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Effects of ionic liquid on the rheological properties of wood flour/high density polyethylene composites

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ABSTRACT

Wood flour was treated with an ionic liquid, 1-(2-hydroxyethyl)-3-methylimidazolium chloride ([Hemim]Cl), to various weight percent gains. The treating effects on the rheological properties of the resulting wood flour/high density polyethylene (HDPE) blends were investigated using a Haake micro-compounder and torque-, capillary-, and rotational-rheometer, respectively. Treatment with [Hemim]Cl caused a decrease in the crystallinity and an improvement in the thermoplasticity of wood flour. At low processing speeds, the melt torque and viscosity increased with increasing [Hemim]Cl content; while at high speed, they decreased or remained the same. [Hemim]Cl can broaden the processing window of wood flour/HDPE composites with stable flow and smooth product surfaces. The dynamic rheological results show that storage and loss moduli and complex viscosity of the composite melts increased with increasing [Hemim]Cl content.

1. Introduction

Wood plastic composites (WPCs) have emerged as viable bio-based composites and thus have attained commercial success [1]. During WPC production, the preferred method for manufacturing is extrusion. The viscosity of WPC melts generally increase with increasing wood content. Higher viscosity requires high torque to efficiently mix the blends; in addition, internal friction can increase and cause local overheating, thermally degrading the wood flour [2]. This requires higher energy consumption and the resulting WPCs may have reduced performance and surface quality [3]. Various methods have been applied to improve the processability of WPCs, such as use of additives [4,5], adjusting die and processing parameters [6,7], and designing specific screw configurations and dies [7–9].

The rigid, crystalline cellulose microfibril reinforcing an amorphous matrix of lignin and hemicelluloses forms a sophisticated architecture, which endows wood cell wall with great strength and rigidity [10]. The rigid cell architecture lacking adequate plastic deformability during extrusion processing, may suffer significant changes due to friction and heating conditions. At high levels of wood, extreme processing conditions may induce structural damage of wood particles, evidenced as buckling, cellular collapse and eventually fracture in cell walls, and consequently poor reinforcing effects [11]. Therefore, current methods, such as altering flow of plastics or controlling die stresses, do not work for high wood flour contents.

If the cell wall can be processed with an approach similar that of thermoplastics, by exhibiting plastic deformation without fracture at high temperatures and restoring rigidity after processing, both the processability and performance of WPCs could be greatly improved [3,12]. Results of our previous work show that removal of lignin can decrease viscosity of WPC melts that results from the highly porous and flexible structure of delignified wood fiber. Also, removal of hemicellulose can increase the melt viscosity that results from enhanced stiffness of the hemicellulose-removed fiber [13]. This indicates that improving the thermoplasticity of rigid cell walls may be a viable strategy to improve processability of WPCs.

Ionic liquids (ILs) know as "green solvents" have been extensively studied for their ability to dissolve cellulose [14], lignin [15], hemicelluloses [16], and even wood [17–19]. Poplar wood treated with a small amount of ILs can achieve a large deformation without cell wall fracture under low pressure (796 kPa) [20]. Plasticized wood cell walls also exhibit increased hydrophilicity due to the high polarity of the ILs. This may enhance filler–filler interaction, which facilitates agglomeration of the wood flours in resulting WPCs [9]. Interfacial tension between hydrophilic wood

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flours and hydrophobic plastic matrix can be increased as well. The increase in filler–filler interaction and interfacial tension can increase the viscosity of composite melts, and thus decrease processability of WPCs [4,21]. This brings up the question of whether plasticizing wood flours with ionic liquid can improve processability of WPCs.

This study aims to elucidate how plasticization of wood flour by ionic liquid affects processing performance of the WPCs. Therefore, we treated wood flour with ionic liquid and assessed the effects of treatments on the rheological characteristics of the resulting high density polyethylene composite melts.

2. Experimental

2.1. Materials

Wood flour (WF) was prepared from poplar (*Populus ussuriensis* Kom.) sapwood chips in a hammer mill to pass sieves measuring 60–100 meshes. Prior to use, WF was dried at 105 °C for 24 h. High density polyethylene (HDPE) pellets (5000S) were purchased from Daqing Petrochemical Co., China, with a density of 0.954 g cm^{-3} and a melt flow index of 0.7 g/10 min (190 °C, 2.16 kg according to ASTM D1238). The HDPE pellets were further ground into a fine powder for use. Ionic liquid (IL), 1-(2-Hydroxyethyl)-3-methylimidazolium chloride ([Hemim]Cl) with a purity of 99.0% was purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences without further purification. Anhydrous ethanol was supplied by JT Baker Chemical Company.

2.2. Treatment of WF

A specific amount of [Hemim]Cl was dissolved in anhydrous ethanol in a flask. Thereafter, the dried WF was added and stirred vigorously to form a homogeneous mixture. The flask was sealed and set for 4 h at room temperature. The treated WFs were vacuum-dried at 60 °C for 24 h and sealed in plastic packing bags for use.

2.3. Preparation of WF/HDPE compounds

WFs were dry-mixed with the HDPE powder at a specific ratio (Table 1), and then compounded using a co-rotating twin-screw extruder (diameter = 18 mm and L/D = 40) (Leistritz ZSE-18, Leistritz Extrusionstechnik GmbH, Germany). The extrusion temperature ranged from 150 to 175 °C over eight zones along the extruder barrel. The extruded strands were cooled in air and pelletized. Portions of the pellets were injection-molded (SE50D, Sumitomo Heavy Industries, Japan) into standard impact test specimens. Injection and mold temperatures were 180 and 50 °C, respectively.

2.4. Characterization of WF

2.4.1. X-ray diffraction (XRD) measurement

Untreated and treated WFs were compression-molded into sheets using a pellet press (FW-4, Uncommon Sci. & Tech. Development CO., Ltd., Tianjin, China) under a pressure of 10 MPa for 20 min at 25 °C and 180 °C, respectively. The compressed sheets were used immediately for XRD analysis.

XRD test was conducted by using an X-ray generator (Ni-filtered Cu Kα radiation) with a voltage of 40 kV and a current of 30 mA (D/max 2200, Rigaku, Tokyo, Japan). The crystallinity index (*CrI*) was calculated according to the method of Segal et al. [22].

2.4.2. Dynamic mechanical analysis

Dynamic mechanical analysis of the untreated and treated WFs was carried out using a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, USA). Approximately 40 mg of WF was loaded into a stainless steel material pocket (Perkin Elmer, USA, Product No. N5330323) with dimensions of 30×14 mm^2. The pocket was then folded in half, crimped closed to form a sandwich approximately 0.9 mm thickness, and clamped into the DMA. The pocket was loaded in a single cantilever mode. The clamps were tightened using a torque wrench to 7 in lb. The test was performed at an oscillating frequency of 1 Hz and amplitude of 15 μm. Samples were heated from −25 to 200 °C at a rate of 3 °C min^{-1}. Five replicates were used for each treatment.

2.5. Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on a thermal analyzer (SDT Q600, TA Instruments, New Castle, USA) under N_2 atmosphere with a purge gas flow of 100 ml min^{-1}. Samples (6–8 mg) were heated from room temperature to 600 °C at a heating rate of 10 °C min^{-1}. Three replicates were used for each sample.

2.6. Interfacial morphological analysis

Sections of the impact test specimens were cryo-microtomed (RMC CR-X cryo-ultramicrotome) perpendicular to the injection flow direction at −120 °C using a glass knife. The sectioned surfaces were subsequently dried, sputter-coated with gold, and then observed with a field emission scanning electron microscope (FE-SEM, Quanta 200F, FEI Company) at an accelerated voltage of 30 kV.

2.7. Rheological analysis

2.7.1. Dynamic microcompounding

The rheological tests of WF/HDPE melts were conducted on a laboratory scale microcompounder (Minilab Rheomex CTW5, Thermo Scientific, Germany). The blend was mixed with a pair of conical co-rotating screws and passed through a recirculating channel (width 10 mm, height 1.5 mm, length 75 mm). Two pressure sensors were positioned at the inlet and outlet of the channel. The torque (T) and pressure drop (ΔP) in the channel were recorded and used to calculate the specific mechanical energy (*SME*, in J g^{-1}) and the final apparent viscosity of the melt, respectively [23].

In this study, six grams of dry-mixed WF/HDPE (Table 1) were fed into the Minilab (within 5 min) and compounded at 175 °C with a screw speed of 40 rpm for 20 min to produce a homogeneous blend. Three replicates were used for each formulation.

2.7.2. Torque rheometry

The rheological behavior of the WF/HDPE melts was evaluated using a Haake torque rheometer (Rheomix 600p, Thermo Scientific, USA) equipped with two counter-rotating roller rotors. The extruded pellets were quickly forced into the mixing chamber when the rotors began to rotate. The measurement was run at 175 °C and 50 rpm for 8 min, with a constant degree of filling of 75%. Three replicates were used for each formulation.

In this paper, equilibrium torque (T_e) and temperature are defined as the average values during the last 2 min of measurement.

Table 1
Formulation of the composites.

Sample	WF (wt.%)	HDPE (wt.%)	[Hemim]Cl (wt.%)
Ctrl	40	60	0
1%	40	59	1
3%	40	57	3
5%	40	55	5