

Rheological Behavior and Mechanical Properties of Sawdust/Polyethylene Composites

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ABSTRACT: We have characterized the melt rheological behavior and the solid tensile properties of sawdust/polyethylene composites prepared in an internal mixer. Various concentrations (from 0 to 60 wt %) and three particle sizes have been tested, in presence of a coupling agent (maleic anhydride grafted polyethylene). In the molten state, for each particle size, a mastercurve of the complex viscosity as function of frequency can be plotted, using a shift factor depending on weight fraction. We show that the shift factors can be described by a

Krieger-Dougherty law, leading to a “universal” viscosity law of the Carreau-Yasuda type. In the solid state, the presence of sawdust increases Young modulus in uniaxial elongation, mainly for small size particles, but reduces dramatically deformation at break and tensile strength. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2559–2566, 2009

Key words: composites; rheology; mechanical properties; viscoelastic properties; polyethylene

INTRODUCTION

In the last 10 years, the use of wood/polymer composites (WPC) has largely developed, for applications in the field of profiles or panels for automotive and building industry. The matrices used are essentially polyolefins (polypropylene PP and high density polyethylene HDPE), and the fillers are wood fibers, wood flour or sawdust of various origins (aspen, maple, eucalyptus, pine). These composites contain generally a high amount of fillers (50–70 wt %, up to 95% in specific cases¹). Compared with mineral fillers, wood is characterized by a lower cost, a lower density and a reduced abrasion in processing machines. Moreover, this material is renewable and can be found in abundance as by-product of the wood industry.^{2–4} However, the hydrophilic wood filler has generally a low compatibility with the hydrophobic polymer matrix. This leads to problems of dispersion of the fillers into the matrix (agglomeration of wood particles) and to poor mechanical properties.^{5–7} To improve adhesion between wood particles and matrix, it is possible to chemically modify wood surface or matrix, or to add a compatibilizer.^{3,6,8–10} This compatibilizer (or coupling agent) is generally a maleic anhydride grafted polyolefin.

Mechanical properties of WPC depend on the properties of the matrix and of the filler, on the filler concentration, on the filler aspect ratio, on the coupling agent (nature, concentration...), and on the processing conditions.^{1–11} Mixing conditions must lead to an homogeneous dispersion of the wood fillers into the matrix, but high temperatures (above 200°C) and high shear rates have to be avoided, to limit wood degradation.¹²

The viscosity of the composite may be largely increased compared with the one of the matrix by the presence of wood particles, mainly at high concentrations. It is thus important to estimate it, if classical processing equipments (twin screw extruder, injection machine...) have to be used, and to try to reduce it to limit the energy required for processing.^{11,12}

In this study, our objectives were to characterize the influence of filler concentration and filler size on the melt rheological properties and solid tensile behavior of WPC made of high density polyethylene and sawdust.

MATERIALS AND METHODS

Materials

The matrix is a high density polyethylene (HDPE) Stanyl 8621, from DSM company. It has a melting temperature of 131°C, a weight average molecular weight of 210,000 g/mol and a polydispersity index

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TABLE I
Average Values of Wood Particles Characteristics

	Fine	Intermediate	Coarse
Area (mm ²)	0.1154	0.7064	1.3457
Major axis <i>L</i> (mm)	0.57	1.48	1.78
Minor axis <i>D</i> (mm)	0.30	0.78	1.15
Aspect ratio (<i>L/D</i>)	1.97	1.92	1.56

of 34. Its melt index is 0.89 g/10 min (190°C, 2.16 kg). The compatibilizer is a maleic anhydride grafted polyethylene (PE-g-MA) Fusabond 226DE, from Du Pont. It has a melting temperature of 120°C and a melt index of 1.5 g/10 min (190°C, 2.16 kg). In all experiments, PE-g-MA content was fixed and equal to 3% of the total weight (HDPE + sawdust). From the literature, it was found that this amount was considered as optimal in the case of HDPE/sawdust¹³ and PP/sawdust.¹⁴

Wood particles come from sifted sawdust, provided by sawmill Tembec (Béarn, Quebec, Canada). It is made of 65 wt % of white spruce (*Picea glauca*), 20 wt % of black spruce (*Picea mariana*) and 15 wt % of balsam (*Abies balsamea*). Sawdust has been dried under vacuum at 85°C for 24 h, then stored into polyethylene bags before use. The residual moisture is expected to be around 2 to 3 wt %, if we compare to conditions from the literature.^{3,15} Sawdust has been sieved to obtain three different classes, according to the diameters *d* of the sifter: $d \leq 0.71$ mm (fine); $0.71 \leq d \leq 1.00$ mm (intermediate) et $1.00 \leq d \leq 1.40$ (coarse). The apparent density of the three classes of sawdust is 0.17 g/cm³. The real one, measured with a helium pycnometer (Accupic model 1330), is 1.48 g/cm³. Major and minor axes and areas of wood particles have been characterized by optical microscopy and image analysis (System Visilog 6.3), on more than 200 particles for each class. Average values are indicated in Table I. We observe that the aspect ratio is higher for the fine class, even if it remains rather low (between 1.6 and 2). Table II presents the length distribution for the three classes. It shows that intermediate and coarse classes are not very different. In fact, particles with length less than 100 μm are not taken into account with Visilog analysis. For the fine class, we used a Fiber Quality Analyser (FQA) (Optest Equipment, Hawkesbury, Ontario) to measure more accurately the fiber length distribution. The results show that these fibers (less than 100 μm) represent effectively 50% of the distribution

Composites preparation

All composites have been prepared in an internal mixer (Haake Rheomix 600), in fixed processing

condition: rotor speed 60 rpm, temperature 170°C, mixing time 4 min. This temperature was chosen to prevent from thermal degradation.¹⁶ HDPE and PE-g-MA were first introduced in the mixer and mixed during 1.5 min. Then, sawdust was introduced in the molten matrix and mixed at the same condition for 4 min. For each of the three classes, six concentrations were studied: 0, 20, 30, 40, 50, and 60 wt %. All WPC have been made twice, to have enough materials for rheological and mechanical characterizations.

Samples for these characterizations were compression molded at 150°C and 20 MPa for 4 min. Samples for rheometry have a diameter of 25 mm and a thickness of 4 mm. Samples for tensile tests are parallelepiped bars of dimensions 125 × 13.8 × 3.65 mm³.

Rheological measurements

Small amplitude oscillatory shear measurements have been performed at 170°C, under nitrogen, on a parallel plate rheometer (Rheometrics RMS 800) equipped with discs of diameter 25 mm and gap 3.5 mm. An important gap is necessary to account for the size of the wood particles.¹⁷ For each class of sawdust, the linear domain has been characterized for a concentration of 30 wt %. The limit strain is around 3% for this concentration. In the linear domain (2%), frequency sweep tests have been conducted from 0.1 to 100 rad/s¹.

The measurements are well reproducible and the thermal stability at 170°C under nitrogen is higher than 4 h.

Mechanical properties

For each WPC, five samples have been tested in uniaxial extension, until rupture. The tests have been carried out 7 days after compression molding, in

TABLE II
Length Distribution of the Wood Particles

Length (mm)	Frequency (%)			
	Fine		Intermediate	Coarse
	Visilog	FQA		
0 to 0.25	15.7	70.9	0	0
0.25 to 0.50	31.7	16.5	0	0
0.50 to 0.75	26.6	6.6	0	0
0.75 to 1.00	15.0	2.8	8.2	0
1.00 to 1.50	9.6	2.6	53.1	28.9
1.50 to 2.00	0.7	0.5	28.6	45.9
2.00 to 2.50	0.7	0.1	10.2	20.0
2.50 to 3.00	0	0	0	2.2
3.00 to 3.50	0	0	0	0.7
3.50 to 4.00	0	0	0	2.2
> 4.00	0	0	0	0

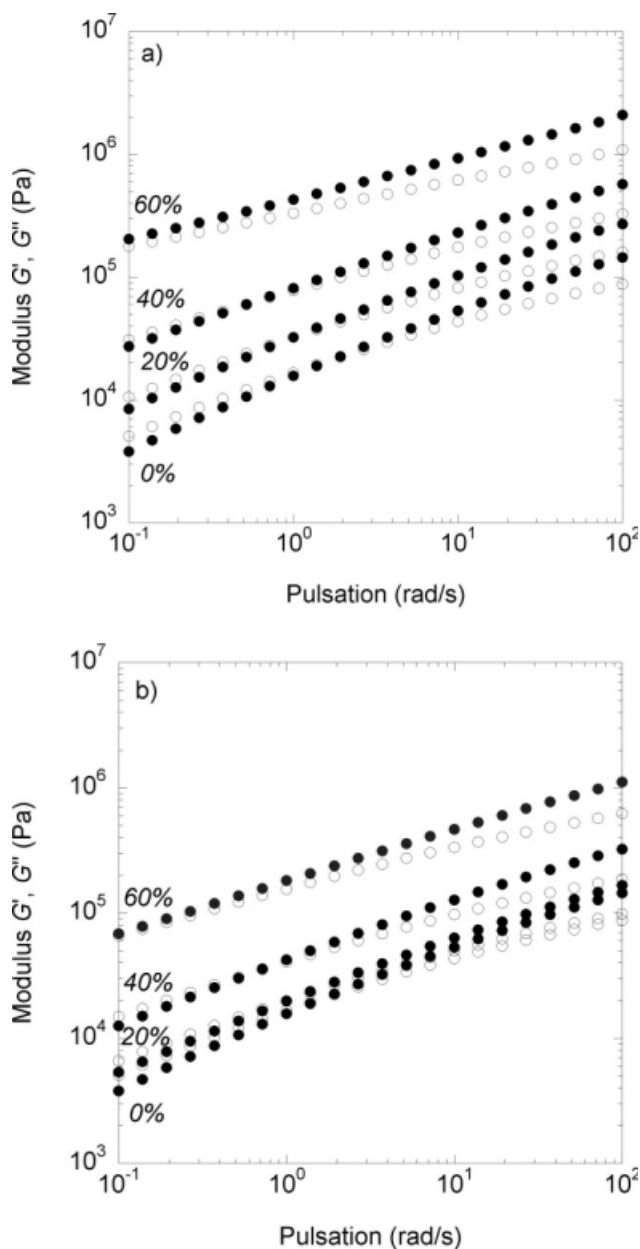


Figure 1 Evolution of storage G' (●) and loss G'' (○) modulus with pulsation at 170°C. (a) fine sawdust, (b) intermediate sawdust.

ambient conditions (around 22°C and 40% relative moisture), on an universal traction machine (Zwick/Z2.5), with a cell of 2.5 kN. Traction speed was 3 mm/min, which led to a sample rupture between 30 s and 2 min (ASTM D5456). We calculated apparent stress/strain curves from the original sample geometry, but the true stresses are assumed to be close to the apparent ones as the strains are small (less than 5%) and no striction occurred before rupture. Young modulus was evaluated using the secant method at 0 and 0.1% total strain.

RHEOLOGICAL BEHAVIOR AND DISCUSSION

Mechanical spectra

First of all, it is worth noting that unsatisfactory results were obtained with the coarse class samples at high sawdust content. At 40 wt %, we observed a sudden decrease of modulus above 20 rad/s^1 . At 50 wt %, this phenomenon appeared at 3 rad/s^1 . This may be due to the onset of wall slip, often observed with WPC at high wood content.^{18–20} We also think that, at high concentration, the strain of 2% is out of the linear domain. Consequently, the

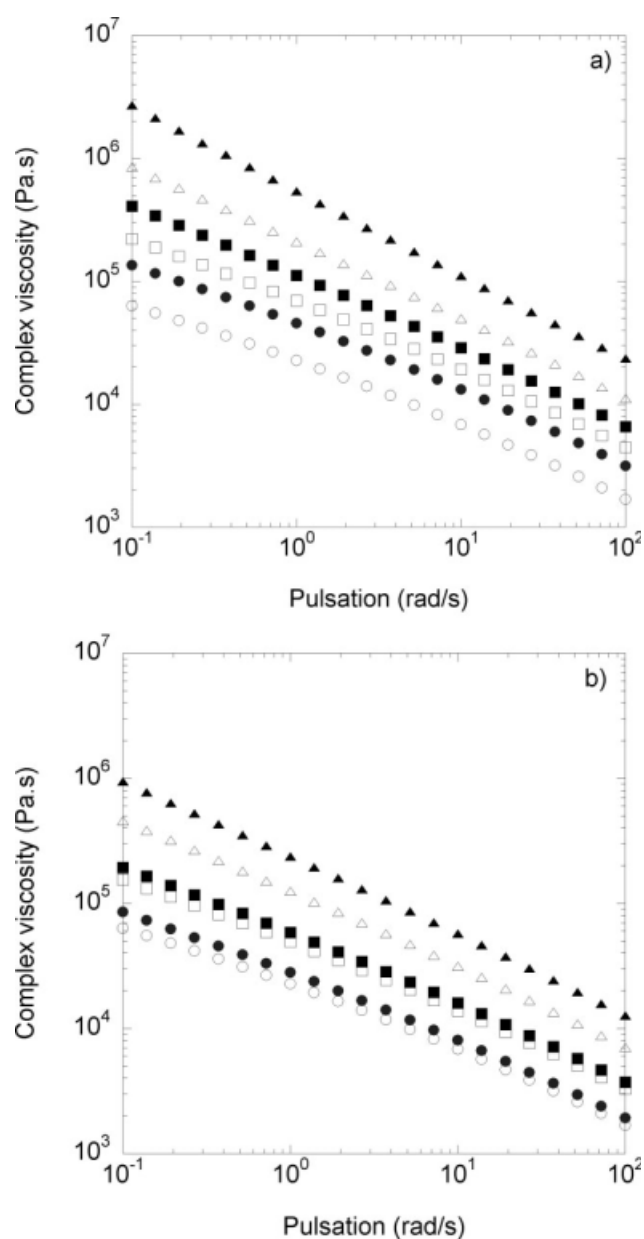


Figure 2 Evolution of complex viscosity with pulsation at 170°C for different concentrations (in weight) ○ 0%, ● 20%, □ 30%, ■ 40%, △ 50%, ▲ 60%; (a) fine sawdust, (b) intermediate sawdust.

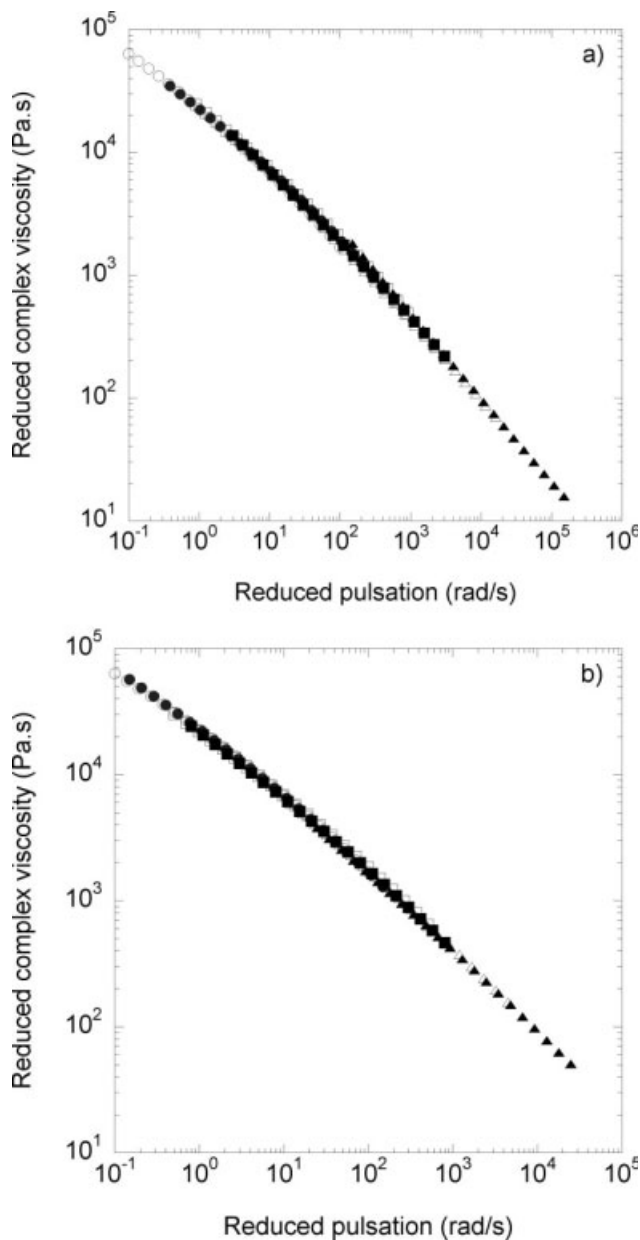


Figure 3 Complex viscosity mastercurves at 170°C of composites at different concentrations (in weight) ○ 0%, ● 20%, □ 30%, ■ 40%, □ 50%, ▲ 60%; (a) fine sawdust, (b) intermediate sawdust.

corresponding data will not be used in the following.

Figure 1 presents an example of evolution of storage modulus G' and loss modulus G'' with pulsation at different concentrations, for fine and intermediate classes. Storage and loss modulus increase with the filler concentration, and the behavior tends to become more elastic, with a crossover of G' and G'' at lower pulsations. Fine samples present higher values of modulus than the intermediate ones. These results are in agreement with the classical observations on WPC behavior.²¹

Complex viscosity

The corresponding complex viscosity curves are presented in Figure 2. Viscosity increases with concentration, mainly at high concentration and for the fine sawdust. From these curves at different concentrations, it is now possible to obtain a unique mastercurve by using a shift factor, which is function of the concentration. This approach has been proposed by Marcovich et al.²¹ for PP/wood flour composites, and more generally by Trappe and Weitz²² for concentrated suspensions of low attractive particles. At any concentration ϕ and any pulsation ω , the complex viscosity η^* can be written:

$$\eta^*(\phi, \omega) = \frac{\eta^*}{a_C}(\phi_0, \omega a_C) \quad (1)$$

where ϕ_0 is a characteristic concentration and a_C the shift factor. Figure 3 shows the reduced viscosity η^*/a_C as a function of the reduced pulsation ωa_C , for the fine and intermediate classes. We observe that the superposition is very satisfactory and allows to define the behavior of the WPC on a wide range of pulsations. Now, if we plot the mastercurves obtained for each class of sawdust, we can see on Figure 4 that they are all perfectly superimposed. It means that it is possible to define a “universal” behavior for this type of WPC, characterized for example by a Carreau-Yasuda law, whose parameters will vary according to the concentration and the size of the wood fillers.

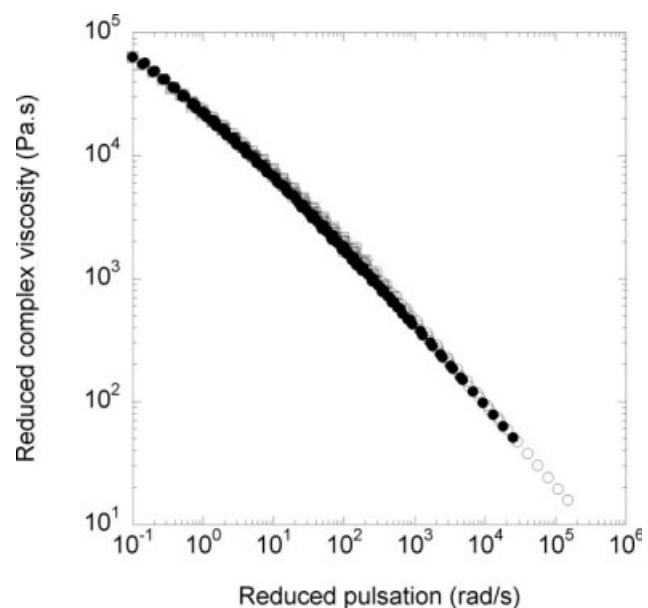


Figure 4 Complex viscosity mastercurves at 170°C of composites made with (○) fine sawdust, (●) intermediate sawdust, (□) coarse sawdust.

$$\eta^*/a_C = \eta_0[1 + (\lambda\omega a_C)^a]^{(n-1)/a} \quad (2)$$

or more explicitly:

$$\eta^* = \eta_0 a_C [1 + (\lambda a_C \omega)^a]^{(n-1)/a} \quad (3)$$

where η_0 is the limit viscosity, λ a characteristic time, n the power law index and a the Yasuda parameter.

The best fit was obtained with the following values: $\eta_0 = 1,519\ 250$ Pa.s, $\lambda = 43.34$ s, $n = 0.28$, $a = 0.19$.

With this formalism, only the limit viscosity η_0 and the characteristic time λ are affected by the presence of wood particles, through the shift factor a_C . In Figure 5, the shift factor is plotted as function of filler concentration, for the three classes of particles. In all cases, it increases with the concentration, more markedly with the fine samples. The values obtained for the coarse samples are unexpected, but we have to keep in mind that, for these samples, some results have not been taken into account, as explained previously.

The evolution of the shift factor with the concentration can be described by a Krieger-Dougherty equation, generally used for concentrated suspensions²³:

$$a_C = \left(1 - \frac{\phi}{\phi_{\max}}\right)^{-[\eta]\phi_{\max}} \quad (4)$$

where ϕ_{\max} is the maximum packing fraction and $[\eta]$ the intrinsic viscosity. Similar approaches for describing the behavior of WPC using Krieger-Dougherty laws have been proposed by Dong et al.,²⁴ Marcovich et al.,²¹ and Li and Wolcott.²⁰ Figure 5 shows that this

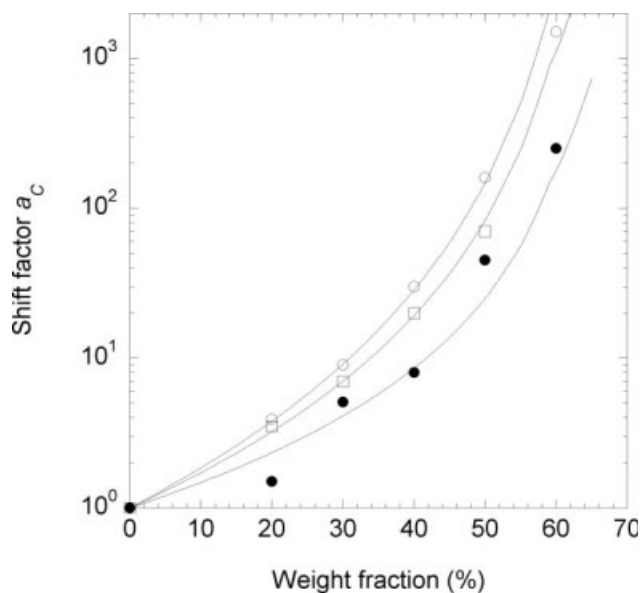


Figure 5 Shift factors for the composites made with fine (\circ), intermediate (\bullet) and coarse (\square) sawdust. Full lines correspond to the best fit by a Krieger-Dougherty law.

TABLE III
Parameters of the Krieger-Dougherty Model for the Three Classes of WPC

Sawdust class	ϕ_{\max} (%)	$[\eta]\phi_{\max}$
Fine	71.5	4
Intermediate	70	2.5
Coarse	71	3.5

type of equation allows a good fit of the experimental shift factors. The best values of the two parameters ϕ_{\max} and $[\eta]\phi_{\max}$ are given in Table III for the three classes. The maximum packing fraction is similar, close to 71%. In fact, in the classical Krieger-Dougherty model, the volume (and not mass) fraction is to be considered and, by taking into account the respective densities of sawdust and matrix, 71 wt % corresponds to an approximate volume fraction of 60%. It is less than the theoretical value for a stacking of monodisperse spheres (74%), but close to the value for a dense random staking (63.7%), what could be explained by the complex morphology of the sawdust. By comparison, Dong et al.²⁴ found a value of 58% for WPC based on linear low density polyethylene and wood fibers (length 240 μm , aspect ratio 10), Marcovich et al.²¹ gave a value of 40% for PP/wood flour composites, and Li et Wolcott¹⁹ proposed 67.5% for HDPE/wood flour composites. The exponent $[\eta]\phi_{\max}$ is often close to two.²⁵ For our samples, it varies between 2.5 and 4, depending on the class. It is found equal to 2 by Li and Wolcott,²⁰ 4 by Marcovich et al.,²¹ and 4.2 by Dong et al.²⁴ To summarize, our results are very similar to the few data available in the

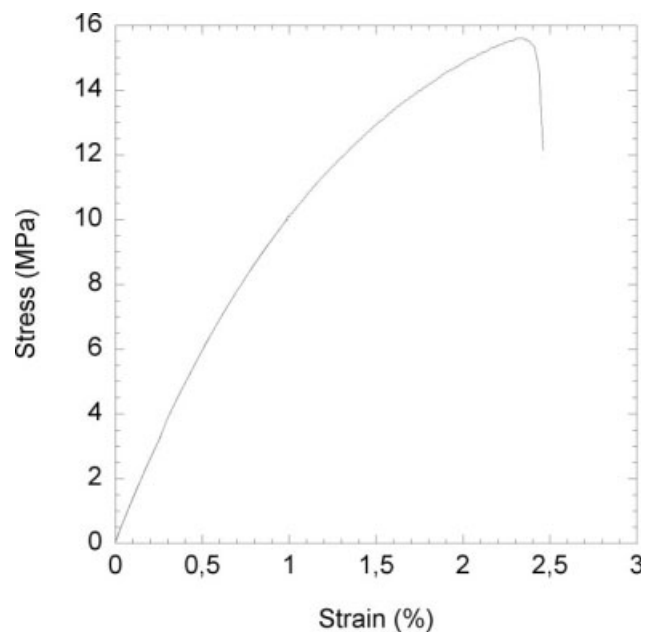


Figure 6 Example of stress-strain curve (40%, intermediate sawdust).

TABLE IV
Mechanical Properties of WPC of Fine Sawdust

Mass concentration (%)	Young modulus E (MPa)	Tensile strength R_m (MPa)	Deformation at break ϵ_R (%)
0	929 ± 33	23.56 ± 2.10	108.3 ± 11.2
20	1573 ± 41	23.08 ± 1.62	5.47 ± 2.20
30	1642 ± 60	24.04 ± 0.66	5.06 ± 1.44
40	1763 ± 77	20.39 ± 0.86	2.99 ± 1.35
40 ^a	1001 ± 120	9.96 ± 1.31	2.55 ± 0.60
50	1757 ± 104	18.02 ± 0.95	1.76 ± 0.34
60	1897 ± 87	17.55 ± 2.25	1.59 ± 0.42

^a without PE-g-MA.

literature. The proposed correlations allow, for all the WPC studied, to predict the values of complex viscosity with a good accuracy for mass concentrations between 0 and 60%.

MECHANICAL PROPERTIES AND DISCUSSION

Figure 6 shows a typical example of stress–strain curve. Tables IV, V, and VI synthesize the main results of the mechanical tests for the three classes of WPC. Listed parameters are Young modulus E , tensile strength R_m and deformation at break ϵ_R .

Young modulus increases linearly with sawdust concentration (Fig. 7). Results are similar for intermediate and coarse classes and much higher with the fine class. Compared to the matrix (929 MPa), the best value (1.9 GPa) is reached for 60% of fine sawdust, which represents an increase of 104%. These results are in agreement with the literature: on HDPE/wood flour composites, Adhikary et al.¹⁵ measured 1.7 GPa at 50% concentration. Raj and Kokta²⁶ obtained 2 GPa at 40% on HDPE/wood fibers composites, when Yam et al.²⁷ cited a value of 1.6 GPa at 50% for a recycled HDPE/wood fibers composite. The best properties obtained with the fine class can be attributed to the ratio surface/volume, which is more important for these particles (see Table I). As the specific surface is

TABLE V
Mechanical Properties of WPC of Intermediate Sawdust

Mass concentration (%)	Young modulus E (MPa)	Tensile strength R_m (MPa)	Deformation at break ϵ_R (%)
0	929 ± 33	23.56 ± 2.10	108.3 ± 11.2
20	1154 ± 44	15.74 ± 1.68	4.08 ± 1.58
30	1189 ± 65	17.50 ± 1.17	3.58 ± 0.27
40	1256 ± 92	14.82 ± 0.97	2.10 ± 0.30
40 ^a	1142 ± 165	10.87 ± 1.49	2.37 ± 1.05
50	1409 ± 91	15.11 ± 2.12	1.67 ± 0.49
60	1449 ± 61	14.04 ± 0.87	1.61 ± 0.44

^a without PE-g-MA.

TABLE VI
Mechanical Properties of WPC of Coarse Sawdust

Mass concentration (%)	Young modulus E (MPa)	Tensile strength R_m (MPa)	Deformation at break ϵ_R (%)
0	929 ± 33	23.56 ± 2.10	108.3 ± 11.2
20	1039 ± 23	15.43 ± 0.98	3.58 ± 0.69
30	1191 ± 23	16.16 ± 0.43	3.09 ± 0.42
40	1315 ± 66	15.98 ± 0.65	2.36 ± 0.63
40 ^a	1051 ± 74	10.22 ± 1.04	2.75 ± 0.93
50	1358 ± 85	14.76 ± 1.32	1.89 ± 0.93
60	1408 ± 57	13.97 ± 1.36	1.40 ± 0.46

^a without PE-g-MA.

more important, chemical bounds through the compatibilizer at the interface wood/polymer are more numerous, which could explain the better mechanical properties. This is generally the explanation proposed by authors who characterized the influence of particle size on WPC mechanical properties.^{28,29}

For the tensile strength, we obtain a value slightly higher than the matrix at 30% of fine sawdust, otherwise all the other values are lower. For each class, a maximum is observed at 30% and the values obtained for the fine class are always higher than for the intermediate and coarse classes. In the literature, results concerning tensile strength are contrasted. Yam et al.,²⁷ Adhikary et al.,¹⁴ and Selke and Wichman³⁰ observed a decrease of tensile strength when increasing concentration, whereas Raj and Kokta,²⁶ Woodhams et al.,³¹ or Kuan et al.³² reported an

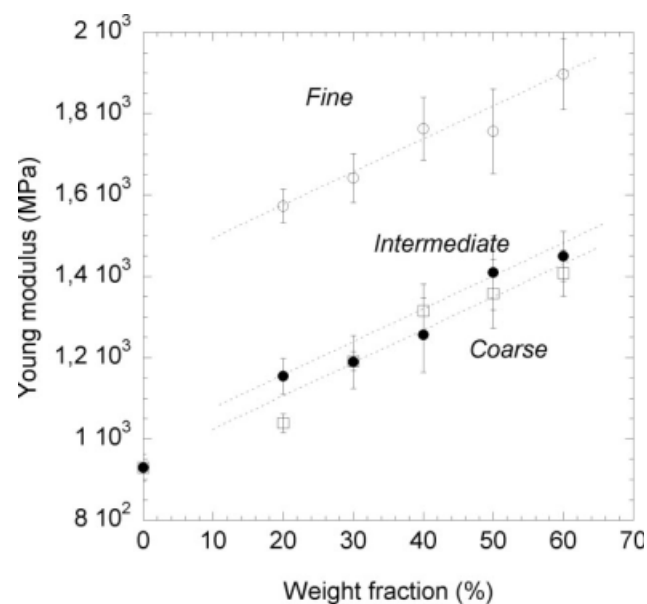


Figure 7 Young modulus of composites made with fine (○), intermediate (●), and coarse (□) sawdust. Dotted lines are just for guiding the eye.

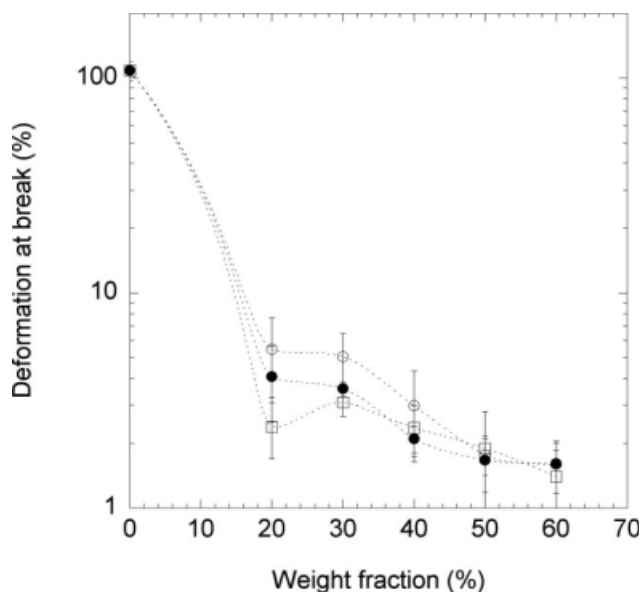


Figure 8 Deformation at break of composites made with fine (○), intermediate (●), and coarse (□) sawdust. Dotted lines are just for guiding the eye.

increase of tensile strength. However, in the last cases, the fillers were wood fibers, with important aspect ratio.

For all our WPC samples, the ductility is dramatically reduced (Fig. 8), whatever the size of the particles. The deformation at break drops from 108% to less than 5%, what is usually observed for WPC.^{15,26,27}

The effect of the coupling agent has been characterized at a concentration of 40%. Without PE-g-MA, the Young modulus of the composite remains slightly higher than the matrix one (1 to 1.1 GPa, compared to 0.9 GPa). However, it is much less than the values reached with 3% PE-g-MA: 1.2 to 1.7 GPa. Moreover, without coupling agent, the tensile strength is also dramatically lowered, around 10 MPa, to compare with the value of 23.6 MPa for the matrix and values between 15 and 20 MPa for the composite with coupling agent. If we consider the rupture aspect of a sample without PE-g-MA, we observe voids corresponding to the delamination between wood particles and matrix. In this case, the break is essentially silent. On the contrary, the rupture with coupling agent was accompanied by a sharp noise, probably due to the break of wood fibers.

CONCLUSIONS

We have characterized the melt rheological behavior and the solid tensile properties of composites made of high density polyethylene, coupling agent and sawdust, at different concentrations and for different particle sizes. We found that:

- Both storage and loss modulus increase with the concentration;
- The complex viscosity increases with the concentration and is more important for the fine sawdust;
- For each class of WPC, we can obtain a master-curve using a shift factor depending on concentration, that allows to describe the rheological behavior of all the composites studied;
- These shift factors are correctly described by a Krieger-Dougherty law, whose parameters depend on particle size;
- Young modulus increases with sawdust concentration and is more important for the fine particles. Elongation at break decreases dramatically with wood concentration;
- 3% of coupling agent allows a better adhesion between wood and polymer, leading to better mechanical properties;
- The best properties obtained with the fine sawdust are probably due to a better surface/volume ratio, facilitating a better adhesion with the matrix.

Therefore, a compromise between high mechanical properties, especially Young modulus, and reduced processing energy (viscosity) must be chosen.

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