Effects of Chemical Modification of Wood Flour on the Rheological Properties of High-Density Polyethylene Blends

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ABSTRACT: Chemical modification of lignocellulosic fibers can improve interfacial adhesion and dimensionally stabilize the resulting plastic composites. This study examined the rheological properties of wood flour/high density polyethylene (HDPE) melts after poplar wood flour was modified with glutaraldehyde (GA, mainly cell wall cross-linking) and 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU, mainly poly-condensation). Results show improvement in both the dispersibility of treated wood flour in the HDPE and its interfacial compatibility. Treatment with GA decreased melt viscosity, moduli, and shear stress as evidenced by rheometry. However, the modifying effects of DMDHEU were not observed, which was mainly due to reduced HDPE content. This study indicates that chemical modification of wood flour is a promising approach to improve the processability of highly filled wood thermoplastic composites via extrusion/injection molding processing. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 41200.

INTRODUCTION

Wood plastic composites (WPC) combine the advantages of natural fibers and thermoplastics, including toughness of fiber and hydrophobicity of plastic. The production of WPC has recently undergone rapid expansion in the U.S. and China. In commercial WPC products, fiber content commonly ranges from 40 to 60 wt % to reduce cost. However, adding large amounts of natural fiber hinders proper interfacial adhesion between polar fiber and nonpolar thermoplastics, and poses challenges in extrusion processing due to insufficient dispersibility of the natural fibers.[1]

Chemical modification of natural fiber is an efficient strategy to reduce the polarity difference between fibers and thermoplastics, thereby promoting the interfacial compatibility and dispersion in the matrix. This can also improve dimensional stability and durability of the resulting composites.[2] Acetylation of natural fiber can plasticize the cell walls via a grafting reaction of the acetyl group onto cell wall polymers. Acetylation of flax fiber can cause a 60 and 30% decrease in moisture absorption and dimensional swelling of resulting polypropylene composites, respectively. Mass loss of the composites due to fungal decay can be reduced up 40%.[3] The tensile and flexural properties of composites filled with 18% acetylated flax fiber have been found to be 25% higher than for untreated composites.[4] Cross-linking

wood cell wall polymers with bi-functional glutaraldehyde can also considerably reduce the water uptake and the resulting dimensional swelling of wood/polypropylene composites up to 39% and 46%, respectively.[5] Modification of wood particles with 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) can affect the properties of wood/polypropylene composites in a similar manner to that of glutaraldehyde. However, the chemical reaction mechanisms are different for these substances. DMDHEU monomers/oligomers penetrate and mainly self-condense, forming rigid thermoset macromolecules to physically deposit in the cell walls (cell wall bulking).[5]

Changes in the molecules and micro-structure of cell walls due to chemical modification may create different rheological properties of natural fiber/thermoplastics. Grafting of monomers/oligomers onto cell wall polymers may enhance the dispersibility of wood fillers in matrix, which may dominate the extrusion processability of modified fiber/plastic composites. Rheological studies have mainly focused on the effects of coupling agents,[6–8] lubricants,[9] fiber morphology,[10,11] and matrix molecules,[12] but few studies have explored the modifying effects of natural fibers.[13]

In this study, wood flour was modified with GA (cross-linking pattern) and DMDHEU (bulking pattern) and the modifying effects on the rheological behavior of the resulting wood flour/

Table I. Formulations of the Blends, Specific Mechanical Energy (SME), Shear Heating (ΔT), and Equilibrium Torque (T_e) Obtained from Minilab and Torque Rheometer

Sample	Wood flour (wt %)	GA/DMDHEU (wt %)	HDPE (wt %)	SME (J g^{-1})[a]	ΔT (°C)[b]	T_e (Nm)[b]
Ctrl	40.0	0.0	60.0	1299	19.9	11.86
GA5	40.0	1.0	59.0	1175	16.5	10.83
GA10	40.0	2.2	57.8	1082	15.9	10.41
GA15	40.0	3.1	56.9	1054	14.0	10.21
DM5	40.0	2.7	57.3	1256	16.1	11.60
DM10	40.0	6.7	53.3	1278	17.4	11.71
DM15	40.0	12.6	47.4	1266	16.0	11.51

[a] Values obtained from Minilab.
[b] Values obtained from torque rheometer.

HDPE blend were investigated using a microcompounder, torque-, capillary-, and rotational-rheometer in order to explore the processability of WPC filled by high content of wood flour.

EXPERIMENTAL

Materials

Wood flour with a size of 40–80 meshes was prepared from poplar (*Populus ussuriensis* Kom.) sapwood chips with a hammer mill. High-density polyethylene (HDPE) pellets (5000S) were purchased from Daqing Petrochemical, China, with a density of 0.954 g cm^{-3} and a melt flow index of 0.7 g 10 min^{-1} (190°C, 2.16 kg according to ASTM D1238). HDPE pellets were ground to a fine powder in a Wiley mill for use.

Modifying agents were a 50 wt % aqueous solution of glutaraldehyde (GA) and 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) supplied by BASF (China). Magnesium chloride hexahydrate (MgCl$_2$·6H$_2$O) purchased from Tianjin Kermel Chemical Reagent. (Tianjin, China) was used as a catalyst for chemical reactions. GA and DMDHEU were used as received, and other chemicals were of analytical purity grade.

Treatments of Wood Flour

Wood flour was immersed into aqueous solutions of 5, 10, and 15% GA or DMDHEU, respectively, in a vacuum (0.06 MPa) for 4 h. The molar ratios of MgCl$_2$·6H$_2$O/GA and MgCl$_2$·6H$_2$O/DMDHEU in the solutions was 0.15 : 1 and 0.05 : 1, respectively. After impregnation, wood flour was dewatered by filtration and air-dried for 24 h, followed by drying in an oven at 60°C for 6 h and curing at 120°C for 24 h. Wood flour treated with water using the same procedure as above was used as an untreated control. The treated wood flour was allowed to cool down and sealed in plastic bags for use.

Preparation of Wood Flour/HDPE Blends

Untreated and treated wood flours were respectively compounded with HDPE at a specific ratio (Table I) using a corotating twin-screw extruder with a diameter of 18 mm and an *L/D* of 40 (Leistritz ZSE-18, Leistritz Extrusionstechnik GmbH, Germany). The screw configuration is shown in Figure 1. The extrusion temperature ranged from 150 to 175°C over eight heat zones along the extruder barrel. The feed rate and screw rotational speed were of 150 rpm and 100 rpm, respectively. The extruded strands were cooled in air and cut into pellets using a pelletizer.

CHARACTERIZATION

Morphological Analysis

Portions of the extruded pellets were injection-molded (SE50D, Sumitomo Heavy Industries, Japan) into impact test specimens measuring 80 mm × 12 mm × 3 mm. Injection and mold temperatures are 180 and 50°C, respectively. Cryo-fractured surfaces were generated by breaking the specimens frozen in liquid nitrogen. The specimens were also cryo-microtomed (CR-X cryo-ultramicrotome, RMC) perpendicular to the injection flow direction at −120°C using a glass knife. The fractured and sectioned surfaces were dried, sputter-coated with gold, and then observed with a field-emission scanning electron microscope (Quanta 200F, FEI, USA) at an accelerated voltage of 30 kV.

Dynamic Microcompounding Analysis

A 6-g mixture of wood flour/HDPE was compounded at 175°C using a laboratory scale microcompounder (Minilab Rheomex CTW5, Thermo Scientific, Germany) equipped with a pair of conical co-rotating screws. The blended melt passed through a recirculating channel (width 10 mm, height 1.5 mm, length
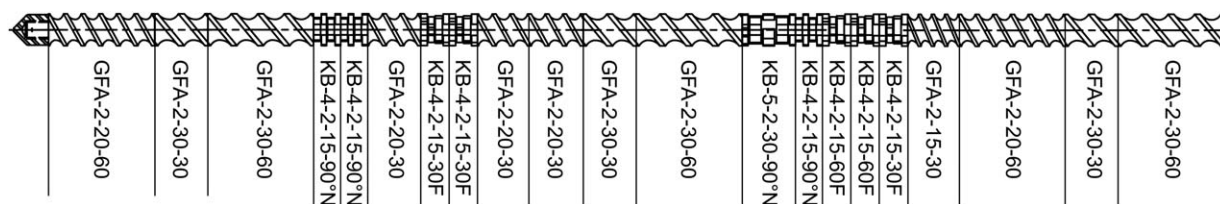
Figure 1. Screw configuration of the corotating twin-screw extruder (Leistritz ZSE-18).
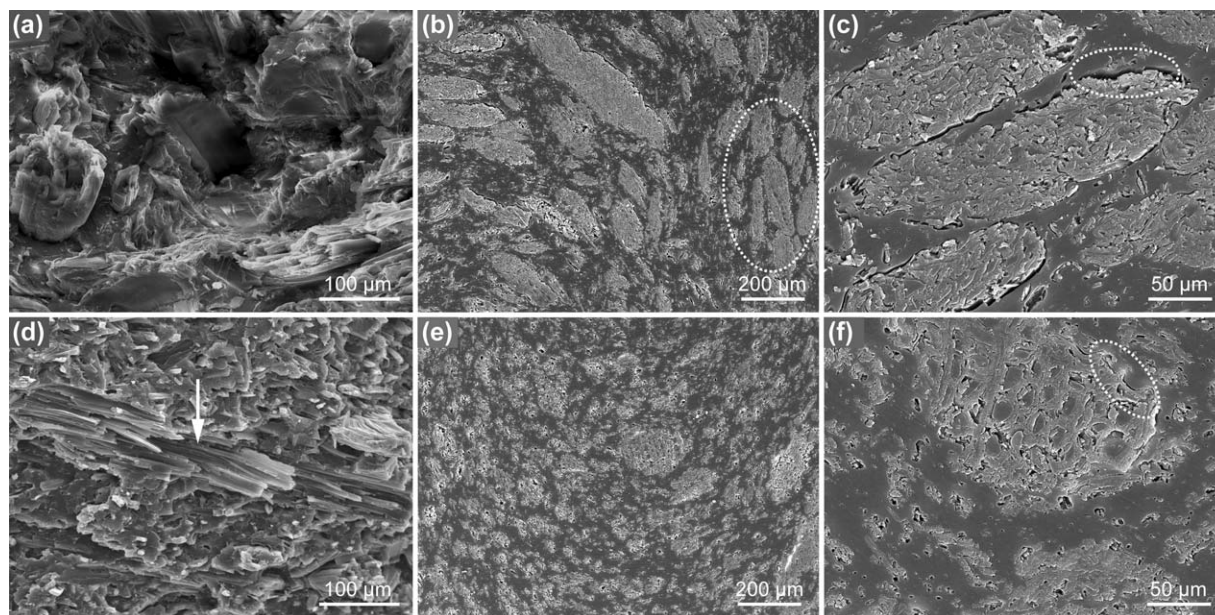
Figure 2. Micrographs of the composites untreated (a, fractured; b & c, sectioned) and treated with 15% GA (d, fractured; e and f, sectioned).

75 mm) and the inner pressure was determined at the inlet and outlet of the channel, respectively. The screw speed was set at 40 rpm and the run lasted 20 min to obtain a homogeneous blend. The torque (T) of screws and pressures were recorded, from which both the specific mechanical energy (SME, in J g^{-1}) and apparent viscosity of the melts were calculated.[14] Three replicates were tested for each formulation (Table I).

Torque Rheological Analysis

The pellets prepared in Preparation of Wood Flour/HDPE Blends Section were quickly fed into the sample chamber of a Haake torque rheometer equipped with two counter-rotating roller rotors (Rheomix 600p, Thermo Scientific, USA). The test was run at 175°C and 50 rpm for 8 min at 75% feeding volume. Three replicates were tested for each formulation. The equilibrium torque (T_e) and temperature are defined as the average values in the last 2 min of the test.

Capillary Rheological Analysis

Shear flow behavior was investigated using a screw-driven capillary rheometer (Rheometric Scientific Acer 2000) equipped with tungsten carbide dies with an entry angle of 180°. The diameter and length of the barrel were 20 and 320 mm, respectively. The capillary die had a length of 30 mm and a diameter of 2 mm. The test temperature was set at 170°C, and shear rates ranged from 20 to 2000 s^{-1}. A zero-length die of 0.2 mm in length was used to make end correction, which was verified by Bagley plots using the dies measuring 2.0 mm in diameter and 5, 10, and 15 in length/diameter ratio, respectively.[15] The pellets prepared in Preparation of Wood Flour/HDPE Blends Section were used, and three replicates were measured for each formulation.

Rotational Rheological Analysis

The pellets prepared in Preparation of Wood Flour/HDPE Blends Section were injection-molded into test samples measuring 25 mm (diameter) × 2.2 mm (thickness) using a mini

injection molder (Haake MiniJet, Thermo Scientific, Germany). Prior to testing, the sample was heated to 175°C and equilibrated for 5 min to erase the previous thermal and deformation history. Tests were run using a rotational rheometer (Discovery HR-2, TA Instruments, New Castle, USA) equipped with a pair of parallel plates (2 mm in working distance and 25 mm in diameter). The dynamic frequency sweep was run at 175°C from 0.1 to 500 rad s^{-1} at a 0.05% strain amplitude in the linear region. Four replicates were tested for each formulation.

RESULTS AND DISCUSSION

Morphological Analysis

Wood flour was pulled out from the matrix, giving rise to voids on the fractured surface of the untreated composites. The surface of the pulled wood flour appeared free of any adhered HDPE matrix [Figure 2(a)]. There was no substantial interfacial adhesion between the wood flour and the HDPE matrix. The wood flours were agglomerated in the HDPE and dispersed unevenly on the sectioned surfaces [Figure 2(b)], which has been attributed to a strong affinity between polar wood flour particles.[16] Interfacial delamination was observed on the sectioned surfaces of the untreated composites [Figure 2(c)]. Compared with the untreated composites, the composites treated with 15 wt % GA showed a smoother fractured surface on which wood particles were broken [Figure 2(d)]. This may have been due to the improved interfacial adhesion between the wood flour and HDPE. The reduced tensile strength of wood due to GA treatment may have also caused the brittle fracture.[17] There was much less interfacial delamination between the wood flour and HDPE on the sectioned surface than on the untreated composites, further confirming the improved interfacial compatibility [Figure 2(f)]. The size of wood particles in the GA-treated composites [Figure 2(e)] was apparently smaller than that in the untreated controls [Figure 2(b)], which is due to
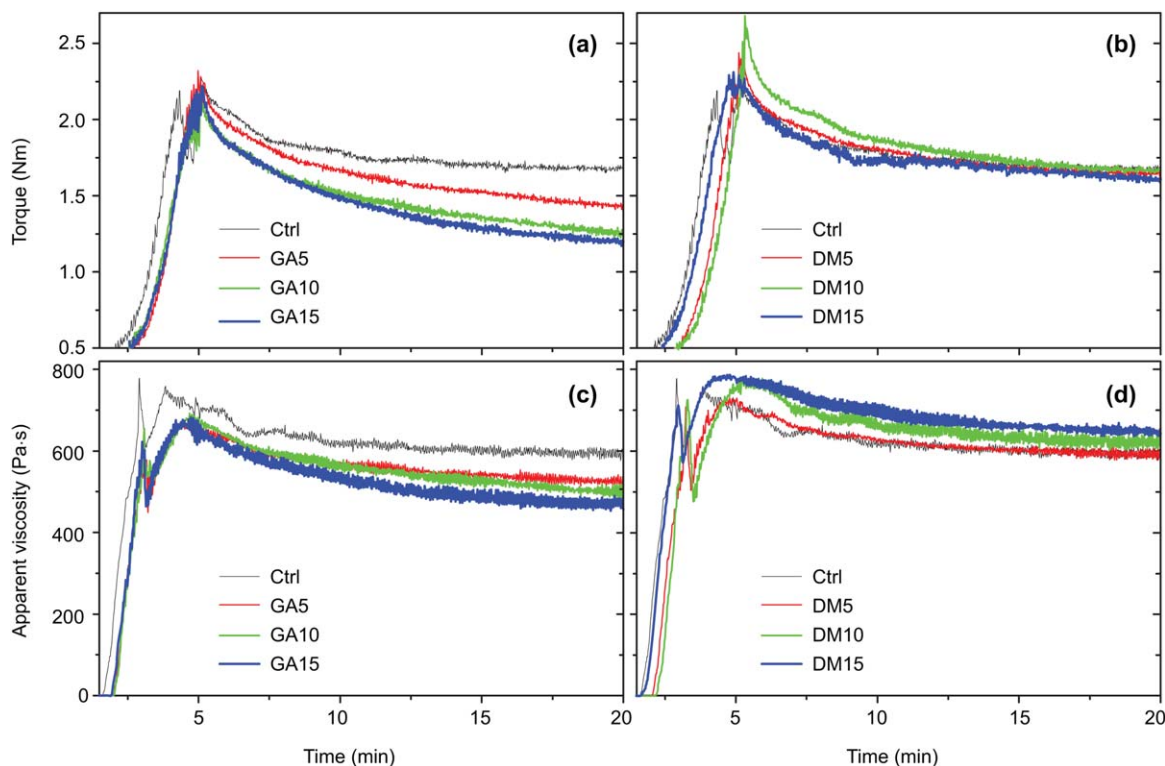
Figure 3. Change of torque (a, b) and viscosity (c, d) of blend melts with time obtained from Minilab. The legends: Ctrl, untreated control; GA, glutaraldehyde; DM, DMDHEU; the number behind shows a concentration of chemical used. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

embrittlement of GA-treated wood flour that was broken into finer fragments during the extrusion and injection molding processes.[5,18] The composites treated with 15 wt % DMDHEU exhibited a comparable appearance to those treated with 15 wt % GA; however, wood particles in the DMDHEU-treated composites were slightly larger than those in GA-treated composites (not shown). This is consistent with our previous results observed in the treated-wood particle/polypropylene composites.[5]

Dynamic Microcompounding and Torque Rheological Analysis

Treatments of wood flour with GA caused a considerable decrease in torque and viscosity during compounding of wood/HDPE blends. Both torque and viscosity decreased with increasing GA content [Figure 3(a,c)]. The blend melt of 15 wt % GA-treated wood flour/HDPE exhibited an 18.9% reduction in specific mechanical energy (SME) compared with the untreated melt (Table I). The reduction in viscosity and SME may mainly be explained by the improved dispersibility of wood flour in HDPE and their interfacial compatibility. GA can react with hydroxyl groups and cross-link the wood cell wall polymers, thereby lowering the surface energy of wood particles.[19,20] As a result, the agglomeration of wood flour was reduced. The finer cell wall fragments resulting from GA treatments and shear [Figure 2(e)] should not contribute to the reduced torque and viscosity due to the fact that changing the particle size of wood

flour does not apparently influence the melt viscosity of wood flour/HDPE composites.[10,21]

Compared with the untreated wood flour, treatments of wood flour with DMDHEU did not substantially influence the torque, but caused slightly higher viscosity during compounding of the wood flour/HDPE blend. DMDHEU is a polyol monomer and tends to condense in the wood cell wall.[22] Treatments with DMDHEU affected the surface energy less than did GA treatments.[23] Dispersion of DMDHEU-treated wood flour in HDPE was more even than that of the untreated wood flour, but less even than that of GA-treated wood flour. With increasing DMDHEU concentrations, the amount of condensed DMDHEU (rigid thermoset) increased up to 12.6% in the blend. As a result, the amount of HDPE decreased accordingly (Table I), which may have reduce the shear flow of the resulting blend melt.[10,24] These combined effects may explain the unchanged torque and the increased viscosity [Figure 3(b,d)]. At a comparable GA/DMDHEU content of 2.1–2.5% (Table I), GA treatment considerably reduced the torque and viscosity of the resulting blend; however, DMDHEU modification did not cause any substantial changes (Figure 3). This comparison further demonstrates the positive effects of cross-linking reactions by GA.

The modifying effect of wood flour on the torque obtained from Minilab was further confirmed by torque rheometry. Treatment with low concentrations of GA (5%) considerably reduced the equilibrium torque of the blend melt. The torque
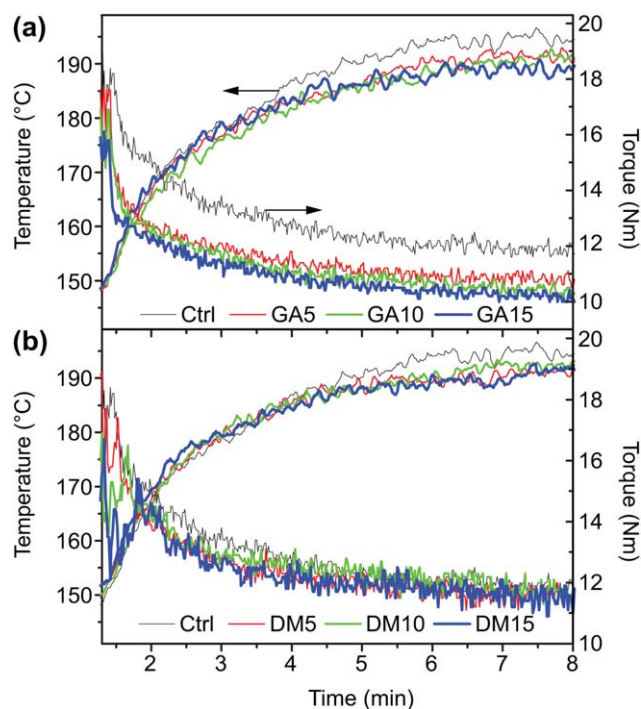
Figure 4. Change of torque and temperature of blend melts with time obtained from torque rheometer. The wood flour was treated with GA (a) and DMDHEU (b) in the blend, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decreased marginally with increasing GA concentrations [Figure 4(a)]. Compared with the untreated blend, DMDHEU treatments did not appear to change the blend's equilibrium torque [Figure 4(b)]. Treatments with both GA and DMDHEU, especially for GA, led to a decrease in shear heating (ΔT) compared with the untreated blend (Table I). This reflects that less heat was produced by friction in the sample chamber, which may be attributed to improved dispersibility of the treated wood flour in the HDPE.

Capillary Rheological Analysis

The wood flour/HDPE blends displayed three flow regimes according to the test (Figure 5). During the shear rate of 20–200 s^{-1}, shear stress increased with shear rate. The flow was stable and the surface of the extrudates showed small-amplitude, periodic distortions (sharkskin melt fracture, not shown) due to surface tearing. In the shear rate region of 200–600 s^{-1}, the blend melt flow was unstable and the shear stress fluctuated. The extrudate appeared alternatively distorted and smooth on the surface (stick-slip flow).[25] At a shear rate of over 600 s^{-1}, the shear stress linearly increased again and the resulting extrudate surface was smooth, as observed in the previous studies.[21,26,27]

Treatments of wood flour with only 5 wt % GA caused a considerable reduction in the shear stress compared to the untreated wood flour through the shear rates [Figure 5(a)]. With increasing GA concentrations, the shear stress curves were similar to those obtained at 5% GA. DMDHEU treatments did not substantially influence the shear stress of the wood

flour/HDPE blend [Figure 5(b)]. These results are consistent with the findings obtained from microcompounding and torque rheological analyses. The steady shear viscosity (η) of the blend melts did not change after modification of wood flour with GA or DMDHEU [Figure 5(a,b)]. This can be explained by the alignment of wood flour along the flow direction, and the formation of a thin layer of HDPE on the capillary wall for all test blends.

Rotational Rheological Analysis

Above studies using rheological analyses mainly reflect the behavior of wood flour/HDPE blend melts. We further prepared the composite samples using these blends to analyze using rotational rheometer, aiming at exploring the internal structure and dispersion state of wood flour in the composite.[9,28] Our study found that the storage modulus (G') of the untreated composites had a nonterminal plateau at low frequencies [Figure 6(a)], which may be due to network structure formed by strong hydrogen bonds in the agglomerated wood flour in the composite.[29]

In treatments of wood flour with GA, both viscosity (η^*) and G' of the resulting composites were decreased over the frequency region, especially in the low-frequency region [Figures 6(a) and 7(a)]. With increasing GA concentrations, the G' value decreased and slope of G' curve increased, respectively, at low-frequency ranges of 0.1–0.4 rad s^{-1}. This suggests an improved
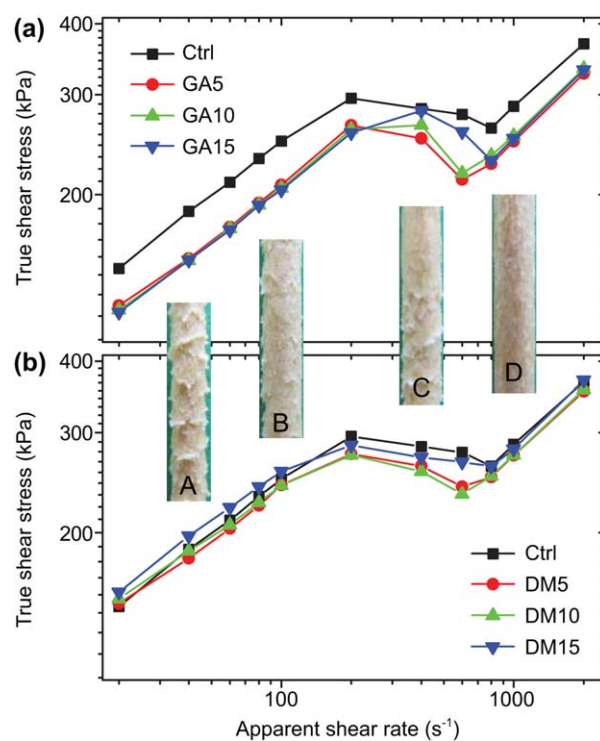
Figure 5. Change of true shear stress of blend melts with apparent shear rate. The wood flour was treated with GA (a) and DMDHEU (b) in the blend, respectively. Insert pictures are the extrudate surface morphology at 40 (A), 100 (B), 400 (C), and 1000 s^{-3} (D), respectively. $D = 2$ mm and $L/D = 15$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
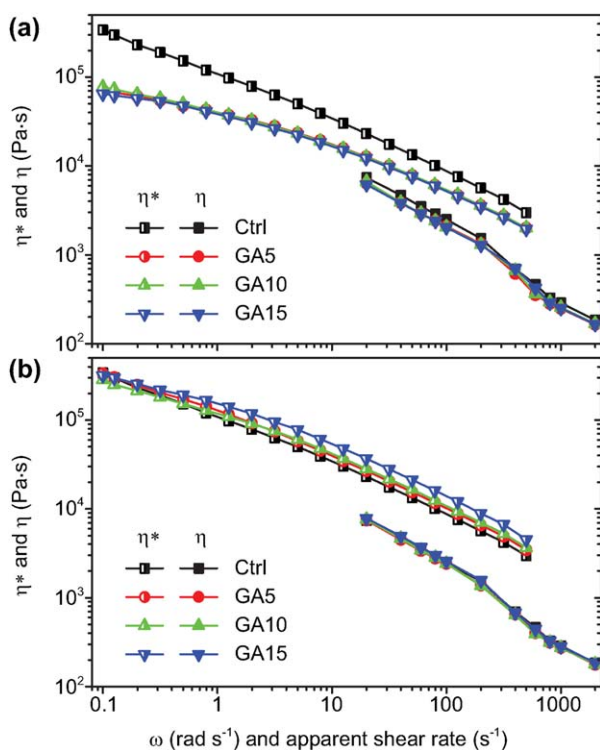
Figure 6. Comparison of apparent shear viscosity η and complex viscosity η^* obtained from capillary- and rotational rheometer, respectively. The wood flour was treated with GA (a) and DMDHEU (b) in the blend, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dispersion of wood flour.[30] Over 0.4 rad s^{-1} the G' was similar and independent of GA concentration [Figure 7(a)]. The viscosity of GA-treated wood flour/HDPE composites was not sensitive to the change of GA concentrations used [Figure 6(a)]. However, the G' value of DMDHEU-treated wood flour/HDPE composites was slightly lower than the untreated composites at frequencies of 0.1–0.4 rad s^{-1} [Figure 6(b)]. This suggests a limited improvement in the dispersion of wood flour. DMDHEU treatment caused a slight increase in both η^* and G' compared with the untreated composites [Figures 6(b) and 7(b)], which can be explained by the reduced HDPE content and incorporation of rigid, condensed-DMDHEU polymer in the composites.

At low frequencies, the loss modulus (G'', not shown) of the composites was higher than G'; over an intersection point, the G'' was lower than G', indicating a transition from viscous to elastic behavior.[9] The intersection point of G' and G'' for untreated composites was located at ~5 rad s^{-1} [arrow in Figure 7(a)]. The intersection point shifted toward higher frequencies of 12, 20, 50 rad s^{-1} with increasing concentrations of DMDHEU or GA [arrows in Figure 7(a,b)]. This suggests that HDPE chains fully relax at high frequencies, especially for GA-treated composites.[9]

A comparison of the steady shear viscosity (η) obtained from the capillary rheometer and the complex viscosity (η^*) obtained from the rotational rheometer is shown in Figure 6. The

viscosity from the capillary rheometer was considerably lower than that obtained from the rotational rheometer, which was also observed in the previous studies.[26,31] This difference is explained by the different internal structures of materials tested. In the blend melt of the capillary rheometer, wood flour is aligned along the flow direction due to combined shear and extensional forces. However, wood flour in the composites used for rotational rheometer is randomly oriented. Compared with the untreated blend, the difference between η and η^* of GA-treated blends was smaller, confirming the improved dispersion of GA-treated wood flour in the HDPE matrix. The DMDHEU-treated blend, by contrast, showed a greater difference between the η and η^*, which can be attributed to lower HDPE proportions in the blend.

CONCLUSIONS

This study examined the effects of chemical modification of wood flour with glutaraldehyde (GA) and 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) on the dispersibility of wood flour in HDPE, and determined the rheological behavior of the resulting high density polyethylene blends. Results demonstrate that treatments of wood flour with GA, even at low concentrations, can promote the flowability of the resulting wood flour/HDPE blend due to improved dispersion. This study indicates that chemical modification of wood flour is a promising approach to improve the processability of highly
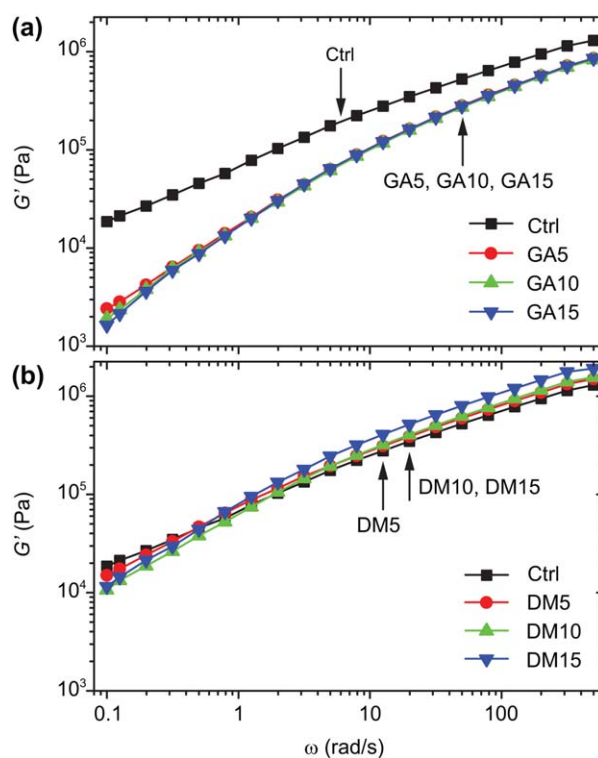
Figure 7. Change of storage modulus G' of the blend melts with angular frequency ω. The wood flour was treated with GA (a) and DMDHEU (b) in the blend, respectively. Arrow indicates the intersection point of G' and loss modulus G''. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

filled wood thermoplastic composites via extrusion/injection molding processing.

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