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Wood plastic composites based on microfibrillar blends of high density polyethylene/poly(ethylene terephthalate)

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ABSTRACT

High-melting-temperature poly(ethylene terephthalate) (PET) was successfully introduced into wood plastic composites through a two-step reactive extrusion technology. Wood flour was added into pre-prepared PET/high density polyethylene (HDPE) microfibrillar blends (MFBs) in the second extrusion at the temperature for processing HDPE. Addition of 25% in situ formed PET microfibers obviously increased the mechanical properties of HDPE, and more significant enhancement by the in situ formed recycled PET microfibers was observed for the recycled HDPE. Adding 2% E-GMA improved the compatibility between matrix and microfibers in MFBs, resulting further enhanced mechanical properties. The subsequent addition of 40% wood flour did not influence the size and morphology of PET microfibers, and improved the comprehensive mechanical properties of MFBs. The wood flour increased the crystallinity level of HDPE in the compatibilized MFB in which PET phase did not crystallize. The storage modulus of MFB was greatly improved by wood flour.

1. Introduction

Global ecological concern has resulted in an interest in renewable natural materials. Natural organic fibers from renewable bio-resources offer the potential to act as biodegradable reinforcing materials, alternative for the use of glass or carbon fibers and inorganic fillers (George et al., 2001; Nabi Saheb and Jog, 1999). Much work has been done in studying and developing general thermoplastic/natural fibers composites, especially wood plastic composites (WPCs). WPCs have successfully proven their application in various fields such as lumber, decking and railing, window profiles, wall studs, door frames, furniture, pallets, fencing, docks, siding, architectural profiles, boat hulls, and automotive components. The global WPC market in North America and Europe has been experiencing double digit growth (Alireza, 2008).

Compared with unfilled thermoplastics, the advantages of WPCs include increased bending strength, stiffness (both flexural and tensile modulus), reduced thermal expansion, and lowered cost. However, mechanical properties such as creep resistance, modulus, and strength are usually lower than those of solid wood. Thus, WPCs are not currently being used in applications that require considerable structural performance, and research is needed towards engineering WPCs (Clemons, 2002). As early as 1984, Klason et al. reported to use cellulose flour to reinforce the polyamides, polyamide 12 (PA-12) and polyamide 6 (PA-6) (Klason et al., 1984). The composites based on PA-6 showed severe discoloration and pronounced pyrolytic degradation. At temperatures needed to process high-melting-temperature (>220 °C) engineering thermoplastics, severe thermal degradation happened to reinforcing cellulose fibers (Sears et al., 2001). The thermal degradation of reinforcing fibers was reduced by using purified pulp fibers whose cellulose content was greater than 80%, and by adding the fibers into pre-melted polymer at downstream of a twin-screw extruder (Caufield et al., 2001; Sears et al., 2001). Thermal stability of cellulose is greater than lignin and hemicellulose, but unfortunately the cellulose content of most natural fibers is lower than 50%. For example, the most widely used pine wood flour usually contains 40–45% cellulose, 20–25% hemicellulose, and 26–34% lignin (Han and Rowell, 1996). Other better ways need to be developed to introduce high melting-point engineering plastics into WPCs to prepare engineered composites.

Microfibrillar blends (MFBs) are a new class of fiber reinforced blends, and the manufacture of in situ MFBs provides a promising route to enhance properties of general thermoplastics using engineering thermoplastics (Denchev and Dencheva, 2008; Evstatiev and Fakirov, 1992). Using a co-rotating twin-screw extruder with a 2-mm strand die, two water baths, and two pullers, high density polyethylene (HDPE)/polyamide (PA) MFBs were prepared (Denchev et al., 2004). Another modified method based on consecutive slit or rod extrusion, hot stretching, and quenching was used to prepare polypropylene/poly(ethylene terephthalate) (PET) and polyethylene (PE)/PET MFBs (Li et al., 2004; Taepaiboon et al.,

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2006; Wan and Ji, 2004). Low density polyethylene (LDPE)/ recycled PET (R-PET) MFBs were also made by Evstatiev et al. (2002). It is noticed that the shaping temperatures for MFBs containing high melting-point engineering plastics are usually lower than the temperature for natural fibers to initially degrade. Thus, engineering plastics can be successfully introduced into WPCs to engineer their performance using this technology. However, little effort has been made so far.

PET and HDPE are used extensively in packaging materials, and their annual rates of growth of production and consumption steadily increase (Akovali et al., 1998). Combining PET and PE can yield unusual properties, and thus recycled HDPE(R-HDPE)/R-PET blends have attracted increased interest for composite manufacturing. In our previous study, in situ microfibrillar R-HDPE/R-PET (75/25 w/w) co-blends were made through reactive extrusion with the aid of three compatibilizers (Lei et al., 2009a). In this study, in situ MFB batches based on both virgin and recycled HDPE and PET were first made through reactive extrusion at the processing temperature for PET, and then wood flour was introduced into the MFBs through the second extrusion at the processing temperature for HDPE. The objectives of the study were (a) to study the influence of wood flour on the morphology of microfibers in MFBs and on the mechanical properties of composites, and (b) to investigate the effect of coupling treatment on the mechanical properties of the WPCs based on MFBs.

2. Experimental

2.1. Materials

Plastics used for the study include both virgin and recycled HDPE and PET. Virgin PET pellets, recycled high density polyethylene (R-HDPE) blocks, and recycled poly(ethylene terephthalate) (R-PET) bottle scraps obtained from Avangard Industries, Ltd. (Houston, TX, USA). The cold crystalline peak temperature and melting peak temperature of the virginal PET are 119.8 °C and 250.8 °C (10 °C/min), respectively, and its density is 1330 kg/m^3. The melt flow index and density of R-HDPE are 0.7 g/10 min (190 °C) and 939.9 kg/m^3, respectively. The melting temperature ranges from 110 to 140 °C with a peak at 131.5 °C (10 °C/min). For R-PET, the cold crystalline peak temperature and melting peak temperature are 133.3 °C and 251.4 °C (10 °C/min), respectively, and its density is 1250 kg/m^3. Virgin HDPE (HD 9856B) with a density of 956 kg/m^3 and a melt index of 0.46 g/10 min (190 °C) was from ExxonMobil Chemical (Houston, TX, USA). A maleated polyethylene (PE-g-MA) compatibilizer (G-2608) with a melt index of 8 g/10 min (190 °C, 2.16 kg) and an acid number of 8 mg KOH/g was obtained from Eastman Chemical Company (Kingsport, TN, USA). An ethylene-glycidyl methacrylate copolymer (E-GMA), LOTADER®AX 8840 with a melt index of 5 g/10 min (190 °C, 2.16 kg) and a glycidyl methacrylate content of 8%, was purchased from Arkema Inc. (Philadelphia, PA, USA). R-PET and PE-g-MA were dried in an oven for 10 h at 105 °C before use. Pine (*Pinus* sp.) flour with a 40-mesh particle size from American Wood Fiber Co. (Madison, MI) was used in the experiment. Pine flour was dried in an oven for 48 h at 90 °C before use.

2.2. Preparation of the composites

The technology to prepare wood fiber reinforced microfibrillar blends (MFBs) containing PET microfibers is shown in Fig. 1. In the first extrusion, the MFB pellets based on HDPE and PET were made at the melting temperature of PET. Formulated raw materials were first tumble mixed, and then melt blended and extruded in a co-rotating twin-screw extruder CTSE-V/MARKII (C.W. Brabender Instruments Inc., Co., Gackensack, NJ, USA) with a screw length/diameter of 25:1. The extrusion temperature profile was 190, 240, 275, 275, and 270 °C, and the screw rotating speed was fixed at 40 rpm. The extrudates were continuously drawn (through neck formation) by a BT 25 pelletizer (Scheer Bay Co., Bay City, MI, USA). After cooling of the extrudates in an icy water cooling bath, they were cut into pellets. HDPE/PET weight ratios were fixed at 75/25 (w/w). Based on the total weight of PET and HDPE, the loading levels of E-GMA were 0% and 2%. The blend pellets were dried at 100 °C before use. The MFBs based on R-PET and R-HDPE were also made using the same technology.

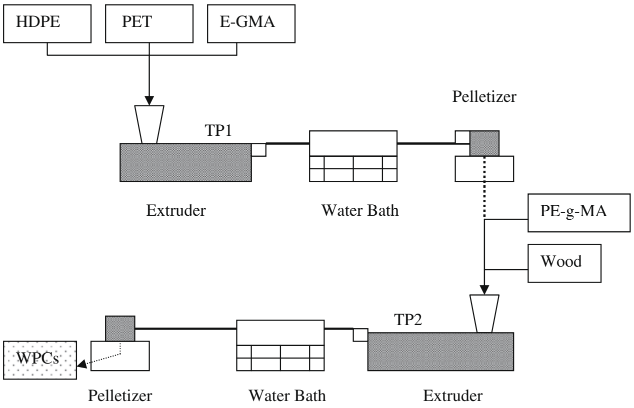

Fig. 1. Scheme of the new technology for preparing wood plastic composites containing high-melting-temperature engineering plastics. TP1: temperature profile 1—190, 240, 275, 250, 270 °C; TP2: temperature profile 2—105, 145, 170, 170, 170 °C.

In the second extrusion, the MFB pellets were melt blended with dried wood flour using the same extruder, with a temperature profile of 105, 145, 170, 170, and 170 °C (i.e. the temperature profile usually for HDPE). The screw rotating speed was set at 50 rpm. The wood flour to plastic weight ratio was 40/60 (w/w). The loading levels of PE-g-MA (a coupling agent) were 0%, 1.2%, 2.4%, and 3.6% based on the total weight of dry wood flour and MFB matrix. The extrudates were cut into pellets after cooling in a water bath. The pellets were dried before injection molding.

The test samples for mechanical properties were made through injection molding, using a PLUS 35 injection system from Battenfeld of American Inc. (South Elgin, IL, USA). The WPC pellets were injection molded at 190 °C with a mold temperature of 85 °C.

2.3. Characterization

Flexural and tensile strength were measured according to the ASTM D790–03 and D638–03, respectively, using an INSTRON 5582 Testing Machine (Instron Co., Grove City, PA, USA). A TINIUS 92T impact tester (Testing Machine Company, Horsham, PA, USA) was used for the Izod impact test. All samples were notched at the center point of one longitudinal side according to the ASTM D256. For each treatment level, five replications were tested.

The crystallization behaviors of HDPE and PET were measured using a differential scanning calorimeter (DSC Q100, TA Instruments, New Castle, DE). Samples of 4–5 mg were placed in aluminum capsules and heated from 40 to 270 °C at 10 °C/min and melt annealed for 5 min to eliminate the heat history before cooling down at 10 °C/min. The heat flow rates and crystallinity levels corresponding to the crystallization of HDPE and PET in the blends and composites were normalized to the mass unit of the specimens.

Dynamic mechanical analysis of the composites was measured with a Dynamic Mechanical Analyzer (DMA Q800, TA Instruments,