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Interrelationship between lignin-rich dichloromethane extracts of hot water-treated wood fibers and high-density polyethylene (HDPE) in wood plastic composite (WPC) production

Abstract: Hot water extraction (HWE) partially removes hemicelluloses from wood while leaving the majority of the lignin and cellulose; however, the lignin partially migrates to the inner surfaces of the cell wall where it can be deposited as a layer that is sometimes visible as droplets. This lignin-rich material was isolated via Soxhlet extraction with dichloromethane to investigate its rheological behavior in blends with high-density polyethylene (HDPE), a common material in wood plastic composites (WPCs). Pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) and electrospray ion mass spectrometry (ESI/MS) confirmed that the isolated material is constituted mainly of low-molecular-weight lignin oligomers. The blends of HDPE/isolated lignin, in varying ratios, were tested by means of dynamic rheology. A "shoulder" was found in plots "shear storage moduli (G′) vs. frequency sweep" and a shift of the terminal zone to lower frequencies was observed. Apparently, this shoulder is caused by the elastic contribution of the interfacial tension between the blend components. The rheology of WPCs produced from HWE wood and HDPE shows a similar shoulder in G′ plots, suggesting that the HDPE/lignin blends are in part responsible for the shape of the G′ curves.

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Introduction

Wood plastic composites (WPCs) are widely used for decking and other purposes such as automobile components. WPC's global market has been growing rapidly and is expected to increase by 13% in the period from 2010 to 2015 (Eder and Carus 2013). Improving appearance and performance, reducing cost, and elevating the environmental friendliness are important factors for better acceptance of WPCs (Ou et al. 2014). Increasing the percentage of wood can be an alternative for this purpose (Wang et al. 2013). However, this possibility is limited by the melt viscosity increment during extrusion, which reduces process ability and impacts the product quality (Li and Wolcott 2005; Klyosov 2007; Wang et al. 2013; Ou et al. 2014). Higher amounts of stiff wood particles raise friction within the partially molten composite and between the melt and the extruder metal walls. These factors increase power consumption for extrusion and thermal degradation of wood as a consequence of overheating (Klyosov 2007; Wang et al. 2013). Adding plasticizers to the composite is one way to mitigate this problem (Klyosov 2007; Wang et al. 2013). Adding organic monomers or low-molecular-weight oligomers with high thermal conductivity, which could penetrate the cell wall, increasing wood thermal conductivity, could be another strategy. Improved thermal conductivity could facilitate lignin softening, which may in turn plasticize the cell wall (Wang et al. 2013), thus enhancing WPC extrusion.

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Each major wood constituent plays a specific role in the manufacture and performance of WPCs. Hemicelluloses' affinity to water negatively affects extrusion. For example, corrosion of extruder walls arises from acidic components of hemicelluloses degradation (Klyosov 2007). Hemicelluloses are largely responsible for high water absorption and poor dimensional stability of WPCs. Minimizing the amount of hemicelluloses in wood could be a remedy (Pelaez-Samaniego et al. 2012; Pelaez-Samaniego et al. 2013), which results in materials enriched in cellulose and lignin. Cellulose provides better mechanical properties to wood. Lignin, on the other hand, acts as a binder of wood carbohydrates, bio-protection agent, water repellent, and as a plasticizer. Thermochemical operations such as hot water extraction (HWE) offer an option to reduce hemicelluloses and increase the lignin concentration (Pelaez-Samaniego et al. 2013). WPCs processing could benefit from a lignin-rich raw material due to the lignin's favorable thermal properties. Lignin softening temperature can vary from ~80°C to 140°C (depending on its origin, testing method, or moisture content) (Goring 1971; Salmén 1982; Irvine 1984). As these temperatures are normally below those used for manufacturing WPCs, higher amounts of lignin could increase wood plasticity and positively impact WPC's extrusion to some extent. HWE-treated wood in WPC manufacture has better compressibility and reduced springback (Pelaez-Samaniego et al. 2014a). Enhanced plasticity and deformation of particles may improve the rheological behavior during extrusion.

A common observation during HWE is that lignin in wood undergoes a series of transformations such as plasticization, depolymerization, and rubbery/liquid flow. These changes in combination with capillary and hydrophobic forces promote its partial migration from the cell wall to the inner surface cell wall, where it is deposited and forms rubbery layers, frequently visible as spherical or semispherical droplets (Selig et al. 2007; Donohoe et al. 2008; Pelaez-Samaniego et al. 2012). Spherical shape is common for soluble macromolecular lignins and have a tendency to aggregate (Goring 1971). This material is partly linked to carbohydrates.

Pelaez-Samaniego et al. (2012) observed that HWE of wood drastically reduced water sorption and thickness swelling of WPCs (mainly due to the removal of hemicelluloses) and the mechanical properties were improved or not affected. The underlying hypothesis of this work is that one of the reasons for better or equal mechanical properties of the WPCs is the presence of the partially migrated and redeposited lignin, which blends with the thermoplastic resin during compounding processes. The objective of this investigation is to gain more insight concerning the potential interaction between the readily accessible lignin-rich depositions on the fiber surfaces and thermoplastic resins in the course of the WPC manufacturing. Particularly, the rheological behavior of high-density polyethylene (HDPE) with the redeposited lignin blends will be in focus.

Materials and methods

Small diameter ponderosa pine (*Pinus ponderosa* Dougl. *Ex* Laws.) logs without debarking (bark content 14.0%±0.5%) were chipped and subjected to HWE (160°C for 90 min) in an M&K digester as described by Chaffee (2011). HWE extracted and control pine chips (P_{HWE} and P_{cont}) were ground and dried to produce WPCs based on HDPE (Bamberger Polymers, Houston, TX, USA) and additives, as described by Pelaez-Samaniego et al. (2012).

Lignin preparation from P_{HWE}

P_{HWE} flour (Pelaez-Samaniego et al. 2012) was dried (24 h at 103°C) and subjected to a Soxhlet extraction process with dichloromethane (DCM) as solvent following the procedure described in the literature (Li et al. 2007; Osman et al. 2012; Pelaez-Samaniego et al. 2014b). By this process, DCM-soluble lignin-rich extractives were isolated, which was expected to be similar to the material deposited on P_{HWE} surfaces. The process was conducted in triplicate with 10 g of P_{HWE} each time. A filter paper (1001–042 Whatman™) was placed at the bottom of the sintered thimble of the extraction apparatus (Kemtech America Synthware) to help retention of small P_{HWE} particles. P_{cont} served for verification that the lignin-rich extractives resulted from the HWE process. Afterward, the DCM extract was evaporated (Buchi R-300 rotary evaporator) and the yields of lignin-rich extracts calculated. The extracts presented an oil-like morphology, as previously observed by Tanahashi (1990) in steam-exploded wood, with very high viscosity. The characterization of these extractives was conducted via pyrolysis gas-chromatography/mass spectrometry (Py-GC/MS) as described in Pelaez-Samaniego et al. (2014b). Data was normalized by dividing the area of the peaks of representative components in the resulting pyrograms by the corresponding weight of the specimen. The molecular weight was determined by electrospray ion mass spectrometry (ESI/MS, LCQ-Deca, Thermo Finnigan). Both the number average molecular weight (M_n) and the weight average molecular weight (M_w) were computed based on the MS detected molecular weights as follows:

$$M_n = \sum M_i N_i / \sum N_i \text{ and } M_w = \sum M_i^2 N_i / \sum M_i N_i$$

where the M_i is the m/z and N_i is the intensity of the ith ion (Goring 1971; Parees et al. 1998).

For the dynamic rheological tests of WPCs, four disc-shaped specimens of P_{cont}/HDPE WPC boards and four of P_{HWE}/HDPE WPC boards (Pelaez-Samaniego et al. 2012) were prepared by means of a planner and a belt sander machine (200-grit sander belt) and dried (103°C, 12 h). Final specimen dimensions: ~25 mm diameter and

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2.3±0.1 mm thick. A rotational rheometer (Discovery HR-2, TA Instruments) equipped with 25 mm diameter parallel plates and controlled by TRIOS software was employed. The critical strain (γ_{crit}), that is, the maximum strain up to which storage modulus (G′) remains constant, was determined under strain sweep conditions using one of the specimens. The γ_{crit} served for setting the next frequency sweep tests. For determining oscillation strain (γ) vs. G′ and γ vs. loss modulus (G″) behavior, the corresponding specimen was placed between the plates and a load of 1 N was applied. The specimen was then equilibrated at 160°C (as in torque rheology tests) for 3 min to erase any thermal and deformation history. Afterward, the frequency (ω) was set to 10 rad s^{-1}, the load was increased to ~40 N, and γ was set to vary from 0.001% to 10% in isothermal conditions. The tests started after 2 min soaking and G′ vs. γ and G″ vs. γ curves were recorded. The linear region was verified up to γ~0.03% for both formulations. Therefore, a constant value γ=0.03% was the basis for dynamic frequency sweep tests under isothermal conditions (160°C). For dynamic frequency sweep tests, the remaining specimens of each formulation were loaded and maintained in the chamber for 3 min. The ω was set to vary from 0.01 to 100 rad s^{-1}, as in Bousmina et al. (1995), and the initial load was again 40 N. The test started after 2 min soaking and G′ vs. ω and G″ vs. ω values were recorded.

For the dynamic rheological tests of HDPE/lignin blends, 50 mg of lignin-rich DCM extracts were manually blended with 100 mg of HDPE (i.e., 2:1 ratio) at room temperature. As in the case of WPC boards, tests in strain sweep conditions were conducted first to determine γ_{crit} of the blends, in which γ changed from 0.005% to 10% with ω=10 rad s^{-1}, keeping a gap of 100 µm between the plates of the rheometer. The soaking time was 120 s. As γ_{crit} was verified to be approximately 0.2% (see typical G′, G″ curves vs. γ in Figure 5), the value of γ for frequency sweep tests was set at 0.03% (the same as for testing the composites), and ω was set to vary from 0.01 to 100 rad s^{-1}. The gap of the plates was again 100 µm, which allowed for a change in load from 2 N at the beginning to 0.8 N at the end of the test, respectively. The test started after 120 s of soaking and 10 points per decade were collected. However, 140°C was applied because it was observed that at higher temperatures the lignin melted too quickly and it was difficult to test the blends under load conditions. A similar procedure was performed with HDPE only and with additional blends of HDPE and lignin-rich extracts. Specifically, 1:1, 3:1, 4:1, and 5:1 HDPE/lignin-rich extracts (mass/mass) were tested under similar conditions. The solidified formulations (after rheology tests) were visualized by SEM (FEI Quanta 200F) and optical microscopy (Olympus BH-2 with ProgRes Digital Camera). Cross-sections of WPC boards were also observed by SEM to compare P_{HWE} and P_{cont} particles during extrusion.

Torque rheometry tests of both formulations (P_{cont}/HDPE, P_{HWE}/HDPE) were conducted in a Haake Rheomix 600 torque rheometer (Thermo Scientific) equipped with counter-rotating roller-blade rotors. The wood flour was applied without additives, whereas the formulations consisted of 60% of dried (103°C, 24 h) P_{cont} or P_{HWE} and 40% of HDPE. The blends were compounded in triplicate for 10 min with 50 g of each formulation (the material covered more than 80% of the chamber volume). The screw speed was 20 rpm at 160°C, that is, the conditions were the same as in the case of WPCs extrusion described by Pelaez-Samaniego et al. (2012).

Results and discussion

Py-GC/MS and ESI/MS of DCM-soluble material

The yield of DCM-soluble material isolated from P_{HWE} flour was ~1.5% based on HWE wood, whereas P_{cont} did not contain DCM solubles; thus, the extract is the result of HWE treatment. The normalized Py-GC/MS chromatogram (pyrogram, Figure 1) shows mostly phenols (Table 1) with retention times (RT) up to 25 min; peaks with RT>25 min corresponding to fatty acids (Pelaez-Samaniego et al. 2014b), but these are not shown because the focus in the present paper is on lignin. Therefore, it can be concluded that the DCM-soluble part of HWE is lignin rich. For simplicity, the extract will be designated as lignin. The ESI/MS spectra of the extract (Figure 2) was the basis for molecular weight determinations, that is, M_w of 942 g mol^{-1} and M_n of 663 g mol^{-1} were found. These data are similar to those obtained by Pelaez-Samaniego et al. (2014b) in the case of torrefaction pretreatment of the same wood species.

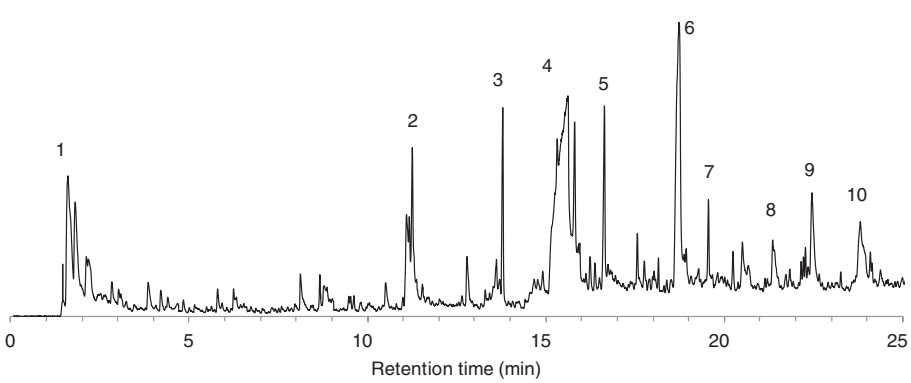

Figure 1: PyGC/MS pyrogram of material isolated from HWE wood by DCM extraction. High amounts of lignin-derived products (phenols) provide evidence that this DCM extract is lignin-rich.

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Table 1: Identification of peaks of Figure 1 (#).

Peak #	RT (min)	*m*/*z*		Compound
1	1.57	44	CO_2	Carbon dioxide
2	11.26	109	$C_7H_8O_2$	Phenol, 2-methoxy-
3	13.79	123	$C_8H_{10}O$	Phenol, 2-methoxy-4-methyl-
4	15.79	137	$C_9H_{12}O_2$	Phenol, 4-ethyl-2-methoxy-
5	16.65	135	$C_9H_{10}O_2$	2-Methoxy-4-vinylphenol
6	18.63	151	$C_{20}H_{28}O_{13}$	Vanillin
7	19.55	164	$C_{10}H_{12}O_2$	Phenol, 2-methoxy-4-(1-propenyl)-, (E)-
8	21.32	137	$C_{10}H_{12}O_3$	2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-
9	22.43	151	$C_9H_{11}NO_3$	α-Amino-3′-hydroxy-4′-methoxyacetophenone
10	25.23	178	$C_{10}H_{10}O_3$	(2E)-3-(4-Hydroxy-2-methoxyphenyl)-2-propenal#

Peak# referes to the numbers of the peaks in Figure 1. RT, Retention time.

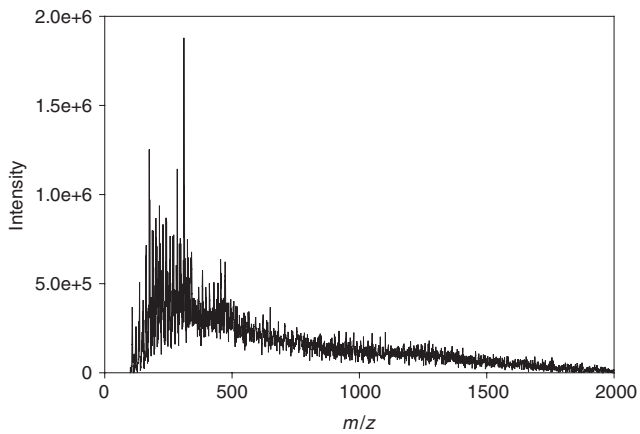

Figure 2: ESI/MS spectra of the DCM-soluble lignin isolated from HWE pine.

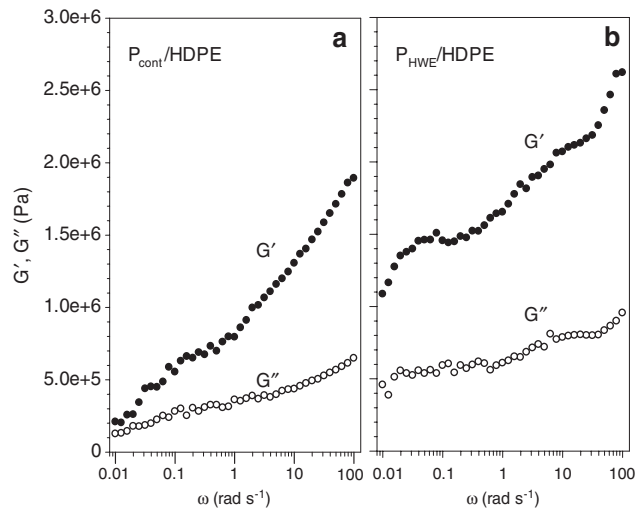

Figure 3: Typical G′ and G″ curves of (a) P_{cont}/HDPE and (b) P_{HWE}/HDPE WPC boards tested in dynamic oscillatory rheology conditions (at 160°C).

Dynamic oscillatory rheology of WPC boards

Results of the dynamic rheological behavior of WPC samples produced from P_{cont}/HDPE and P_{HWE}/HDPE (Figure 3) show that in both formulations the storage modulus (G′) is higher than the loss modulus (G″) in the entire range of frequencies (ω) tested, except from 0.01 to ~0.02 in the case of P_{cont}/HDPE. At very low frequencies (ω<0.03), G′ and G″ are close for P_{cont}, which could indicate that P_{cont} behaves either as plastic or as elastic material (transitional state) at these frequencies. Thus, the melt rheology of both WPC samples presents mostly an elastic behavior under the test conditions. A decreasing trend of G′ and G″ as a function of ω decrement is common in both formulations. However, G′ is higher in P_{HWE} than in P_{cont} formulations, showing that in the case of P_{HWE} the elastic forces are more important. Another key difference in the G′ curves is the presence of a shoulder for the P_{HWE}/HDPE composite in the range from 0.3 to 0.01 rad s^{-1}, which could be associated to the contribution of the interfacial tension of two liquids (Bousmina et al. 1995).

As presented in Figure 4a, the complex viscosity (η^*) of both formulations increases with decreasing ω. Higher viscosity of P_{HWE} formulations at ω=0.01–1.0 rad s^{-1} shows, presumably, that in this frequency range the interaction between the wood particles and the plastic is more intense than for P_{cont} formulations. This is probably due to the relatively higher amount of lignin in P_{HWE}. Both complex viscosities converge at ω~1.0 rad s^{-1} and have similar values at ω>1 rad s^{-1}. The η^* of HDPE is also presented in Figure 4a for comparison. Expectedly, the HDPE's η^* is lower than that of the composites. The damping factor tan δ (tan δ=G″/G′) is <1 in the whole range of ω (Figure 4b), which can be interpreted that elasticity dominates the compounding process.

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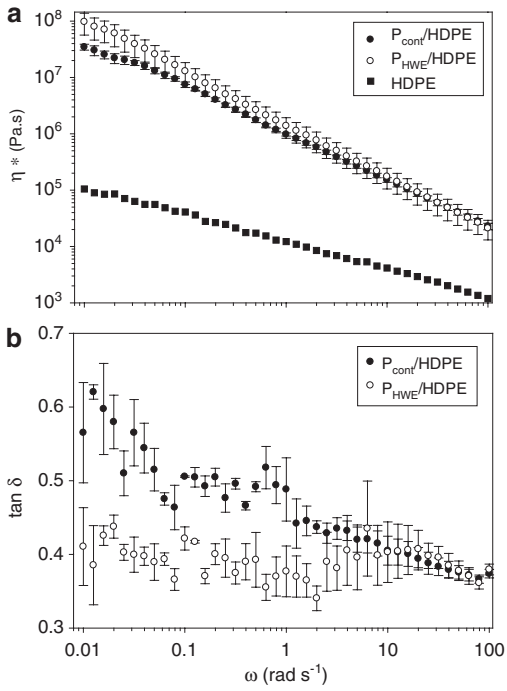

Figure 4: (a) Complex viscosity and (b) damping factor tan δ of the WPC melts.

Dynamic oscillatory rheology of the blends

Dynamic oscillatory rheological studies of HDPE/lignin blends were performed to understand better the observations in Figure 3b and the role of lignin in the composite's rheology. In Figure 5, typical plots of G′, G″ vs. γ data of HDPE/lignin at a 2:1 ratio under strain sweep are presented, whereas the behavior of the blends under frequency sweep (G′, G″ vs. ω) is visible in Figure 6a. Although both HDPE's G′ and G″ curves follow a smooth decreasing linear trend with decreasing ω (Figure 6a), the curves of the HDPE/lignin blends fluctuate along the ω sweep. Both curves of HDPE and the blends show a crossover point at ω~20 rad s^{-1}. Attention should be paid to the behavior of the G′ curve at low frequencies (at ω<0.2 rad s^{-1}) (arrow in Figure 6a). This curve shows a shoulder-like shape in the same position of the shoulder observed in the G′ curve of WPC melts produced with P_{HWE} (Figure 3b). The interpretation is that interfacial tension effects between HDPE and the lignin-rich extract are in part responsible for such distinctive shoulder of the composite's G′ curve. A similar feature has been reported previously by Bousmina et al. (1995) and Bousmina (1999) on emulsions of thermoplastics (polystyrene/polyethylene-PS/PE) under small amplitude deformations, which was also the case in

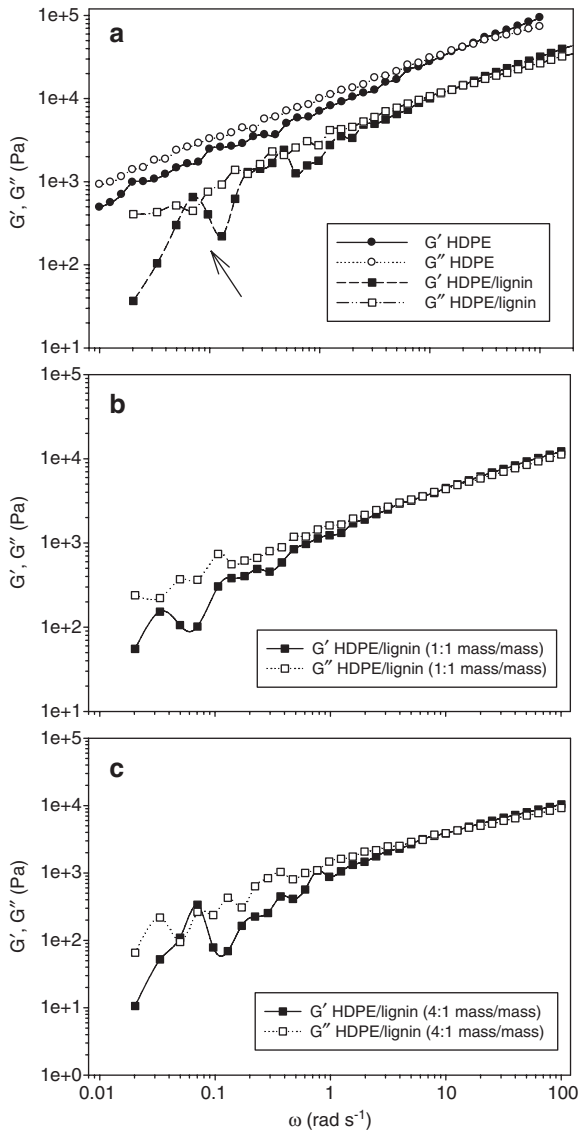

Figure 6: Typical rheological behavior of HDPE/lignin blends (2:1, 1:1, and 4:1) under frequency sweep.

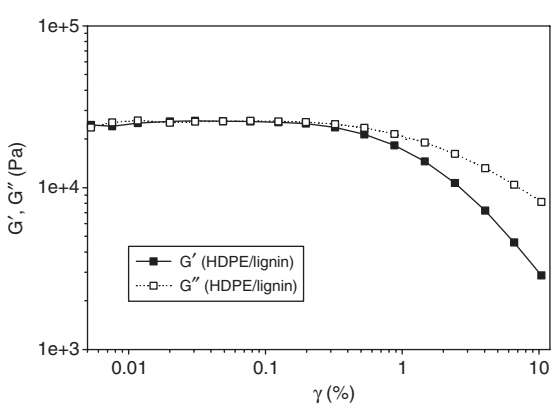

Figure 5: Typical G′, G″ vs. γ curves of HDPE/lignin blends (2:1) under strain sweep.

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polypropylene-PP/PS blends (Elias et al. 2007). The shoulder is characteristic of the viscoelastic behavior of molten immiscible polymer blends and is a manifestation of the interfacial tension effects, leading to a shift of the terminal zone to lower frequencies, that is, to longer relaxation times (Bousmina et al. 1995; Bousmina 1999).

Long relaxation time processes are common in multiphase systems and are attributable to the deformability of suspended droplets under strain. The mechanism can be described by theory that considers a balance between hydrodynamic (responsible for particles deformation) and interfacial forces (responsible for trying to keep the spherical or equilibrium shape). The explanation provided by Bousmina et al. (1995) appears pertinent for this study because the lignin in the blends in focus of this study also have a spherical morphology (Figure 7a). Moreover, the dynamic rheology curves of the HDPE/lignin blends show a shoulder in the same frequency than in the case of the G′ curve of PS/PE blends (Bousmina et al. 1995). Figure 6b and c presents results of the rheology tests of other HDPE/lignin blends with ratios of 1:1 and 4:1, respectively, which also show the same shape as described above.

The SEM images for the blend with the 2:1 HDPE/lignin ratio (Figure 7a and c) and the optical microscopy images (Figure 7b and d) demonstrate the immiscibility of the phases and the deformability of lignin-rich droplets subjected to dynamic rheology tests. Concentration of lignin-rich extracts (Figure 7c and d) was observed in materials at the edge of the rheometer's plate. The shape of some particles of deformed lignin in Figure 7c and d resembles the shape of the ribbon-type dispersion model of incompatible polymers (Van Oene 1978). Only rapid quenching or crystallization of the disperse phase preserves this type of morphology during flow. When the blend is melted again, the ribbons break up rapidly to form again small droplets (Van Oene 1978). This observation suggests that in melt conditions, the blend HDPE/lignin (droplets observed on P_{HWE} particles' surfaces) is subjected to deformation/relaxation similar to other immiscible blends with phase separation, which influences to some extent the rheological behavior of P_{HWE}/HDPE blends.

Torque rheometry

Results of the torque rheology tests (Figure 8) show that the torque at the beginning under loading conditions (or peak torque) up to ca. 1 min after loading is less in the P_{HWE} than in the P_{cont} formulations. The mean of the torque required for compounding each formulation in the interval 0–1 min was computed for comparison. In this region, P_{HWE} required ~10% less torque than P_{cont} formulations.

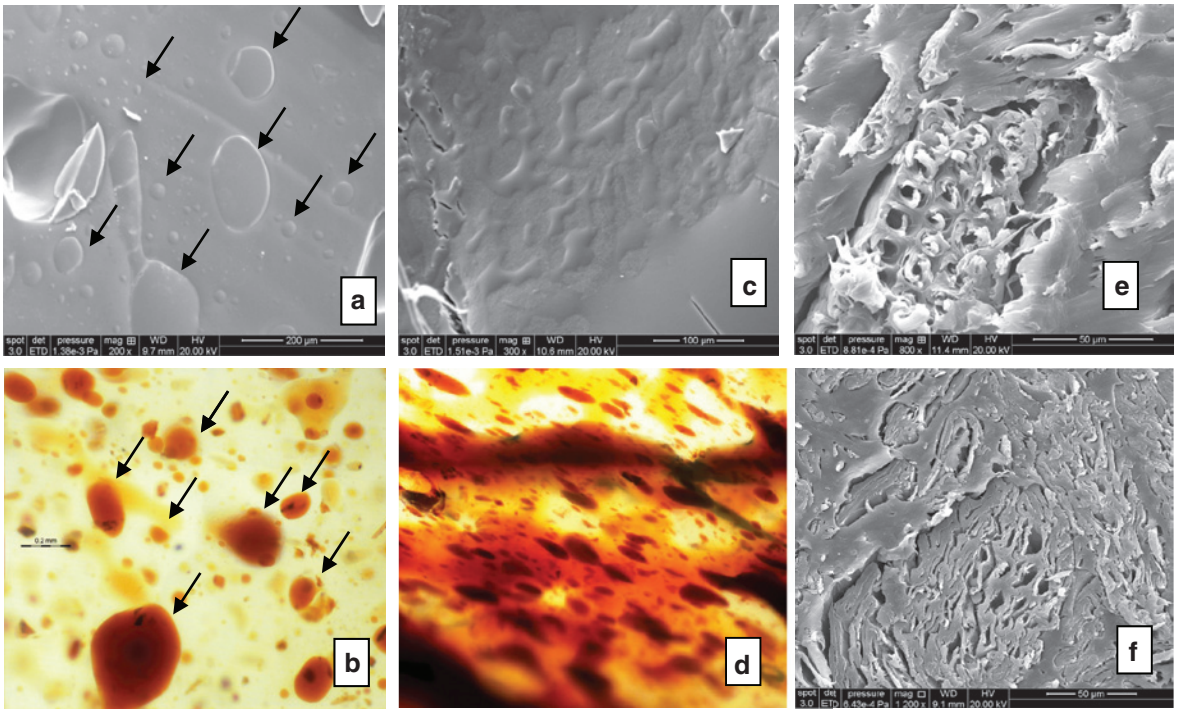

Figure 7: SEM (a, c) and optical (b, d) microscopy pictures of HDPE/lignin blend (2:1) after dynamic rheological tests. Disperse phase is constituted by lignin droplets (see arrows). SEM micrograph of cross sections of (e) P_{cont}/HDPE and (f) P_{HWE}/HDPE WPCs.

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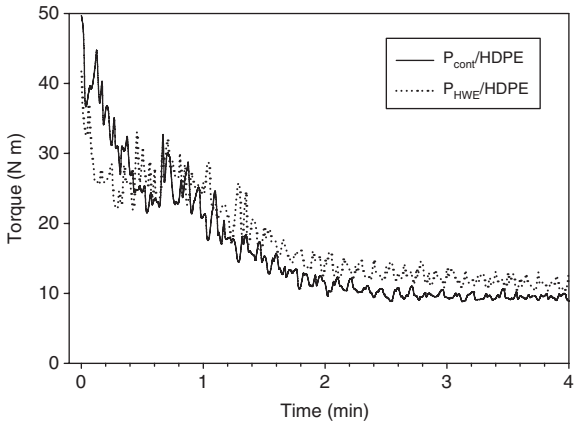

Figure 8: Torque rheology of compounding P_{cont} and P_{HWE} with HDPE at 160°C.

This behavior could result from the better flexibility and reduced mechanical properties of HWE particles as a consequence of the removal of hemicelluloses (Pelaez-Samaniego et al. 2014a), a relatively higher amount of lignin in the cell wall, presence of lignin droplets on the cell surfaces, and/or the deformation/relaxation behavior of the HDPE/lignin-rich layer. SEM micrographs of the cross-section of WPC boards produced with P_{HWE} verify better flexibility and higher deformability of particles during WPC extrusion process, as observed by the transverse collapse of fiber cell walls of the P_{HWE} particles during the extrusion of WPCs (Figure 7e and f). Pelaez-Samaniego et al. (2014a) observed a similar behavior of P_{HWE} particles.

Conclusions

HWE promotes softening, flowing, and partial migration of lignin from the cell wall to the cells' inner surfaces, where it is deposited as droplets layer. This lignin-rich material blends with the HDPE during compounding of WPCs and impacts to some extent the rheology of the composite. In particular, dynamic rheology results can be interpreted that the lignin layer promotes longer relaxation times to the HDPE/lignin-rich blends under melt conditions. This was revealed by a shoulder in G′ vs. frequency plots. This shoulder results from the interfacial tension between the lignin-rich material and HDPE due to the deformability of the lignin droplet in the blend under strain. Thus, the HDPE/lignin rubbery layer appears to contribute to improved linkage between wood particulates and HDPE during compounding. This is one of the reasons why no loss of mechanical properties of WPCs occurs with HWE wood.

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