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Short Communication

A novel wood flour-filled composite based on microfibrillar high-density polyethylene (HDPE)/Nylon-6 blends

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ABSTRACT

A novel wood flour (WF)-filled composite based on the microfibrillar high-density polyethylene (HDPE) and Nylon-6 co-blend, in which both in situ formed Nylon-6 microfibrils and WF acted as reinforcing elements, was successfully developed using a two-step extrusion method. At the 30 wt.% WF loading level, WF-filled composite based on the microfibrillized HDPE/Nylon-6 blend exhibited higher strengths and moduli than the corresponding HDPE-based composite. The incorporation of WF reduced short-term creep response of HDPE matrix and the presence of Nylon-6 microfibrils further contributed to the creep reduction.

1. Introduction

Wood and plastic composites (WPCs) have been gaining more and more widespread applications in building, automotive, and infrastructure fields in light of their superior properties and a climate of heightened environmental awareness. Due to the poor thermal stability of wood above 200 °C, low-melting polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC) resins are still the most commonly used thermoplastic matrix until now. However, inherently undesirable mechanical properties (e.g. creep-resistant properties) of the polyolefin matrix impeded further applications of the WPCs as structural composite materials. In order to overcome these drawbacks, some efforts have been made through silane-crosslinking of wood/PE composites (Bengtsson et al., 2005), the use of high-performance engineering thermoplastics (e.g. Nylon-6) (Jacobson et al., 2001) as single polymeric matrix, the modification of the matrix by incorporation of organoclay (Zhong et al., 2007), and stretching wood/PP composites (Newson et al., 2000).

During the last decade, a new type of polymer–polymer composites, known as microfibrillar composites (MFCs), was developed (Evstatiev and Fakirov, 1992). In such composites, a low-melting and isotropic thermoplastic matrix was reinforced with in situ formed microfibrils of another higher-melting-point thermoplastic. It has been reported that they exhibited Young's moduli and tensile strengths about 30–50% higher than the weight-average values of the components becoming comparable to those of the corresponding glass fiber reinforced systems. Until now, very limited work has been done to develop wood/natural fiber-filled MFCs.

The compatibilizing effects of immiscible high density PE (HDPE)/Nylon blends on morphologies and properties of their resulting banana fiber-filled composites were studied in our previous work (Liu et al., 2009). It was found that the compatibilization contributed to reinforcing effect of minor Nylon-6 component in the final composites. In this work, we developed wood flour (WF)-filled MFCs based on the compatibilized HDPE/Nylon-6 blend. The objective of the study was to demonstrate morphological, mechanical, thermal, and creep properties of such kind of composites.

2. Experimental

2.1. Materials

HDPE (grade HD6706.17) with a melt index of 6.1 g/10 min (190 °C/2.16 kg) was obtained from Exxon-Mobil Chemical Co. Nylon-6 resin (grade Aegis H8202NLB) was provided by Honeywell Co. Maleic anhydride grafted high-density polyethylene (grade Fusabond MB100D; HDPE-g-MA) having MA grafting ratio of about 1 wt.% and melt flow index 2 g/10 min (190 °C/2.16 kg), was supplied by Dupont Co. and used as compatibilizer (CA) for immiscible HDPE/Nylon-6 blends. Wood flour (WF) with 40 mesh particle size was provided by the American Wood Fibers Co. Prior to

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use, Nylon-6 resin and WF were thoroughly dried at 90 °C for 24 h in a convection oven.

2.2. Sample preparation

Two-step melt compounding was performed following steps schematically outlined in Fig. 1 using an intermesh, counter-rotating Brabender twin-screw extruder (Brabender Instruments Inc., Hackensack, NJ). Prior to the first extrusion step, HDPE pellets were dry-mixed with Nylon-6 and a compatibilizer (i.e., HDPE-g-MA) pellets in the weight ratio of 70/30/3. The barrel temperature profile during the first extrusion varied from 200 to 235 °C with a fixed screw speed of 40 rpm. The extruded bristles (3 mm in diameter) were firstly cooled in a cold water bath, immediately continuously drawn, and finally pelletized into pellets (~3 mm in length and ~1 mm in diameter), which was designated as 'PEA30E3#', namely MFCs' precursor. The specimens for mechanical testing were prepared using an Injection Molding Machine (Batenfeld Plus 35, Batenfeld Inc., NJ). In the case of the above 'PEA30E3#' pellet, two different injection temperatures (190 °C vs. 250 °C) were chosen to reveal post-processing temperature on the morphology of Nylon-6. The obtained specimens were designated as 'PEA30E3-190#' and 'PEA30E3-250#', respectively.

The 'PEA30E3#' pellets, WF, and HDPE-g-MA in a weight ratio of 70/30/1.1 were extruded during the second extrusion step. The temperature profile of barrels was set to range from 160 °C to 175 °C with a fixed screw speed of 40 rpm. The pre-dried extrusion granules were injection-molded into standard mechanical test specimens using the same injection machine at 190 °C. The resulting composite was designated as 'PEA30E3C-190#'. As a comparison, the corresponding HDPE-based composite having the same WF and HDPE-g-MA content was also prepared under the same condition, and designated as 'PEE3C-190#'.

2.3. Characterization

Tensile and flexural properties of the composites were measured using an Instron 5582 testing machine (Instron Co., Norwood, MA) according to the ASTM D638 and D790 standards, respectively. A crosshead speed of 5 mm/min and a gage length of 50 mm were used in the tensile test. Notched Izod impact strength was determined using a Tinius Olsen Mode 1892 impact tester (Tinius Olsen Inc., Horsham, PA) according to the ASTM D256 standard. Five replicated specimens of each composition were tested for each property. TA Q800 Dynamic Mechanical Analysis (DMA) instrument (New Castle, DL) was used for short-term creep tests using a 3-point bending mode. In each test, the sample was heated to 35 °C and allowed to equilibrate for 5 min. A static stress level of 4 MPa was then applied for 12 h, and sample deformation was measured. The experimental data was then predicted

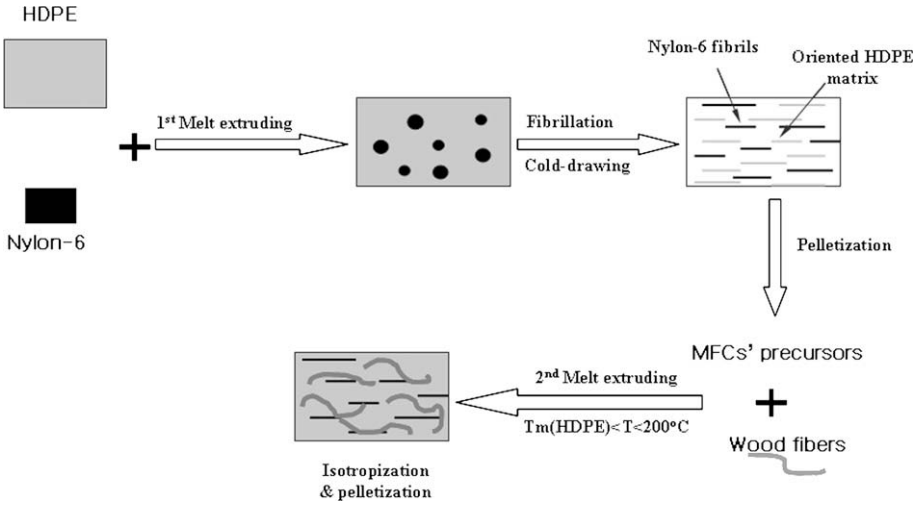

Fig. 1. Schematic diagram for preparation method of HDPE/cellulosic fiber hybrid composites reinforced with in situ Nylon-6 fibrils.

Table 1
Effect of different injection temperatures on mechanical properties of as-drawn HDPE/Nylon-6/HDPE-g-MA (70/30/3, w/w) blends, together with as-extruded HDPE.

Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Izod notched impact strength (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)
As-extruded HDPE	17.8 ± 0.4	0.53 ± 0.03	8.59 ± 0.21	18.7 ± 0.5	0.67 ± 0.01
PEA30E3-250#	21.8 ± 0.3	1.06 ± 0.04	3.86 ± 0.36	25.5 ± 1.0	0.76 ± 0.02
PEA30E3-190#	24.2 ± 0.3	1.23 ± 0.14	4.52 ± 0.87	30.9 ± 0.8	1.00 ± 0.05

Table 2
Comparison of mechanical properties of both WF-filled composites.[a]

WF content (wt.%)	Tensile strength (MPa)	Tensile modulus (GPa)	Izod notched impact strength (kJ/m^2)	Flexural strength (MPa)	Flexural modulus (GPa)
PEA30E3C-190#					
30	30.2 ± 2.4	3.37 ± 0.19	3.06 ± 0.09	48.6 ± 2.2	2.57 ± 0.12
PEE3C-190#					
30	26.1 ± 0.6	2.55 ± 0.09	3.84 ± 0.16	39.4 ± 1.1	1.99 ± 0.06

[a] During the second extrusion step, the weight ratio of added HDPE-g-MA to WF was fixed at 3.75% and loading level of WF was kept at 30 wt.% for both cases.

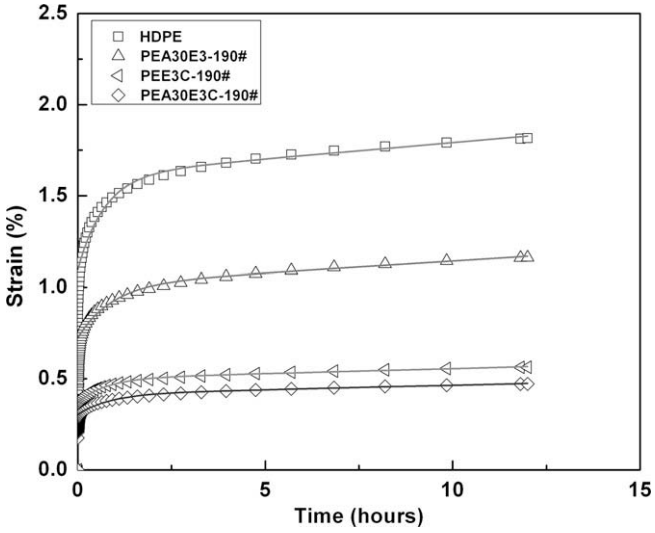

Fig. 2. Creep strain (dot) as a function of time during creep experiment at 35 °C, together with the corresponding fitted curves of Burgers model (line).

using a four-element Burgers model. Derived from this model, the total creep strain, $\varepsilon(t)$, at a time (t) is expressed by the following equation:

$$\varepsilon(t) = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{\sigma}{E_1} + \frac{\sigma}{E_2}\left[1 - \exp\left(-t\frac{E_2}{\eta_2}\right)\right] + t\frac{\sigma}{\eta_3} \quad (1)$$

where ε_1 is the elastic strain, ε_2 is the viscoelastic strain, and ε_3 is the viscoplastic strain; σ is the applied stress, E_1 the elastic constant of the Hookean spring, E_2 the delayed elastic constant of the spring in the Kelvin element, η_2 the viscous constant of the dashpot in the Kelvin element, and η_3 the viscous constant for the permanent deflection.

3. Results and discussion

SEM micrographs revealed that the in situ formation of Nylon-6 fibrils were able to be mostly retained when the post-processing temperature was well-controlled below the melt temperature of Nylon-6. Table 1 lists mechanical properties of the ternary blends prepared via different injection temperatures (190 °C vs. 250 °C), together with as-extruded HDPE as a control. Higher mechanical properties were universally found for the 'PEA30E3-190#' blend, which was evidently attributed to the reinforcing role of in situ forming Nylon-6 microfibrils in this case. Table 2 further presents mechanical properties of WF-filled composites (i.e., 'PEA30E3C-190#') prepared from MFCs' pellets, together with the corresponding HDPE-based composite (i.e., 'PEE3C-190#'). At the WF loading of 30 wt.%, compared to the 'PEE3C-190#' composite, tensile and flexural strengths of 'PEA30E3C-190#' one were increased by 16% and 23%, respectively. And the improvement of 32% and 29% in tensile and flexural moduli were achieved, respectively, for the 'PEA30E3C-190#' composite with respect to the 'PEE3C-190#' one.

Usually, poor creep performance of PE itself is a major obstacle to make it structural plastics, and therefore, to make PE-based WPCs structural composite materials. As shown in Fig. 2, the creep response of as-extruded HDPE was decreased with addition of minor rigid Nylon-6. In the presence of the compatibilizer (HDPE-g-MA), the addition of WF remarkably increased the creep-resistance of the composite with reduced creep strain. Moreover, the introduction of Nylon-6 microfibrils further improved the creep property of the HDPE/WF composite, but such effect was less pronounced in HDPE/WF composite than in pure HDPE. This may be attributed to two factors: relatively lower content of Nylon-6 microfibrils with respect to WF, and partial loss of anisotropic Nylon-6 microfibrillar morphologies during the post-processing. Therefore, further work on optimization of Nylon-6 microfibrils in the final composites is still needed. Besides, it was shown that the Burgers model offered a good fitting for the creep curves of the composites.

4. Conclusion

A novel kind of WF-filled composite based on the microfibrillar HDPE/Nylon-6 blend was developed using two-step extrusion followed by injection molding. It was confirmed that Nylon-6 microfibrils were formed in the drawing step. Compared to the corresponding HDPE/WF composite, the resultant composite based on the as-drawn HDPE/Nylon-6 blend exhibited superior strengths, moduli, and short-term creep-resistance performance. The two-step extrusion approach successfully avoided undesired thermal degradation of WF and retained integrity of majority of Nylon-6 microfibrils having high melting temperature ($T_m > 200$ °C) by effectively combining isotropization of HDPE microfibrils with dispersion of WF into a single step.

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