Effects of Filler–Filler and Polymer–Filler Interactions on Rheological and Mechanical Properties of HDPE–Wood Composites

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Received 1 April 2008; accepted 15 September 2008
DOI 10.1002/app.29336
Published online 3 December 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: High-density polyethylene (HDPE)–wood composite samples were prepared using a twin-screw extruder. Improved filler–filler interaction was achieved by increasing the wood content, whereas improved polymer–filler interaction was obtained by adding the compatibilizer and increasing the melt index of HDPE, respectively. Then, effects of filler–filler and polymer–filler interactions on dynamic rheological and mechanical properties of the composites were investigated. The results demonstrated that enhanced filler–filler interaction induced the agglomeration of wood particles, which increased the storage modulus and complex viscosity of composites and decreased their tensile strength, elongation at break, and notched impact strength because of the stress concentration. Stronger polymer–filler interaction resulted in higher storage modulus and complex viscosity and increased the tensile and impact strengths due to good stress transfer. The main reasons for the results were analyzed. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 2806–2812, 2009

Key words: composites; interfaces; mechanical properties; polyethylene (PE); rheology

INTRODUCTION

During the last several decades, fillers are widely used to increase the performance and reduce the cost of polymeric materials. Among various factors affecting the properties of filled polymeric composites, filler content is no doubt an important one in consideration of the combination of economical competition and mechanical performance. Thus, it is important to increase the filler content without the loss of the mechanical performance of composites.

The addition of fillers into polymers results in two different interactions, that is, polymer–filler interaction and filler–filler interaction. These two interactions affect the flow behavior and mechanical performance of the composites.[1–7] Guo et al.[1] investigated the fiber–fiber and polymer–fiber interactions of glass fiber-filled linear low-density polyethylene using model prediction and experimental measurement. It was found that a strong fiber–fiber interaction causes an increase of the steady shear-viscosity, and a strong coupling effect between polymer and fiber results in a higher zero shear viscosity, an earlier shear-thinning transition, and a stronger shear-thinning behavior. Ray and Bhowmick[2] found that the surface modification of silica filler significantly reduces the formation of filler–filler networking, especially at high filler loadings. The use of maleic anhydride-grafted polyethylene enhances polymer–fiber interaction and therefore increases the tensile strength of wood-filled high-density polyethylene (HDPE).[3]

Recently, plastics–wood flour products have attracted increasing attention because of the economical competition. The wood flour content may be as high as $\sim$ 50 wt % in commercial plastics–wood products. However, increasing the wood content increases the viscosity of plastics–wood composite[8–11] and reduces its mechanical properties.[12–17] Thus, different additives, such as compatibilizer, lubricant, and elastomer, were added to improve the processibility and/or mechanical properties of plastics–wood composites. However, limited research paper has reported the effects of filler–filler and polymer–filler interactions on the rheological and mechanical properties of composites.

Therefore, the aim of the present work was to investigate the effects of filler–filler and polymer–filler interactions on the rheological and mechanical

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 10672061.
Contract grant sponsor: Teaching and Research Award Program for Outstanding Young Teachers in Higher Education Institutions of the Ministry of Education, People's Republic of China.

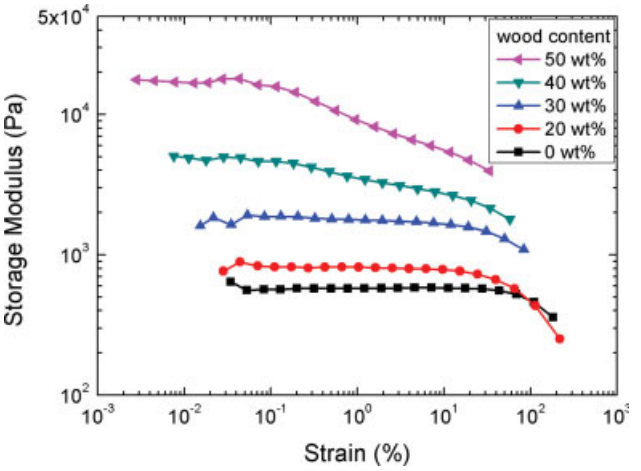

Figure 1 Storage modulus versus strain of HDPE1–wood composites with different wood content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

properties of the HDPE–wood composites. Different filler–filler and polymer–filler interactions were achieved by using four wood contents and three HDPE melt indexes and adding the compatibilizer.

EXPERIMENTAL

Materials

In this work, three HDPE grades with different melt indexes were used: grade 5218EA (Dushanzi Petroleum, China), grade 60550AG (Lanzhou Petroleum, China), and grade 5300B (Sinopec Group Daqing, China). They have a melt index of 15, 7.2, and 0.41 g/10 min (at 190°C and 2.16 kg) and are denoted as HDPE1, HDPE2, and HDPE3 in this work, respectively. The poplar wood flour with a 60-mesh size (Shuyang Wood Flour, China) was used. The maleic anhydride-modified polyethylene with a melt index of 6 g/10 min and a graft ratio of 1.1% (Lushan Chemical, China) was used as compatibilizer.

Sample preparation

The wood flour was dried at 80°C in a vacuum oven for 12 h. Then HDPE and wood flour with or without compatibilizer were compounded using a corotating twin-screw extruder (Ruiya, China) with a screw diameter of 35 mm and a length to screw diameter ratio of 40 : 1. The barrel temperature was set at 80-120-150-160-170-170-170°C (toward the die). The extruded strands were cooled in water bath and palletized. The pellets were dried at 80°C in a vacuum oven for 12 h. Then some pellets were compression molded into disks with a size of $\phi 25 \times 1$ mm at 170°C and 15 MPa for 20 min, which were used to measure the dynamic rheological properties. Some pellets were injection molded into standard specimens, which were used to measure the mechanical properties.

Characterizations

Dynamic rheological measurements, including amplitude sweep and frequency sweep, were conducted using Bohlin Gemini 200 Rheometer System with parallel plate of 25 mm diameter at 170°C. Amplitude sweep was performed at a controlled stress mode from 1 to 5000 Pa at a frequency of 1 s^{-1}. Frequency sweep was performed from 100 to 0.01 s^{-1} at a low strain level of 0.1%. The sample was loaded between two parallel plates with a gap of 1 mm and soaked for 15 min at the test temperature.

The tensile tests were performed according to GB/T1040-1992 at room temperature and a cross-head speed of 50 mm/min on a tensile tester (tensi TECH, USA). The Izod impact tests were conducted according to GB/T1843-1996 on an impact tester (Chengde, China). The average values of five repeated tests were taken for each sample.

Samples were immersed in liquid nitrogen and then fractured. The fractured surface was gold-coated

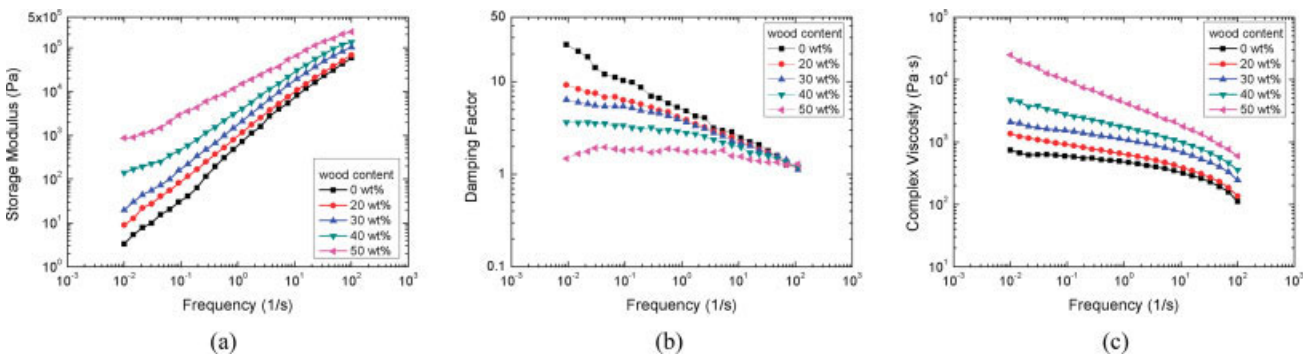

Figure 2 (a) Storage modulus, (b) damping factor, and (c) complex viscosity versus frequency of HDPE1–wood composites with different wood content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

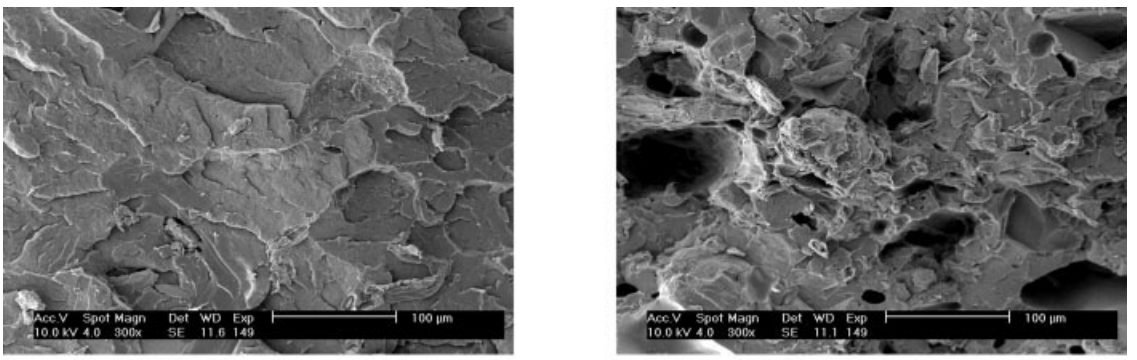

Figure 3 SEM micrographs on fracture surfaces of HDPE1–wood composites with wood content of (a) 20 and (b) 50 wt %.

before being examined using an environmental scanning electron microscope (XL-30 ESEM, Philips).

RESULTS AND DISCUSSION

Effects of wood content

For highly filled polymeric composites, small amplitude dynamic oscillation test is believed to be the most suitable method for assessing their internal structure as well as the dispersion state of the filler because small amplitude strain is indestructible to the internal structure. Thus, the dynamic amplitude sweep and frequency sweep were performed on the composites prepared in this work. Since the dynamic response of composites is sensitive to the level of strain, a small strain of 0.1% was selected for the frequency sweep to ensure that all frequency sweeps were performed in the linear viscoelastic region. The results of HDPE1–wood composites without compatibilizer are given here to reveal the effect of wood content.

The storage modulus versus strain for the HDPE1–wood composites with different wood content in the dynamic amplitude sweep test is shown in Figure 1. From Figure 1, it can be seen that the nonlinear viscoelastic region is shifted to the lower strain side as the wood content increases. Figure 2 shows the frequency sweep results of the HDPE1–wood composites with different wood content. It is evident that when increasing the wood content and sweep frequency, both storage modulus and complex viscosity of the composites increase, and their damping factor decreases. Moreover, the increase or decrease is more obvious at higher wood contents and low frequencies.

From the aforementioned dynamic rheological data, it can be seen that the composites with higher wood contents exhibit more solid like response, such as, the storage modulus is higher and varies less with frequency, and the damping factor is low. This may be due to the presence of agglomerates in highly filled composites.[18] With higher wood flour loadings, the filler–filler interaction in composites is enhanced, which induces the agglomeration of wood particles. The presence of agglomeration is confirmed by the SEM micrographs on the fracture surface of the HDPE1–wood composites, as shown in Figure 3. It can be seen that on the fracture surface, no void exists for the composites with 20 wt % wood content, but some voids exists for the composites with 50 wt % wood content. These voids are formed due to the agglomeration caused by filler–filler interaction. Furthermore, the agglomeration is

TABLE I
Tensile Properties of Three Neat HDPEs and Their Composites with Different Wood Content

Material component		Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)	Notched impact strength (kJ/m^2)
HDPE1/wood/compatibilizer (phr)	100/0/0	21.5 ± 0.2	0.85 ± 0.09	82.55 ± 1.56	11.2 ± 1.3
	80/20/0	19.0 ± 0.3	0.83 ± 0.10	19.22 ± 0.12	9.9 ± 1.2
	70/30/0	18.8 ± 0.2	0.90 ± 0.10	13.09 ± 0.68	8.2 ± 1.2
	60/40/0	18.5 ± 0.3	0.91 ± 0.08	7.43 ± 0.32	7.4 ± 1.3
	50/50/0	17.8 ± 0.2	1.16 ± 0.10	3.42 ± 0.11	6.1 ± 1.1
	50/50/5	34.4 ± 0.4	1.75 ± 0.11	7.67 ± 0.13	6.6 ± 1.2
HDPE2/wood/compatibilizer (phr)	100/0/0	23.5 ± 0.2	0.81 ± 0.08	83.02 ± 1.20	13.3 ± 1.3
	50/50/0	21.0 ± 0.3	1.48 ± 0.09	3.18 ± 0.32	7.5 ± 1.0
HDPE3/wood/compatibilizer (phr)	100/0/0	24.1 ± 0.2	0.93 ± 0.10	127.95 ± 2.13	37.6 ± 1.4
	50/50/0	23.6 ± 0.3	1.54 ± 0.12	4.95 ± 0.09	11.5 ± 1.2

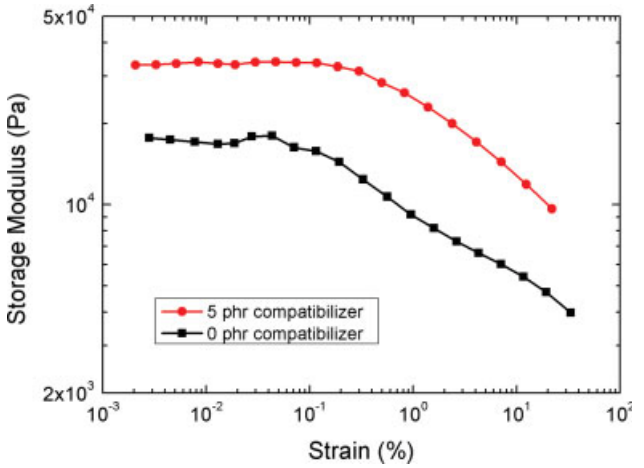

Figure 4 Storage modulus versus strain of HDPE1–wood (50 wt %) composites with and without compatibilizer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

sensitive to the imposed external strain. Thus, in dynamic amplitude sweep test, a smaller strain can destroy the internal structure and decrease the storage modulus of the composites with higher wood contents, as shown in Figure 1.

The tensile and impact properties of neat HDPE1 and its composites with different wood content are given in Table I, which shows that with the increase in the wood content, the tensile strength of composites decreases slightly, whereas tensile modulus increases. In addition, elongation at break decreases dramatically when adding wood into the HDPE1. This enhancing rigidity phenomenon was also observed for composites filled with high stiff filler.[19,20] The impact strength of composites decreases gradually with increasing wood content. The reason for lower tensile and impact strengths of the composites with higher wood contents can be explained as follows. Failure of a composite is governed by the crack initiation and crack propagation.[21] Increasing the wood content results in the increase of the probability for wood agglomeration, creating regions of stress concentration that require less energy to initiate or propagate a crack. Thus, in the composites with higher wood contents, voids formation in the stress concentration region and their subsequent coalescence in large voids and cracks lead to premature brittle fracture at low stress level and elongation.

Effects of compatibilizer

The HDPE1–wood composite containing 50 wt % wood flour was used to investigate the effect of compatibilizer. The effects of compatibilizer on amplitude and frequency sweep results are illustrated in Figures 4 and 5, respectively. From the amplitude sweep results, it can be seen that the addition of compatibilizer has little influence on the nonlinear viscoelastic region. From the frequency sweep results, an increase of storage modulus and complex viscosity caused by compatibilizer are obvious at lower frequency region. The reason for the latter may be explained as follows. The compatibilizer increases the polymer–filler interaction, which restricts the mobility of the polymer chains at the polymer–wood interface to change conformations. The increased polymer–filler interaction can be examined by SEM photographs on fracture surfaces of the composites with and without compatibilizer, as shown in Figure 6. It can be seen that there is an obvious gap between polymer and wood filler on the fracture surface of HDPE1–wood composite

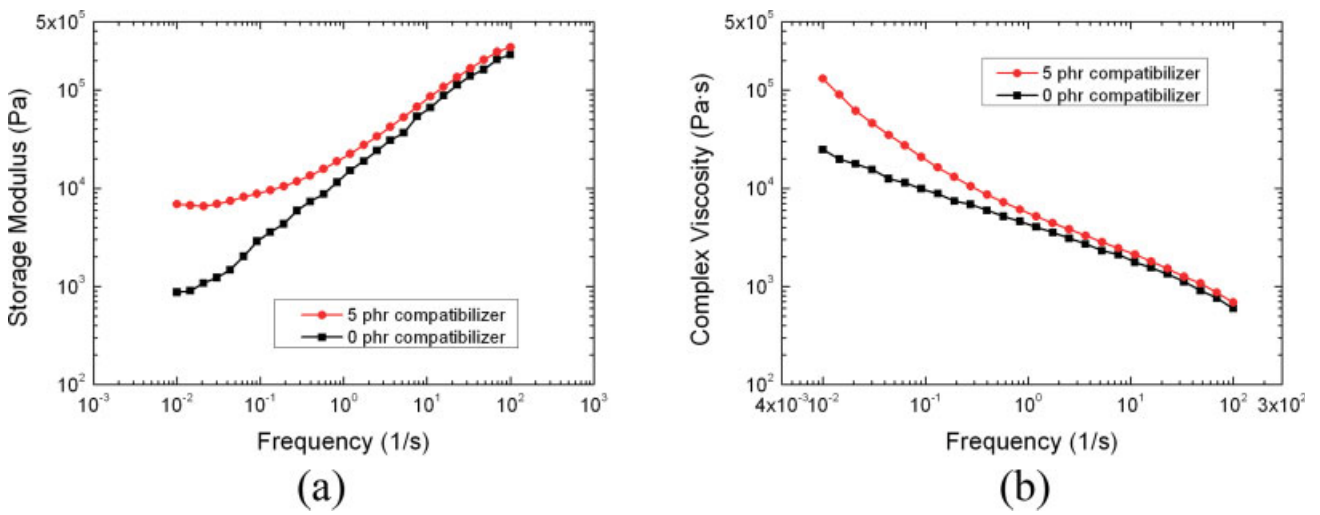

Figure 5 (a) Storage modulus and (b) complex viscosity versus frequency of HDPE1–wood (50 wt %) composites with and without compatibilizer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

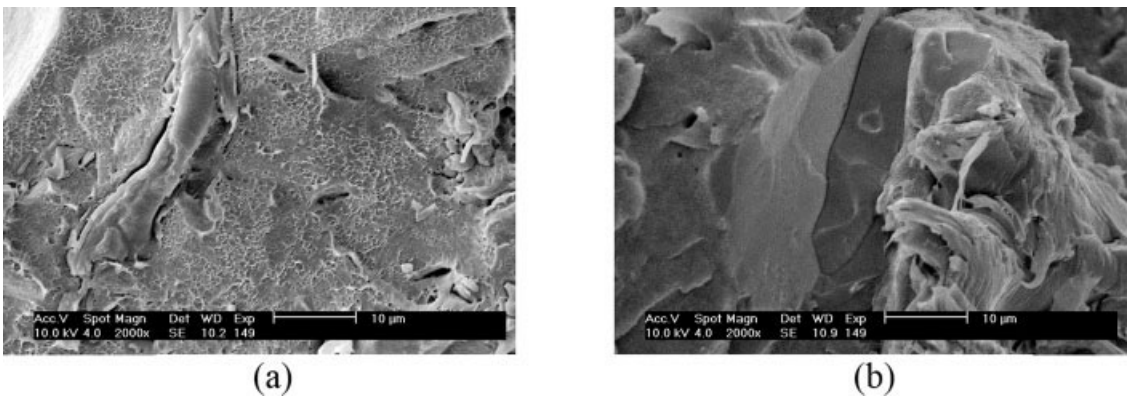

Figure 6 SEM micrographs on fracture surfaces of HDPE1–wood (50 wt %) composites (a) without and (b) with compatibilizer.

without compatibilizer. When adding compatibilizer into the composite, no gap exists between polymer and wood filler, indicating a strong polymer–filler interaction.

The effect of compatibilizer on the tensile and impact strengths of HDPE1–wood composites are also given in Table I. It is obvious that the addition of compatibilizer improves the tensile and impact strengths of the composite, especially the former. The improved tensile and impact strengths are also attributed to increased polymer–filler interaction, which is beneficial to the stress transfer and so reduces the stress concentration and increases the fracture initiation energy.

The difference of notched and unnotched impact strengths of HDPE1–wood composites is investigated and the results are shown in Figure 7. It is interesting to observe that there is a largely different response in notched and unnotched impact strengths when adding the compatibilizer into the HDPE1–wood composite. The compatibilizer increases the notched and unnotched impact strengths of the composite by 8 and 49%, respectively. Similar result was also reported by Nunez et al.,[22] who found that the compatibilizer has little effect on the notched impact strength of PP–wood flour composites. This can be explained as follows. Unnotched impact strength of a composite is the result of the combination of the crack initiation and the crack propagation energy, whereas notched impact strength is mainly attributed to the crack propagation energy because the crack initiation energy is minimized because of the presence of the very sharp notch.[23] With compatibilizer addition, improved polymer–filler interaction increases the crack initiation energy more significantly because of the decreased stress concentration, whereas changes the crack propagation energy a little.

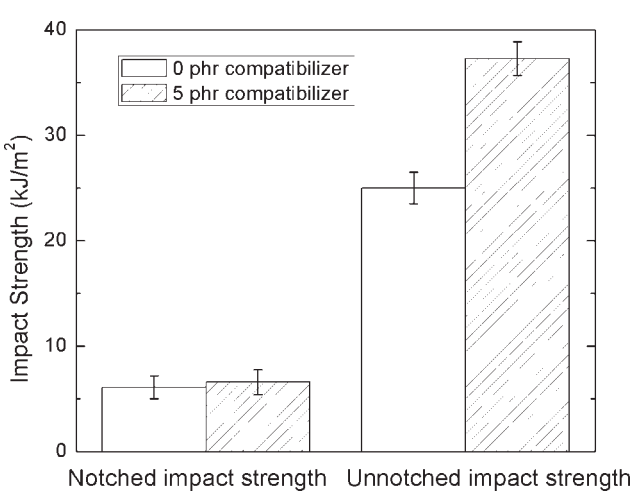

Figure 7 Notched and unnotched impact strengths of HDPE1–wood (50 wt %) composites with and without compatibilizer.

Effects of HDPE melt index

Three different composites combining different HDPE with 50 wt % wood were used to investigate

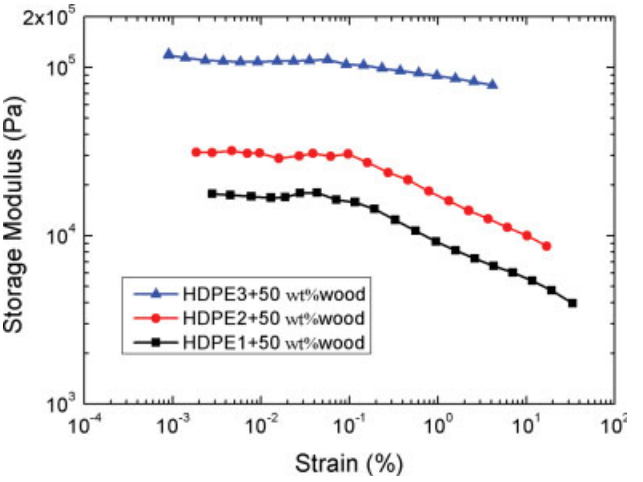

Figure 8 Storage modulus versus strain of HDPE–wood composites with different HDPE melt index. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

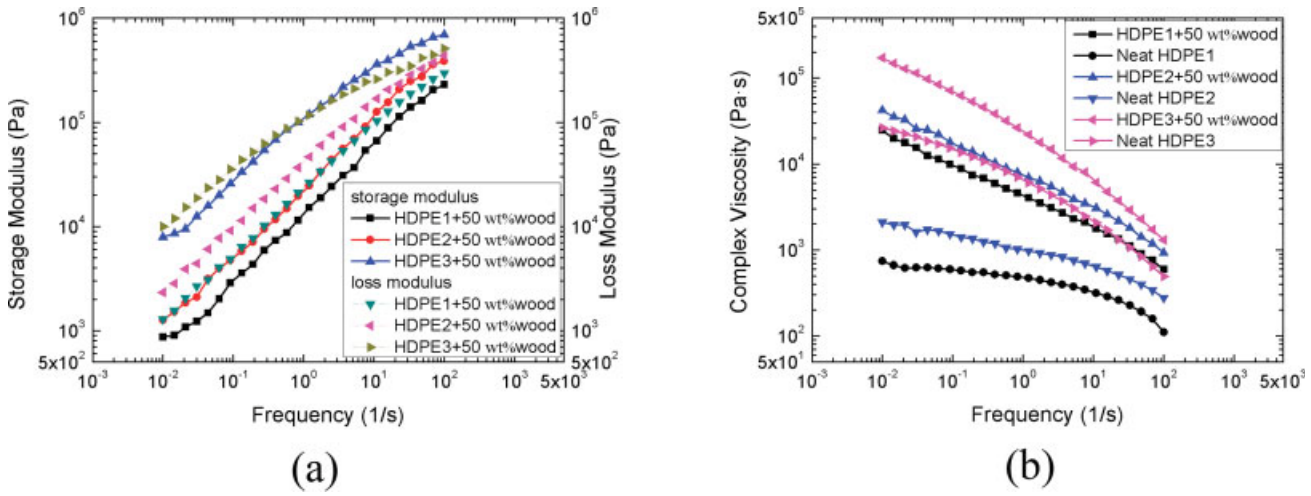

Figure 9 (a) Storage modulus and (b) complex viscosity versus frequency of three neat HDPEs and their composites with 50 wt % wood. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the effect of HDPE melt index. No compatibilizer was added. Figure 8 illustrates the storage modulus versus strain for the three composites in dynamic amplitude sweep test. It is evident that the melt index of the HDPE has little influence on the nonlinear viscoelastic region, but the decrease of storage modulus as strain increases is more pronounced for HDPE1–wood composites. The frequency sweep results of the three composites are shown in Figure 9. It can be seen that the loss modulus is higher than the storage modulus for HDPE1– and HDPE2–wood composites at all frequencies tested, whereas for HDPE3–wood composite, the storage modulus is higher than the loss modulus at higher frequencies. Moreover, the effect of wood on increasing the complex viscosity is more significant in HDPE1– and HDPE2–wood composites. That is, the complex viscosities of higher melt index HDPE–wood composites exhibit more significant increase compared to those of corresponding neat HDPEs. The reason may also be attributed to the improved polymer–filler interaction because of good wettability of wood in higher melt index HDPEs.

The tensile and notched impact strengths of three neat HDPEs and their composites with 50 wt % wood flour are also shown in Table I. The tensile strengths of three HDPE–wood composites are lower than those of corresponding neat HDPEs. The HDPE1– and HDPE2–wood composites exhibit little decrease in the impact strength compared with corresponding neat HDPE1 and HDPE2, whereas the HDPE3–wood composite shows much lower impact strength than neat HDPE3. The aforementioned strong polymer–filler interaction results in smaller decrease of notched impact strength in higher melt index HDPE–wood composites.

CONCLUSIONS

The rheological and mechanical properties of HDPE–wood composites were studied. Different filler–filler and polymer–filler interactions were achieved by using four wood contents and three HDPE melt indexes and adding the compatibilizer. With higher wood flour loadings in the composites, the filler–filler interaction is enhanced, which induces the agglomeration of wood particles. The agglomeration results in higher storage modulus and complex viscosity in dynamic rheological response. The tensile and notched impact strengths of composites decrease with increasing filler–filler interaction because of the stress concentration caused by the agglomeration.

Adding the compatibilizer or using higher melt index HDPE increases the polymer–filler interaction. The stronger interfacial interaction restricts the mobility of the polymer chains, which results in the increase of the storage modulus and complex viscosity. The tensile and impact strengths are improved because of the good stress transfer resulting from stronger interfacial interaction.

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