1-30	M_5-30
MOE (MPa)	756	1697 (213)	1761 (51)	2338 (198)	3048 (397)
Maximum stress σ_{Max} (MPa)	15.5	13.9 (0.7)	21.8 (0.01)	15.1 (0.9)	13.8 (0.7)
MOR (MPa)		12.1 (1.2)	20.8 (0.37)	13.5 (0.76)	13.4 (0.8)
Strain at failure (%)		10.6 (0.9)	9.6 (1.6)	5 (0.2)	3.9 (0.3)

HDPE: high-density polyethylene; WPC: wood plastic composites.

mechanical properties at room temperature are studied. At this stage, only the WPC formulations containing 30% of wood fibers were investigated: the two standard formulations (WPC30 and aWPC30, with additive) and the two acetylated formulations with three carbons (M_1-30 and M_5-30, with additive). For a comparison, a specimen of pure HDPE was also tested. Figure 1 shows some stress–strain curves of these HDPE–wood fibers composite samples under tensile loading. As expected, the tensile curves showed a global non-linear behavior. As an illustration, a fitting of the Maxwell–Bingham model of equation (1) for the aWPC30 formulation was also plotted in Figure 1. Some mechanical properties were deduced from these curves: the MOE calculated from the fitting of the experimental curve by the Maxwell–Bingham model as MOE ab (see above), the maximum stress σ_{Max} reached by the specimen, also called the ultimate tensile strength, the modulus of rupture (MOR) in tension evaluated by the stress value at failure of the specimen and the maximum strain at failure. These properties are shown in Table 3. It was observed first that the pure HDPE clearly presented the lower MOE without rupture at the maximum measured strain (25%): the pure HDPE had a MOE value of 756 MPa while the MOE of the WPC30 formulation was 1697 MPa. The addition of wood fibers led the composite material to become stiffer;[13,22] however, the maximum stress σ_{Max} could decrease. Moreover, composites without carbon chains grafted (WPC30 and aWPC30) exhibited clearly a lower MOE and a strain at failure almost twice that of the ones with carbon chains grafted of three carbons (M_1-30 and M_5-30). It was also observed that the addition of MAPE to the composite, either with (M_5-30) or without carbon chains grafted (aWPC30), increased the MOE of the composite: the MOE of the M_5-30 specimens was almost 30% higher than that of the M_1-30 specimens, and the MOE of the aWPC30 specimens was almost 5% higher than that of the WPC30 specimens without additive. This could be explained by the

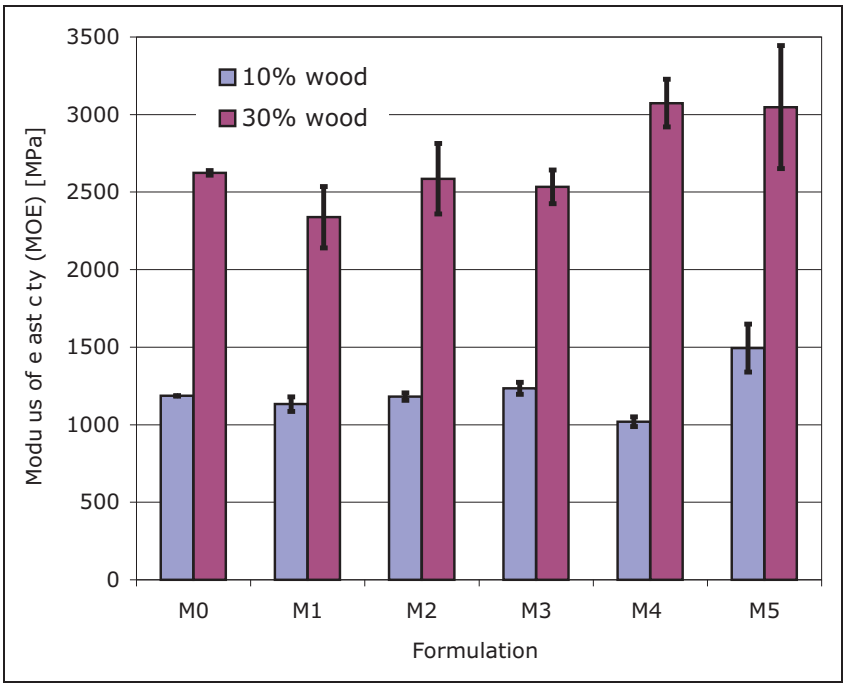

Figure 2. Modulus of elasticity obtained from the tensile tests performed for each grafted chains formulation.

formation of ester bonds between the anhydride carbonyl groups of MAPE and the hydroxyl groups of wood fibers.[22] Furthermore, the MOR in tensile test ranged from 12.1 to 13.5 MPa for all formulations, which was much less variable than the MOE excepted for the aWPC30 formulation for which a very significant value of 20.8 MPa was measured. The same observations could be made concerning the maximum stress. In fact, this stress value is more related to the fiber matrix interface performance than the MOE, which is delimited by the elastic linear domain defined at very low stress level for this kind of composite materials.[18] These results emphasize, first, that the addition of 30% wood fibers greatly improved the elastic properties of WPC and the grafting of carbon chains enhanced the interfacial adhesion,[12] and second, that the addition of MAPE increased compatibility between the hydrophobic matrix and the hydrophilic wood fibers.

Effect of the length of the carbon chains on the mechanical properties

In this section, the results of tensile tests of specimens containing several carbon chain lengths and with 10% or 30% of wood fiber are discussed. Figure 2 shows the MOE for the six formulations of carbon chains grafted and for the 10% or 30% of wood fiber. As no rupture was reached for the 10% wood fiber content, at least for moderate strain values, i.e. less than 25%, it was chosen to plot the maximum stress values reached by all the formulations (tensile strength) instead of the MOR. Results are presented in Figure 3.

Results showed that the increase of wood content led largely to improvement in the elastic properties,[23] whatever the formulation. Moreover, the use of MAPE additive (M_5) seemed to enhance this effect but this was less noticeable that for the formulations without carbon chains grafted: values of MOE obtained for the M_5 formulations, whatever the wood content, were not much higher than the others. The MOE of the different formulations without MAPE was found to lie in the range from 1020 MPa (M_4) to 1235 MPa (M_3) for 10% of wood content and from 2338 MPa (M_1) to 3074 MPa (M_4) for 30% of wood content. On the one hand, the MOE did not really increase with the length of carbon chain: for example the M_0-30 sample presented a higher MOE than the M_1-30 sample (see Figure 2). This indicates that the length of the chains did not influence the elastic characteristics significantly. On the other hand, the impact of the carbon chains was more pronounced for the 30% wood samples than for the 10% wood samples.

Considering the maximal stress plotted in Figure 3, it decreased slightly by around 10% with the increase of wood content. In addition, whatever the wood content, σ_{Max} increased with the length of carbon chain (without MAPE) at least from the M_0 to the M_3 formulations, σ_{Max} for the M_4 formulations then showing a small decrease. The M_5 formulations (with MAPE) presented the lower values of σ_{Max}. These results showed that the

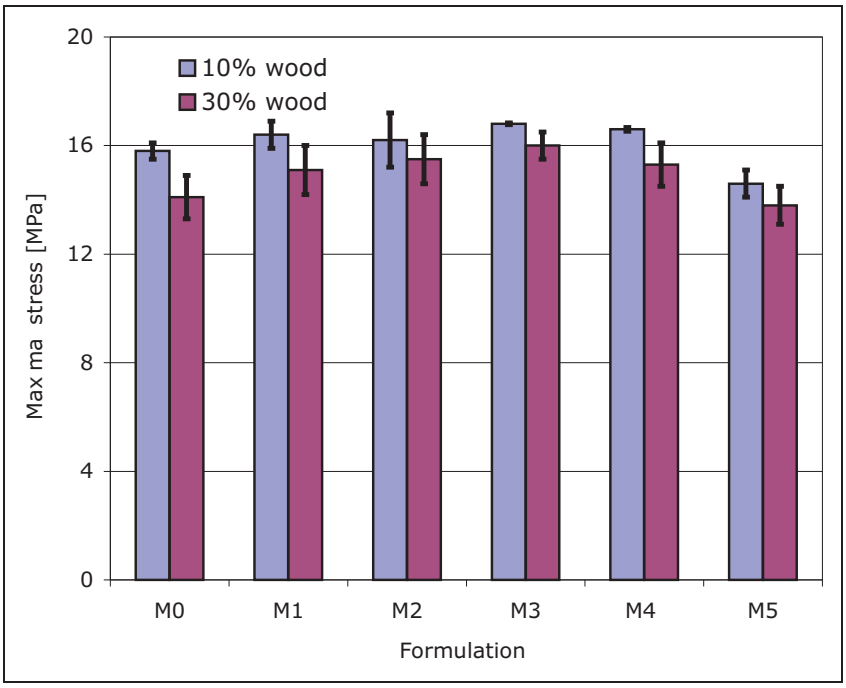

Figure 3. Maximal stress obtained from the tensile tests performed for each grafted chains formulation.

Table 4. Modulus of elasticity (MOE) and maximal stress σ_{Max} for WPC formulations with 10% or 20% gain of mass for the carbon chains grafted, and for 10% or 30% wood content. Values in parentheses are the standard deviation values from all experiments.

	3Cgm10 (10% gain of mass) 10% wood	3Cgm20 (20% gain of mass) 10% wood	3Cgm10 (10% gain of mass) 30% wood	3Cgm20 (20% gain of mass) 30% wood
MOE (MPa)	1133 (47)	1266 (124)	2338 (198)	3099 (315)
Maximum stress (MPa)	16.4 (0.5)	16.2 (0.3)	15.1 (0.9)	15.3 (0.8)

WPC: wood plastic composites.

larger the length of the carbonaceous chain, the more the stress the composite could take. However, what is important to keep in mind is that as the gain of mass was almost 10% for all length of grafted chains, their number decreases as their mass (or length) increases. It was thus difficult to emphasize if it was preferable for the stiffness of the WPC to promote a small amount of long carbon chains or a large amount of small ones.

Effect of the number of the carbon chains on the mechanical properties

In order to evaluate the influence of the number of grafted chains on the mechanical properties, we conducted some experiments with formulations that were made up of a gain of mass of the wood fiber after the reaction of acetylation of around 20% instead of 10%; that means that there were twice as much of grafted chains. This was done only for chains of three carbons (–O–CO–CH_2–CH_3). Results are presented in Table 4 for 10% and 30% wood content. In both cases of wood content, it appeared that the number of grafted chains improved the MOE of the composite by 12% (32%, respectively) for 10% (30%, respectively) of wood fibers. As a result, the more the grafted chains, the more connections between the lingo-cellulosic fibers and HDPE matrix, resulting in enhancing the stiffness of the composite. However, the maximum stress was not influenced by the number of grafted chains.

Microscopic evaluation of the samples

First, microstructure of the fracture surfaces of WPC30 and aWPC30 tensile specimens (without and with additive) were examined using SEM imaging to characterize the morphology of the wood fiber–HDPE interfaces. The SEM was operated at an accelerating voltage of 15 kV, spot 5.0. Figure 4(a) and (b) show a stretching

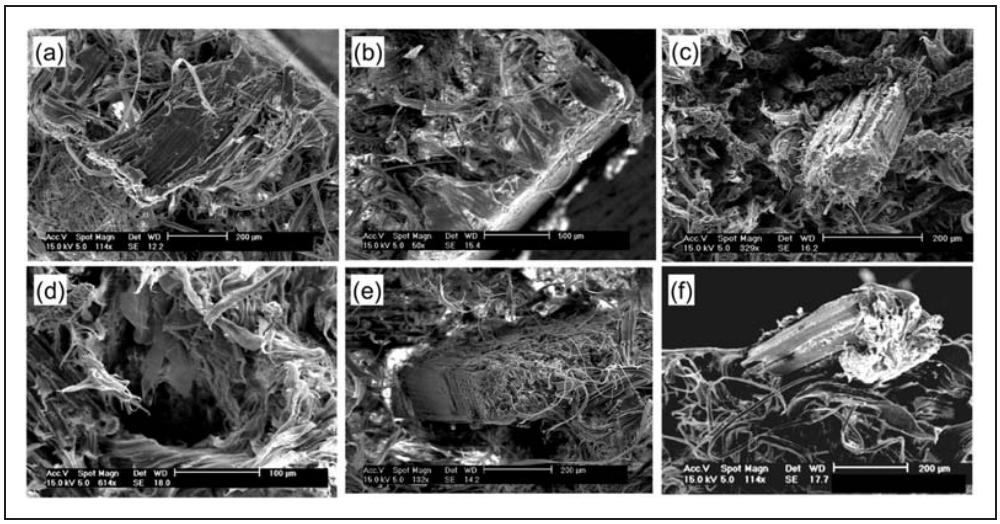

Figure 4. SEM micrographs of fracture surfaces (a) (e): WPC30 sample, (a) 114×, (b) 50×, (c) 329×, (d) 614× and (e) 132×; (f) aWPC30 sample at 114×.
WPC: wood plastic composites; SEM: scanning electron microscopy.

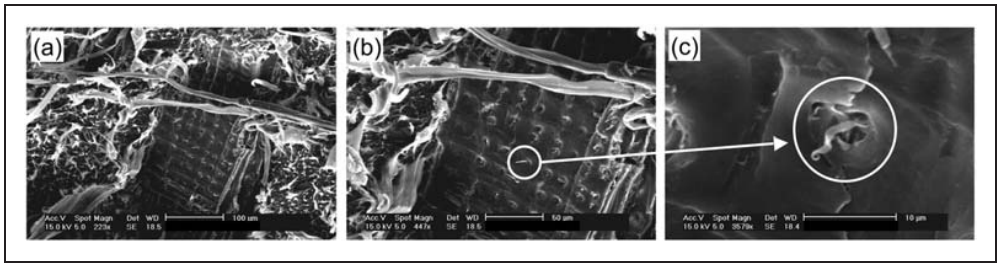

Figure 5. SEM micrographs of fracture surfaces for M_1-30 sample: (a) 223× (b) 447× and (c) 3579×.
SEM: scanning electron microscopy.

of the HDPE matrix before the rupture on the specimen edges. Indeed, during the tensile test, the longitudinal strain field measured by 3D-DIC had shown more important high strain gradients on the edges of the specimen, as discussed in the study of Ben Mbarek et al.,[13] suggesting that the propagation of preexisting microcracks or microvoids was easier at the free edges than in the middle of the sample. The cause of the final rupture could be explained by the fact that at the beginning of the test, a stretching of the HDPE on the edges generated a weakening of the sample. Here, the wood fibers intervened to avoid the rupture. Therefore, the composite mechanical properties depended on the wood fiber content and orientations. In fact, if the fiber was oriented along the tensile direction, loosening of fiber was observed as the fiber was pulled-off (see Figure 4(c)). In addition, Figure 4(d) displays, in this case of uncoupled composites (neither grafted chain nor MAPE), a rough morphology presenting a hole from pull-out fibers. It confirmed the weakness of the interfacial bonding between the wood fiber and the HDPE matrix. In the case of other fiber orientations, the fiber was broken, as seen in Figure 4(e). Finally, the observation of the morphology presented in Figure 4(f) shows that when MAPE was added to the WPC, the wood fiber seemed to be coated with HDPE.[24] This indicated good interfacial adhesion, thus revealing the better affinity between the HDPE-matrix and the wood fiber. The presence of the coupling agent changed the morphology of the fracture surface of the material by improving the interfacial bonding between the wood fiber and the PE matrix.[25]

The fracture surface morphology is now examined on M_1-30 samples. The grafted chains with three carbons acted as a nucleating load on the matrix. The sites of grafting can be seen in Figure 5 on a wood fiber. The HDPE fixed itself by van der Waals bonding.[26] Figure 5(a) shows that the HDPE got into the pores of the wood, thus increasing the contact surface of the interface. Since the stresses had been better distributed,

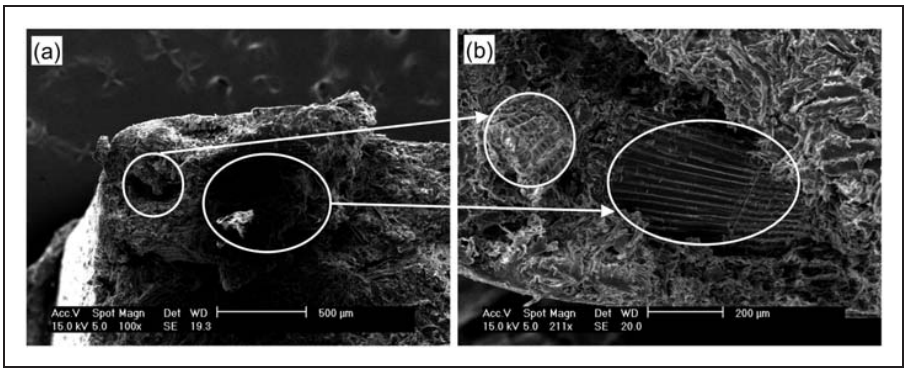

Figure 6. SEM micrographs of fracture surfaces for M_1-30 sample: (a) one side of the fracture surface (100×) and (b) corresponding other side (211×).
SEM: scanning electron microscopy.

the mechanical properties of the composite were improved. This was due to the polarity of wood fibers, which became lower after the transformation of the hydroxyl groups of hemicellulose and lignin into the acetyl groups, which will confer them a higher compatibility with the non-polar HDPE matrix. At large magnification (Figure 5(b) and (c)), it is clearly observed that the polymer was bounded to the wood fiber.

On the other hand, also for the M_1-30 samples and particularly at the edges of the specimen, the presence of cavities (Figure 6(a)) and pulled-out fibers (Figure 6(b)) was detected. This kind of morphology of fracture was observed when the fiber was oriented along the tensile direction before the rupture (see the circles in Figure 6). In this case, the fiber left its imprint on the other side of the fracture surface. This could be explained by a lack of compatibility in this region (there was no MAPE in this case), which led to a poor bonding at the interface between the HDPE matrix and the wood fibers.

Conclusions

In this study, specimens with various lengths and number of carbon chains grafted, coupling agent and wood content were investigated. It was reported first that the addition of wood fibers led to the composite material becoming stiffer, but generally less flexible. Second, the carbon chain-treated wood improved the interfacial adhesion properties between the chains grafted to the wood fiber and those of the HDPE polymer: the MOE was increased, whereas a lower strain at failure was reported. Finally, the coupling agent increased the compatibility between the hydrophobic HDPE matrix and the hydrophilic wood fibers, but mainly in the case where there was no grafted chain. Finally, with regard to the influence of carbon chains, on the one hand their length did not appear to significantly influence the elastic stiffness of the composite material, in the case where the gain in mass was kept constant by using small amount of long carbon chains or large amount of small ones. The other important parameter was the number of grafts, which on the other hand greatly improved the elastic properties: many connections prevented slippage between the fiber and the matrix, making the material more rigid.

The observation of the post-mortem surface fractures by the SEM confirmed, without additive, the weakness of the interfacial bonding between the wood fibers and the HDPE matrix: there were pull-out fibers or broken fibers, depending on their orientation with regard to the tensile direction. With the MAPE, the presence of coupling agent that enrobed the wood fibers was observed. The fracture surface was then clean; the composite behaved as if there was only one component, thus demonstrating the effectiveness of the copolymerization of wood with HDPE. Finally, the grafting of carbon chain improved also, to a lesser extent, the interfacial bonding, and in this case it was observed both a better adhesion of the matrix to the pores of the wood fibers as well as ruptures at the interface between fiber and matrix.

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