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Morphology, mechanical properties, and dimensional stability of wood particle/high density polyethylene composites: Effect of removal of wood cell wall composition

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ABSTRACT

Variation in the chemical composition of wood cell walls has a significant influence on the properties of wood plastic composites (WPCs). This study investigated the effect of removal of hemicellulose and/or lignin on the mechanical properties and dimensional stability of WPCs. Four types of wood particles with various compositions including native wood flour (WF), hemicellulose-removed particle (HR), holocellulose (HC), and α-cellulose (αC) were prepared and compounded with high density polyethylene (HDPE) in an extruder, both with and without maleated polyethylene. Injection molding was used to make test specimens. The HR-based composites exhibited the best water resistance. The HC-based composites obtained a greater tensile modulus but a lower water resistance. The highest values for tensile strength, elongation at brake, toughness, and impact strength were achieved by the composites filled with αC.

1. Introduction

Lignocellulosic fibers exhibit many advantages over synthetic fibers (e.g. carbon, glass and aramid), such as biodegradability, renewability, wide availability, low density, low cost, and high specific strength and stiffness [1,2]. Wood plastic composites (WPCs) made from lignocellulosics and thermoplastic polymers have emerged as viable bio-based composites with low water absorption, recyclability, high yield efficiency, and various geometries in a cross section [3,4]. The ultimate performance of WPCs depends on the intrinsic properties of lignocellulosic fillers such as stiffness of structure and the chemical composition (cellulose, hemicellulose, and lignin) of cell walls.

Lignin is a branched hydrophobic heteropolymer that provides mechanical strength to plant cell walls. For composite applications, lignin can serve as a nucleating agent [5], antioxidant [6,7], compatibilizer [8,9] or even base matrix [10,11]. Karimi et al. [12] investigated hot-pressed polypropylene (PP) composites filled with delignified hornbeam fiber by a Kraft pulping process at 170 °C. They showed that delignification improved the tensile strength, tensile modulus, and water resistance of the resulting composites. Fabiyi et al. produced high density polyethylene (HDPE) [13] and polyvinyl chloride [14] composites from pine, extractives-free pine, and pine holocellulose (delignified). They found that holocellulose-based composites showed the lowest change in total color and lightness for both outside and xenon-arc weathering. Beg and Pickering [15] found that Kraft wood fiber (*Pinus Radiata*) with higher residual lignin content enabled creation of PP composites with lower tensile and impact strength.

Hemicelluloses interact with cellulose microfibrils and lignin to form a unique natural composite structure [16]. Hosseinaei et al. [17,18] investigated injection-molded PP composites filled with hemicellulose-extracted Southern yellow pine by means of liquid hot-water treatment (extraction at 140, 155, and 170 °C for 60 min). They found decreased water absorption, increased tensile properties, and improved mold resistance in the resulting composites. These improvements were attributed to the decreased hygroscopicity of the extracted wood. Pelaez-Samaniego et al. [19] used hot water extracted ponderosa pine with bark to make HDPE and PP composites. Water resistance of these composites was enhanced with unchanged or even improved mechanical properties compared to the unextracted controls. Removal of hemicelluloses by alkali treatment can improve the mechanical properties of lignocellulosic fibers [20,21] and composites including them [22–25]. This is because cellulose microfibrils tend to come in closer contact with one another, forming a more aggregated and compact fibrillar structure when the hemicellulose that coats the cellulose microfibrils is removed [26].

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Cellulose fiber is professed to be a better reinforcing filler than wood fiber. Owing to a complex network of inter- and intro-molecular hydrogen bonds, cellulose chains have the ability to pack themselves in a tight, high-strength and high stiffness crystalline edifice [27]. Ashori and Nourbakhsh [28] used microcrystalline cellulose as a reinforcing agent in wood flour/PP composites. Results show that tensile, flexural, and impact strengths of the composites were significantly enhanced with addition of microcrystalline cellulose. Partial replacement of coarse spruce wood flour with microfibrillated cellulose (10 wt.%) resulted in improvements in almost all mechanical properties of the resulting WPCs [29].

Our study was designed to determine the effects of the removal of hemicellulose and lignin (together or respectively) on the mechanical properties and water absorption of the resulting high density polyethylene composites. The interfacial adhesion in composites was characterized with scanning electron microscopy and dynamical mechanical analysis.

2. Materials and methods

2.1. Materials

Wood flour was prepared from poplar (*Populus ussuriensis* Kom.) sapwood chips in a hammer mill to pass through sieves measuring 80–100 mesh. High density polyethylene (HDPE) pellets (5000S) purchased from Daqing Petrochemical Co., China, bear 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 chilled and ground to a fine powder for use. Maleated polyethylene (MAPE, A-C® 575A) was supplied by Honeywell International Inc., USA, with a MA grafting ratio of 3 wt.% and a saponification value of 35 mg KOH/g.

2.2. Preparation of wood particles

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

(1) WF – Extracted wood particle: 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 wood particle: hemicelluloses were removed from the WF according to TAPPI 203 [30], leaving lignin and cellulose.
(3) HC – Holocellulose (delignified wood particle): the WF was delignified using a $NaClO_2$ treatment, leaving hemicelluloses and cellulose [31].
(4) αC – α-Cellulose (both hemicellulose and lignin removed wood particle): the HC was further treated with a 17.5% NaOH aqueous solution to remove hemicelluloses according to TAPPI 203 [30].

Table 1
Formulations of the composites.

Sample	Fiber type	Fiber (wt.%)	HDPE (wt.%)	MAPE (wt.%)
WF/PE	WF	40	60	0
HR/PE	HR	40	60	0
HC/PE	HC	40	60	0
αC/PE	αC	40	60	0
WF/PE/MA	WF	40	58	2
HR/PE/MA	HR	40	58	2
HC/PE/MA	HC	40	58	2
αC/PE/MA	αC	40	58	2

These chemical treatments can potentially alter the size of wood particles. To remove the confounding variable of particle size, all particles were pulverized to 100–160 mesh using an herb grinder with knife. These particles were dried at 105 °C for 24 h, and then stored in a sealed container for use. In our previous paper, the Fourier-transform infrared analysis of the wood particles showed that hemicellulose was completely removed and a trace residue of lignin was found in HC [32].

2.3. Preparation of composite specimens

Wood particles were dry-mixed with the HDPE powder and MAPE at a specific ratio as shown in Table 1. They were compounded using a co-rotating twin-screw extruder (diameter = 8 mm and L/D = 40) equipped with a volumetric feeder and a strand pelletizer (Leistritz ZSE-18, Leistritz Extrusionstechnik GmbH, Germany). The extrusion temperature ranged from 150 to 175 °C over eight zones along the extruder barrel. The extrudate was cut into pellets using the strand pelletizer. The pellets were then injection-molded (SE50D, Sumitomo Heavy Industries, Japan) into standard specimens for mechanical testing. Injection and mold temperatures were 180 and 50 °C, respectively.

2.4. Characterization

2.4.1. Morphological analysis

The impact specimens were frozen in liquid nitrogen for 5 min and broken by hand. The fractured surfaces were subsequently dried, sputter-coated with gold, and then observed with a field emission scanning electron microscope (FE-SEM, Quanta 200F, FEI Company, USA) at an accelerated voltage of 30 kV.

2.4.2. Mechanical test

Type-I dumbbell-shaped tensile specimens measuring 165 × 13 × 3 mm^3 were tested using a screw-driven universal testing machine (Model 4466, Instron Inc., Canton, OH, USA) with an 8.9 kN load cell according to ASTM: D638. The tests were conducted at a crosshead speed of 5 mm min^{-1} with deflections measured using a 50 mm extensometer (MTS 634.12E-24). Izod impact strength was determined from specimens measuring 63.5 × 12.7 × 3 mm^3 using a BPI-0-1 Basic Pendulum Impact tester (Dynisco, MA) according to ASTM: D256. All test specimens were conditioned at 23 °C and 65% relative humidity for 7 days prior to testing. Six replicates were used for each formulation.

2.4.3. Water absorption test

Specimens measuring 30 × 20 × 3 mm^3 were cut from the ends of dumbbell-shaped composites, oven-dried and then weighed. The specimens were subsequently immersed in distilled water at 23 °C for 2 months with a daily change of water. The weight and thickness of each specimen were determined at stated periods. Water absorption of each specimen was expressed as water weight absorbed, divided by the dry weight of the specimen. The thickness swelling of each specimen was calculated based on its dry dimensions. Five replicates were used for each formulation.

2.4.4. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties of the composites were measured using a dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, USA). Tests were performed using single-cantilever strain-controlled mode with an oscillating amplitude of 15 μm and a frequency of 1 Hz. The temperature was swept from 25 to 135 °C at 3 °C min^{-1}. The specimen dimension was 35 mm × 12.0 mm × 3 mm. Three replicates were used for each formulation.