WATER UPTAKE AND FLEXURAL PROPERTIES OF NATURAL FILLER/HDPE COMPOSITES

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Composites of flour from different lignocellulosic sources with high-density polyethylene were prepared, and their water absorption and flexural properties were studied. Flour samples from loblolly pine, hybrid Euro-American poplar, and wheat straw were mixed with the polymer at 35 wt % lignocellulosics content and either zero or 2% compatibilizer. Water absorption tests were carried out on injection-molded specimens for temperatures of 30, 45, 60, and 75°C. Results indicated a significant difference among different lignocellulosic types, of which wheat straw composites exhibited the highest and the pine composites showed the lowest water absorption values. The composites with 2% MAPE showed lower water absorption compare to the composites without MAPE. This indicates that the compatibilizer plays an important role to repel the water molecules. For all four temperature conditions, rising temperature increased water absorption significantly. Composites with poplar had the highest flexural strength and modulus. Adding compatibilizer to the composites boosted the flexural properties by improving the adhesion between natural filler and the polymer matrix.

Keywords: High density polyethylene; Natural filler; MAPE; Water absorption; Flexural properties

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INTRODUTION

Natural fillers have a number of techno-ecological advantages over synthetic fillers, since they are renewable and abundant resources, being less damaging to the environment, and cause less abrasive wear to processing equipment. There is a wide variety of lignocellulosic materials that can be used to reinforce thermoplastics. These include wood fibers, as well as a variety of agro-based fibers such as wheat straw.

A problem associated with using lignocellulosic materials in natural fiber thermoplastic composites is moisture absorption (Sanadi et al. 1997). A moisture buildup in the fiber cell wall can lead to thickness swelling and dimensional changes in the composite (Rowell 1997). The thickness swelling can lead to reduction in the adhesion between the fiber and the polymer matrix. Thus, the water absorption can have undesirable effects on the mechanical properties of the composites (Espert et al. 2004). Temperature may severely influence amount of water absorption, and its subsequent irreversible effects and environmental aging can have major practical repercussions (Bao and Yee 2002). The temperature has a significant effect on water absorption (Kazemi Najafi et al. 2007). The water uptake of natural fiber composites can be reduced considerably by using coupling agents to assist with fiber-matrix adhesion (Joseph et al. 2002).

Shebani et al. (2009) investigated the mechanical properties of linear low-density polyethylene (LLDPE)-filled wood fillers of different species (acacia, eucalyptus, pine, and oak). They showed that with the exception of the water absorption properties, the best WPC performance was achieved with acacia, followed by oak, eucalyptus, and pine. Berger and Stark (1997) investigated the mechanical properties of polypropylene filled with wood flours of different species (ponderosa pine, loblolly pine, maple, and oak). They found that hardwood flours provided an improvement in mechanical properties over softwood flour.

There are few reports about the effect of lignocellulosic type and temperature on the water absorption of natural fiber/thermoplastic injection molded composites. The objective of this study is to evaluate the effect of lignocellulosic type (softwood, hardwood, and non-wood), temperature, and compatibilizer on the water absorption of natural filler/ HDPE composites. Flexure properties of the composites were also analyzed.

EXPERIMENTAL

Materials

Lignocellulosic fillers were obtained by milling and screening softwood (Loblolly pine), hardwood (hybrid Euro-American poplar), and non-wood (wheat straw) materials to 50-mesh particle size. Virgin high density polyethylene (Arak Petrochemical Company, Iran), with a density of 0.95 g/cm^3 and the melt flow index of 8 gr/10min, was used in this study as the polymer matrix. The Maleic Anhydride grafted Polyethylene (MAPE) as compatibilizer was Eastman G-2608 with a melting point of 122°C and molecular weight of 65,000.

Composites Preparation

The lignocellulosic filler was dried for 24 h at 105±2°C. The materials were melt-blended at 180°C and 40 RPM for 10 min in a Haake Buchler apparatus. From the compounds which had been granulated, specimens were injection molded by an injection molder at molding temperature of 185°C, and the injection pressure was 3 MPa. Formulation of the natural filler HDPE composites prepared for this study is given in Table 1.

Table 1. Formulation of Natural Filler HDPE Composites

Formulation No.	Wheat straw (wt %)	Pine (wt %)	Euro-American Poplar (wt %)	HDPE (wt %)	MAPE (wt %)
1	35	-	-	65	0
2	35	-	-	63	2
3	-	35	-	65	0
4	-	35	-	63	2
5	-	-	35	65	0
6	-	-	35	63	2

Chemical Analysis of Natural Fillers

The chemical analysis of natural fillers used in the composites was carried out in accordance with TAPPI test methods (2000a,b) for the different components, namely: T 222 om-98 for acid-insoluble lignin, and T 223 cm-84 for pentosans. Alpha cellulose was determined in accordance with ASTM D1103-60 method.

Water Absorption Tests

Water absorption studies were performed following the ASTM D 570-98 method. Water absorption of the composites was determined after 2 h and 24 h immersion in distilled water at 30°C, 45°C, 60°C, and 75°C. Five specimens of each formulation were dried in an oven for 24 h at 105±2°C. The dried specimens were weighed with a precision of 0.001 g and were placed in distilled water. At the end of the immersion periods, the specimens were removed from the distilled water, the surface water was wiped off using blotting paper, and wet weight values were determined. Water absorption percent was calculated using the following formula,

$$M(\%) = (m_t - m_o) / m_o \times 100 \quad (1)$$

where m_o and m_t denote the oven-dry weight and weight after time *t*, respectively.

Flexural Properties

Three-point static flexural tests were carried out according to ASTM-D790-00 specification. The flexural tests were carried out at load rate of 5 mm/min. The modulus of rupture (MOR) and flexural modulus (MOE) were calculated using the following equations,

$$\begin{aligned} MOR &= 3PL / 2bd^2 \\ MOE &= L^3 m / 4bd^3 \end{aligned} \quad (2)$$

where *P* is the maximum applied load, *L* is the length of support span, *m* is the slope of the tangent, and *b* and *d* are the width and thickness of the specimen, respectively. Five specimens were tested, and the average values are reported.

RESULTS AND DISCOSSION

Water Uptake

The water absorption in natural filler thermoplastic composites is mainly due to the presence of lumens, fine pores, and hydrogen bonding sites in the natural filler, the gaps and flaws at the interfaces, and the micro-cracks in the matrix formed during the compounding process (Stokke and Gardner 2003). The water absorption of different uncompatibilized composites as a function of temperature after 2 h and 24 h immersion in water are presented in Fig. 1. All the composites showed a low uptake of water, which is attributed to the low content of lignocellulosics present in the composites.

It can be seen that the wheat straw composite absorbed more water than the poplar and pine composites. This may be due to the presence of a high amount of pentosans and low amount of lignin in wheat straw filler (Table 2). Cellulose and hemicelluloses are mostly responsible for the high water absorption of natural fibers, since they contain numerous accessible hydroxyl groups. Lignin is a hydrophobic material.

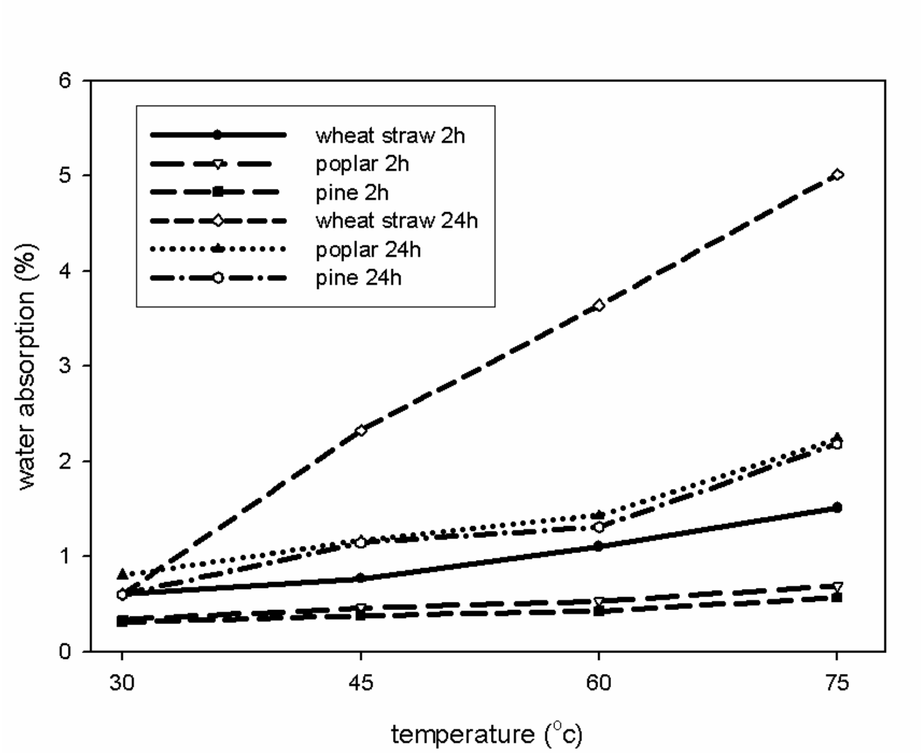

Fig. 1. Comparative water absorption curves of uncompatibilized composites after 2 h and 24 h immersion as a function of temperature

It can also be seen that water absorption values of composites from loblolly pine after 2 h and 24 h immersion in water were less than those of composites from poplar. Namely, the water absorption obtained in softwood was lower than in hardwood. This difference can be attributed to the anatomical properties of the wood of the species, because the cell cavities are larger in hardwoods, the cell walls are thinner and more permeable, and the openings of the pits are larger than in softwoods (Var and Oktem 1999). Another reason for less water absorption in pine could be fewer free hydroxyl groups. The fewer free hydroxyl groups in loblolly pine can be attributed to the lower cellulose and pentosans contents.

Table 2. Chemical Composition of Natural Fillers Used in the Composites

Natural filler type	Alpha cellulose (%)	Lignin (%)	Pentosans (%)
Loblolly Pine	44.9	26.5	12.3
Euro-American poplar	46.7	21.5	17.8
Wheat straw	41.3	17.3	24.6

Statistical analysis indicated that temperature had a significant influence on water absorption of the composites ($p<0.05$). Figure 2 shows the water absorption of 2% compatibilized composites as a function of temperature after 2 h and 24 h immersion in water. The diffusion coefficient is the most important parameter for water absorption, as it shows the ability of solvent molecules to penetrate inside the composite structure. Water absorption of the composites increases with temperature, since temperature activates the diffusion process. In addition, the higher absorption of water may be due to the micro cracks developed on the surface and inside the material and/or natural filler swelling due to moisture, as well as the resulting filler debonding from the matrix due to the moist and high temperature environment (Panthapulakkal and Sain 2007).

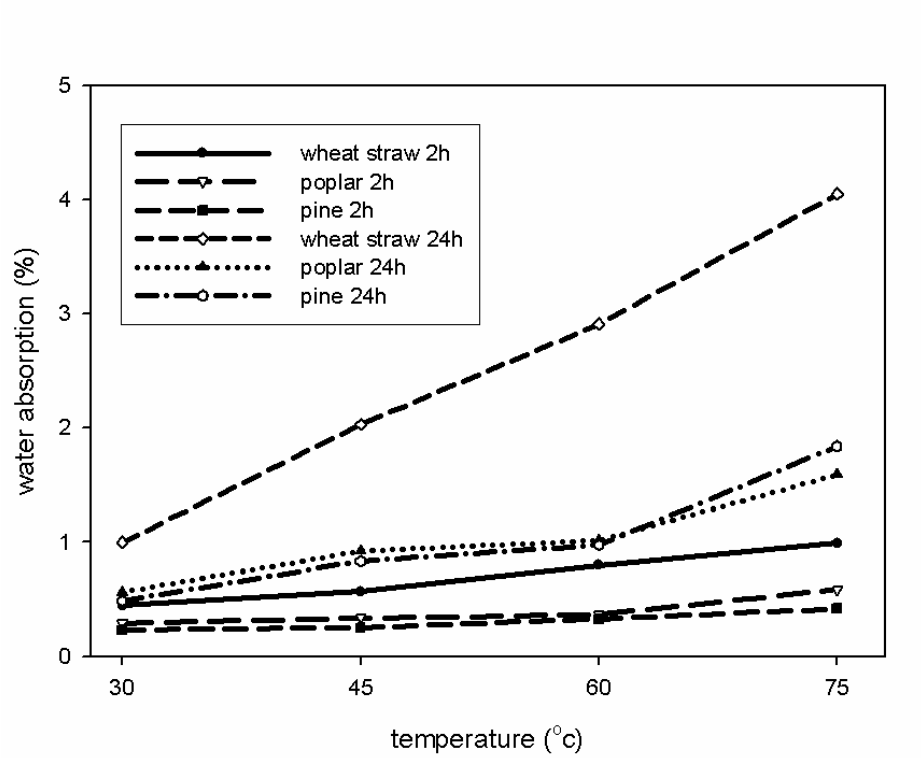

Fig. 2. Comparative water absorption curves of composites with 2wt% compatibilizer after 2 h and 24 h immersion as a function of temperature

The composites with 2% compatibilizer showed lower water absorption compared to those without compatibilizers. The extent of water absorption of compatibilized samples was about 25, 15, and 26 percent less than that of uncompatibilized wheat straw, poplar, and pine composites, respectively for 2 h immersion and 33, 30, and 18 percent for 24 h immersion time. The anhydride groups present in the MAPE can covalently bond to the hydroxyl groups of the filler surface (Sanadi et al. 1997). The decrease of the water absorption therefore may be attributed to the occupation of free hydroxyl groups. The most cost effective benefit for improving moisture resistance along with mechanical performance of natural fiber thermoplastic composites has been found with coupling agents, which play an important role in improving compatibility and adhesion between polar natural fiber and non-polar polymer matrices. Bridges are formed with chemical bonds between the fiber and the matrix (Lu et al. 2000).

At all temperatures, pine composites showed the lowest water absorption, whereas wheat straw ones exhibited the highest water uptake. The highest water absorption was obtained with 24h immersion time for uncompatibilized wheat straw composites at 75°C, and the lowest was obtained with 2h immersion time for 2% compatibilized loblolly pine composites at 30°C. The water absorption of the poplar composite was greater than those of pine.

Flexural Behavior

The flexural strength and modulus of the composites are given in Table 3. The flexural behavior of the composites varied significantly with filler type. Composites made with poplar showed the highest strength and flexural modulus, whereas wheat straw composites exhibited the lowest properties. It was found that composites with 2% compatibilizer provided significantly higher flexural strength and modulus, compared with untreated samples. Moreover, poplar composites showed the highest flexural properties with 2% MAPE. The strength of the composites depended on the properties of constituents and the interfacial interaction.

Table 3. Flexural Properties of Natural Filler/HDPE Composites

Formulation name	Flexural strength (MPa)	Flexural modulus (GPa)
Wheat straw/HDPE	36.68	2.389
Wheat straw/HDPE/MAPE	44.32	2.597
Pine/HDPE	38.56	2.453
Pine/HDPE/MAPE	47.86	2.847
Poplar/HDPE	40.43	2.664
Poplar/HDPE/MAPE	54.23	2.935

CONCLUSIONS

1. Water absorption was highest in wheat straw composites and the lowest water absorption was found in pine composites. This was due to the chemical properties and anatomical properties of the lignocellulosic fillers.
2. The amount of water absorption was clearly dependent upon the temperature.
3. Flexural properties were highest in poplar composites, and the lowest flexural strength and modulus were found in wheat straw ones.
4. Flexural properties of the composites treated with MAPE were significantly superior to those of untreated ones.

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Article submitted: November 20, 2009; Peer review completed: Dec. 18, 2009; Revised version received and accepted: Dec. 23, 2009; Published: Dec. 24, 2009.