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Effect of wood cell wall composition on the rheological properties of wood particle/high density polyethylene composites

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ABSTRACT

This study investigated the effect of wood cell wall composition on the rheological properties of wood particle/high density polyethylene (HDPE) blends. Four types of wood particle with different compositions were prepared: native wood flour (WF), hemicellulose-removed particle (HR), holocellulose (HC), and α-cellulose (αC). The particles were characterized in terms of functional groups, crystallinity, particle size, and morphology. Wood particle/HDPE composite formulations were melt-blended using a twin-screw extruder and the rheological properties of the blends were characterized using a Haake microcompounder, torque rheometer, capillary rheometer, and rotational rheometer. Results show that removal of lignin and/or hemicelluloses changed the crystallinity and microstructure of cell walls. These changes in cell wall composition and morphology altered the melt torque, shear stress, viscosity, and storage and loss moduli. Specifically, the melts viscosity decreased as αC/HDPE > HR/HDPE > WF/HDPE > HC/HDPE. This demonstrates that the composition of cell walls substantially affect the rheological behavior of wood particle/HDPE composites.

1. Introduction

Typical processing techniques for wood plastic composites (WPCs) include profile extrusion, injection molding, and compression molding. Extrusion is the most commonly used approach. In general, large amounts of wood are preferred to achieve good appearance and performance, low costs, and increased environmentally friendliness. In commercial products, wood content is typically in the range of 50–60% (by weight), which is close to the maximum packing content [1]. However, high wood content leads to a considerable increase of the melt viscosity, which creates miscellaneous processing difficulties such as flow instabilities, surface defects, and even failure of extrusion [2,3].

The processability of WPCs using extruder can be improved by several methods, such as use of additives [4], increasing processing temperature and/or speed [2], and designing specific dies and screw configurations [5,6]. Incorporation of coupling agents and/or lubricants can improve extrusion processability [4,7]. Maleated polyolefins can improve compatibility between wood particle and plastic matrix and enhance the dispersion of wood particle in matrix, which decrease the melt viscosity (and thus an increase in the processability) [2]. In addition, because of its relatively low molecular weight, a maleated polyolefin can act as an internal lubricant, decreasing the overall melt viscosity of WPCs [4]. Internal lubricant decreases melt viscosity by increasing wettability and external lubricant facilitates wall slip between composite melts and extruder [2,4,7].

Increasing barrel temperature can decrease melt viscosity by reducing the relaxation time of WPC melts. However, this is limited by the thermal degradation temperature of wood particles (~200 °C). At high extruding speeds, wood particles align along the melt flow direction, which reduces collisions among the particles [8]. A migration of wood particles may also take place, forming a virtually particle-free region near screw and barrel wall, which facilitates wall slip between polymer chains and extruder [9]. Consequently, melt viscosity decreases with increasing extruding speed.

A rotating die system was developed for a single-screw extruder, which can considerably moderate extrusion loads and entrance pressure drop for wood/polypropylene composites with high wood content [5]. Designing screw configurations to provide medium dispersive and distributive mixing cyclically can improve the uniformity of wood particle dispersion in high density polyethylene, and thus improve the processability [6].

The change of the inherent properties of wood particle may also be an option. Wood cell walls are basically comprised of a rigid cellulose microfibril reinforced an amorphous matrix of lignin and hemicellulose [10]. The sophisticated arrangement of the compositions endows cell wall with great strength and rigidity. The rigid

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cell structure lacks adequate plastic deformability during extrusion processing at high temperatures. If wood particles can be processed with an approach similar that of thermoplastics, by showing plastic flow at high temperatures and restoring rigidity after processing, both the processability and performance of WPCs could be greatly improved [11,12]. The plasticity of wood particle is closely related to the cell wall compositions and their interactions. Variation of cell wall composition may influence the rigidity or plasticity of wood particles and accordingly the processing or rheological performance of the composites.

This study aims to elucidate how variation of cell wall composition of wood particle affects the processing performance of WPCs. Therefore, we remove hemicellulose and lignin (together or respectively) from wood particle and assess their effects on the rheological characteristics of the resulting high density polyethylene composite melts.

2. Experimental

2.1. Materials

Wood flour was prepared from poplar (*Populus ussuriensis* Kom.) sapwood chips in a hammer mill to pass through 80–100 mesh sieves. 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 ground to a fine powder for use. Other solvents and reagents were reagent grade and used without further purification.

2.2. Preparation of wood particles

Four types of wood particle were prepared from the 80 to 100 mesh poplar flour, following methods reported in the previous literature:

(1) *WF – Extracted wood flour*: Wood flour was extracted in a Soxhlet extractor with a mixture of ethanol and toluene (1:2 in volume) for 6 h to remove soluble extractives.
(2) *HR – Hemicellulose-removed particle*: Hemicelluloses were removed from the WF according to TAPPI 203 [13], leaving lignin and cellulose.
(3) *HC – Holocellulose (delignified particle)*: The WF was delignified using a $NaClO_2$ treatment, leaving hemicelluloses and cellulose [14].
(4) *αC – α-Cellulose*: The HC was further treated with a 17.5% NaOH aqueous solution to remove hemicelluloses according to TAPPI 203 [13].

These chemical treatments can potentially alter the size of wood particles. To remove the confounding variable of particle size, all the four prepared particles were pulverized to 100–160 mesh using an herb grinder with knife. Wood flours with a particle size of 80–100 mesh and over 160 mesh were also prepared and extracted, as described above.

2.3. Preparation of wood particle/HDPE compounds

Wood particles were dry-blended with the HDPE powder (2:3 in weight) and then compounded using a 18 mm co-rotating twin-screw extruder with an *L*/*D* ratio of 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.

2.4. Characterization of wood particles

2.4.1. FT-IR analysis

Fourier-transform infrared spectra of the wood particles were obtained using a spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc., Madison, USA) with 40 scans at a resolution of 4 cm^{-1}. The signals were collected using a liquid nitrogen-cooled MCT-A detector.

2.4.2. X-ray diffraction

X-ray diffraction test of the wood particles was conducted by using an X-ray generator (Cu Kα radiation) at 40 kV and a 40 mA (D8 Focus, Bruker AXS Ltd., UK). The crystallinity index was calculated according to the Segal method.

2.4.3. Particle size and morphology

Particle size distribution of the wood particles was detected using laser diffraction (Mastersizer 2000, Malvern Instruments Ltd., UK) equipped with a Hydro 2000MU wet dispersion unit with distilled water as the suspension liquid. The size of a non-spherical particle is usually expressed in terms of an equivalent sphere diameter. The $D[4,3]$ is the volume mean diameter and $D[3,2]$ is the area mean diameter. The specific surface area (SSA) was calculated as $SSA = 6/D[3,2]$ [15].

The particle geometry was observed using a stereomicroscope (Leica, Model MZ8) with fiber optics (NCL 150). The images were produced using a Leica camera (Model DFC 425C) and recorded with the software (Leica Application Suite 35).

2.5. Interfacial morphological analysis

Portions of the extruded pellets were injection-molded (SE50D, Sumitomo Heavy Industries, Japan) into standard impact test specimens. Injection and mold temperatures were 180 and 50 °C, respectively. Sectioned surfaces of the specimens were cryo-microtomed (CR-X cryo-ultramicrotome, RMC) 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 (Quanta 200F, FEI Company) at an accelerated voltage of 30 kV.

2.6. Rheological analysis

2.6.1. Dynamic microcompounder

The rheological tests were conducted on a laboratory scale microcompounder (Minilab Rheomex CTW5, Thermo Scientific, Germany). The blends were 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 final apparent viscosity of the melts, respectively.

In this study, six grams of dry-mixed wood particle/HDPE was 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.

2.6.2. Torque rheometry

The rheological behavior was evaluated using a Haake torque rheometer (Rheomix 600p, Thermo Scientific, Germany) 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