EFFECT OF FILLER LOADING ON PHYSICAL AND FLEXURAL PROPERTIES OF RAPESEED STEM/PP COMPOSITES

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The objective of the study is to develop a new filler for the production of natural filler thermoplastic composites using the waste rapeseed stalks. The long-term water absorption and thickness swelling behaviors and flexural properties of rapeseed filled polypropylene (PP) composites were investigated. Three different contents of filler were tested: 30, 45, and 60 wt%. Results of long-term hygroscopic tests indicated that by the increase in filler content from 30% to 60%, water diffusion absorption and thickness swelling rate parameter increased. A swelling model developed by Shi and Gardner can be used to quantify the swelling rate. The increasing of filler content reduced the flexural strength of the rapeseed/PP composites significantly. In contrast to the flexural strength, the flexural modulus improved with increasing the filler content. The flexural properties of these composites were decreased after the water uptake, due to the effect of the water molecules.

Keywords: Composite; Rapeseed; Thickness swelling; Water absorption; Flexural properties

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INTRODUCTION

Today, the use of agricultural residues is common in wood-limited countries, since they are easily available and inexpensive. Rapeseed (*Brassica napus*) stalk is an agricultural industrial residue produced as a by-product. It is widely cultivated throughout the world for the production of animal feed, vegetable oil, and biodiesel fuel. It is one of the most important oilseeds in the world, ranking fourth with respect to production after soybean, palm, and cottonseed (Rashid and Anwar 2008). Rapeseed is mostly used as a general term to describe different species that are quite close in appearance but sometimes very different in their chemical composition or botanical origin (Donald and Bassin 1991). According to the Food and Agriculture Organization (FAO), world harvesting area of rapeseed is growing rapidly, with 30.8 million hectares harvested during the year 2006–07. Iran has about 220 thousand hectares of rapeseed harvesting area. The biomass produced per unit area by rapeseed varies from 5 to 10 t/ha (Enayati et al. 2009).

Natural fiber thermoplastic composites can be manufactured using a variety of production techniques. A simple technique to produce such composites is hot pressing. The advantages of the technique are flexibility in altering the density of the composite panels produced, and the possibility to produce layered panels (Tajvidi and Haghdan 2009).

Although there has been considerable research devoted to the physical and mechanical properties of agro-based fiber thermoplastic composites (Panthapulakkal et al. 2009; Zabihzadeh et al. 2010; Talavera et al. 2007; Yang et al. 2007; Yao et al. 2008), there are no experimental data about the physical and mechanical properties of rapeseed filled thermoplastic composites. This work establishes the hygroscopic and flexural performance of rapeseed filled polypropylene composites produced by hot pressing. Flexure properties of the composites as a function of filler loading before and after water absorption were analyzed. Long-term water absorption and thickness swelling behaviors of composites were also investigated.

EXPERIMENTAL

Materials

Polypropylene (Lotte Daesan Petrochemical Corp., South Korea) with a density of 0.90 g/cm^3, and the melt flow index of 25 g/10min at 230 °C was used in this work as the polymer matrix. Natural filler was obtained by milling and screening rapeseed residue to 40-mesh particle size. Maleic anhydride grafted polypropylene (MAPP) was used as compatibilizer.

Composite Preparation

Table 1 shows formulation of the composite panels prepared for this study. A dry-blending method and hot pressing were used to produce composite panels. The mixture of PP powder, oven-dried rapeseed flour, and MAPP was spread into a steel mold with dimensions of 25 cm × 15 cm × 1 cm. The formed mats were pressed in a cold press to maintain the shape. The formed mats were then pressed in a hot press for 15 min at a pressure of 35 bar and a temperature of 190 °C. The composite panels were transferred to the cold press and stayed there for about 5 min at a pressure of 35 bar. Four composite panels were manufactured for each formulation. The manufactured composite panels were kept at room temperature for two weeks in order to allow the condition of the composite to reach equilibrium.

Table1. Formulation Composite Panels

Code	PP (wt %)	Rapeseed flour (wt %)	Compatibilizer (wt %)
PP/R30	67	30	3
PP/R45	52	45	3
PP/R60	37	60	3

Hygroscopic Tests

Hygroscopic behavior studies were performed following the ASTM D 570-98 method. Four specimens of each composite 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 their thickness was measured with a precision of 0.001 mm. Then they were placed in distilled water. At predetermined time intervals, the specimens were removed from the distilled water, the surface water was wiped off using blotting paper, and their wet mass and thickness were determined. Water absorption and thickness swelling were calculated using the following formulas,

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

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

$$S(\%) = (T_t - T_o)/T_o \times 100 \quad (2)$$

where T_o and T_t denote the oven-dry dimension and dimension after time t, respectively.

Flexural Properties

Three-point flexural tests were performed according to the ASTM D 790-00 specification. The tests were carried out before and after water absorption at a crosshead speed of 5 mm/min. The modulus of rupture (*MOR*) and flexural modulus (*MOE*) were calculated. Each value obtained represented the average of four samples.

RESULTS AND DISCUSSION

Hygroscopic Behavior

Figure 1 shows the water absorption curves of composite panels at room temperature, where percentage of moisture absorbed is plotted against the square root of the immersion time. Generally, the water absorption increased with the filler content and immersion time until equilibrium conditions were reached. The water absorption in natural fiber thermoplastic composites is mainly due to the presence of hydrogen bonding sites in the natural fiber. Cellulose and hemicelluloses are mostly responsible for the high water absorption of natural fibers, since they contain numerous accessible hydroxyl groups. The water absorption of all the composites increased with the immersion time until maximum water absorption was reached. The maximum water absorption for composite with 30, 45, and 60% rapeseed flour was 12.09, 22.13, and 29.88%, respectively. The equilibrium time for composite with 30, 45, and 60% rapeseed flour was 1245, 876, and 756 h, respectively. It can be seen that the filler loading also has a significant effect on initial water uptake (slope of water absorption at the initial stage). The composite with higher filler content reaches the equilibrium moisture content more quickly.

For all three formulations, the water absorption increased with $t^{0.5}$ during the first stages until reaching a certain value at which the water content remained constant, indicating a Fickian mode of diffusion. Fick's second law states that

$$\frac{\partial M}{\partial t} = D.\frac{\partial^2 M}{\partial Z^2} \quad (3)$$

where D, M, T, and Z denote diffusion coefficient, moisture content, time, and the thickness dimension, respectively.

Under conditions of non-steady state diffusion, the apparent diffusion constant, D_A may be described by:

$$D_A = \pi \left[\frac{h}{4M_{Sat}} \right]^2 \left[\frac{\partial M_t}{\partial \sqrt{t}} \right]^2 \tag{4}$$

where h is the thickness of the sample, M_{sat} is the water absorption at saturation, and $\frac{\partial M_t}{\partial \sqrt{t}}$ is the slope of the water absorption versus square root of time.

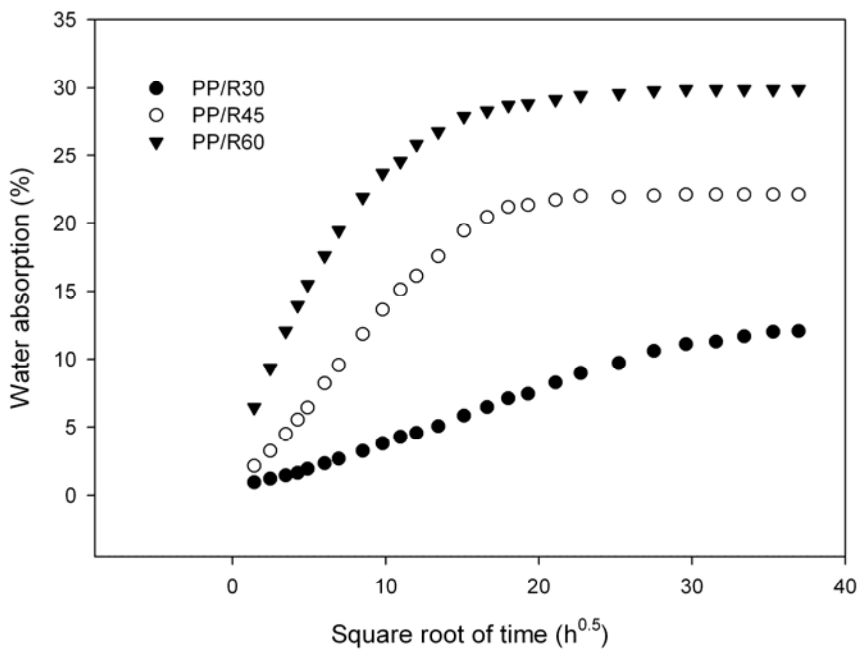

Fig. 1. Effect of filler loading on water absorption for PP/rapeseed composites

Table 2 summarizes maximum water absorption, water diffusion coefficient, maximum thickness swelling and swelling rate parameter for the composite panels. The magnitude of the diffusion coefficients obtained in this study (1.37×10^{-6} to 7.86×10^{-6} mm^2/s) was close to the reported values in previous works. Adhikary et al. (2008) reported a diffusion coefficient of 3.43×10^{-6} mm^2/s for hot pressed 50 wt.% Radiata pine (*Pinus radiata*) sawdust- PP composite coupled with MAPP. Espert et al. (2004) published a diffusion coefficient of 1.09×10^{-6} mm^2/s for PP composites containing 30 wt.% coir fiber and a diffusion coefficient of 1.83×10^{-6} mm^2/s for composites containing 30 wt.% luffa fiber. Wang et al. (2006) published a diffusion coefficient of 4.63×10^{-7} mm^2/s for hot pressed 50 wt.% rice hull-HDPE composites coupled with MAPP.

Table 2. Hygroscopic Properties of Composite Panels

Code	Maximum water Absorption (%)	Water diffusion coefficient ($10^{-6}mm^2/s$)	Maximum thickness swelling (%)	Swelling rate parameter (10^{-3} h^{-1})
PP/R30	12.09	1.37	4.63	1.25
PP/R45	22.13	4.42	8.03	5.63
PP/R60	29.88	7.86	13.05	13.43

Figure 2 shows the long-term thickness swelling behavior of the composite panels. The higher the filler content, the higher the thickness swelling. The maximum thickness swelling for composite with 30, 45, and 60% rapeseed flour was 4.63, 8.03, and 13.05%, respectively. A moisture buildup in the natural fiber cell wall can lead to fiber swelling and dimensional changes in the composite, particularly in the direction of the fiber thickness (Rowell 1997). Dimensional stability of natural fiber thermoplastic composites is one important physical property in outdoor applications. A problem associated with thickness swelling is a reduction in the adhesion between the natural fiber and the matrix, leading to a reduction in the mechanical properties of the composite. The thickness swelling of the composites follows a similar trend to the water absorption behavior, increasing with immersion time until an equilibrium condition is attained.

The swelling rate parameter was determined by using Shi and Gardner model (Shi and Gardner 2006),

$$TS(t) = \left[\frac{h_{\max}}{h_o + (h_{\max} - h_o)e^{-K_{SR}t}} - 1 \right] \times 100 \qquad (5)$$

where $TS\ (t)$, h_o, and h_{max} are the thickness swelling, initial, and equilibrium composite thickness, respectively. K_{SR} is a constant called the intrinsic relative swelling rate.

Rearranging and taking natural logarithm of both sides of Equation 5 gives (Tajvidi et al. 2010):

$$\ln\left[\frac{100h_{\max}}{TS(t) + 100} - h_o \right] = \ln\left(h_{\max} - h_o\right) - K_{SR}t \qquad (6)$$

The swelling rate parameter was obtained from the slope of the linear part of the plot of $\ln(\frac{100h_{\max}}{TS(t)+100} - h_o)$ vs. time (Table 2).

Figure 2 also exhibits the predicted curves of thickness swelling of composites produced by using the Shi and Gardner model. It can be seen from Fig. 2 that the swelling model fit the experimental data well for all of the composites.

The swelling rate parameter of the composite panels is given in Table 2. The magnitudes of the swelling rate parameter in this study were 1.25×10^{-3} to 13.43×10^{-3} h^{-1}. The maximum K_{SR} value was calculated for composite made of 60% rapeseed flour. It is important to note that K_{SR} is dependent not only on the initial rate of swelling but also on the equilibrium thickness swelling of the composites (Shi and Gardner 2006). The composite with 60% rapeseed flour will take less time to reach the equilibrium thickness, for which reason it will contribute to a greater magnitude of the swelling rate parameter. Adhikary et al. (2008) published a swelling rate parameter of 2.76×10^{-3} h^{-1} for hot pressed 50 wt.% Radiata pine sawdust-PP composite coupled with MAPP. Kazemi Najafi et al. (2008) reported a swelling rate parameter of 21.5×10^{-3} h^{-1} for hot pressed 50 wt.% wood flour-virgin PP composite.

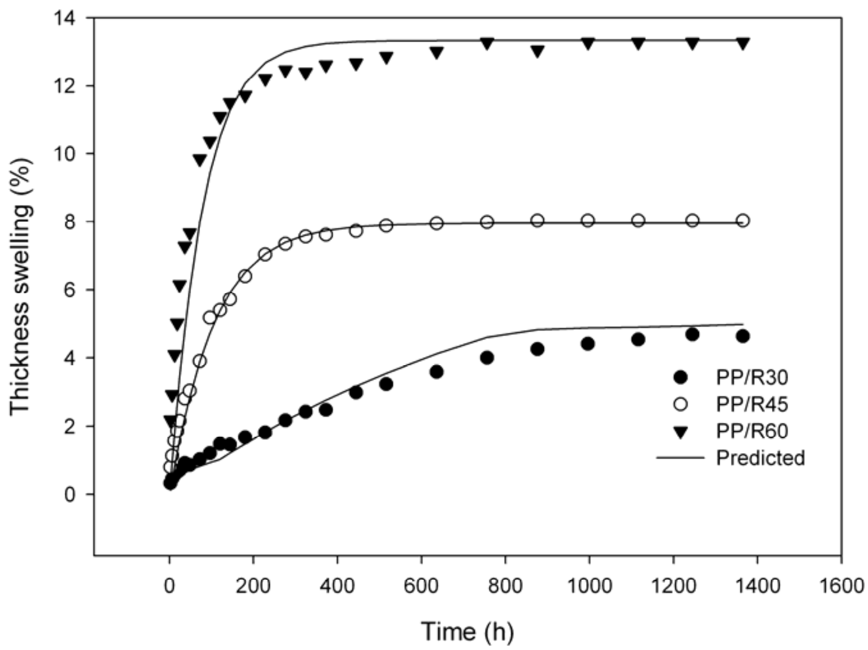

Fig. 2. Effect of filler loading on thickness swelling for PP/rapeseed composites

A good linear relationship was found between thickness swelling and water absorption (Fig. 3). The relationships were established as,

PP/R30 composite panels:

$$T_s = 0.3978W_a - 0.2179 \qquad R^2 = 0.93 \tag{7}$$

PP/R45 composite panels:

$$T_s = 0.3651W_a - 0.1388 \qquad R^2 = 0.98 \tag{8}$$

PP/R60 composite panels:

$$T_s = 0.4037W_a - 0.5119 \qquad R^2 = 0.79 \tag{9}$$

where T_s and W_a are thickness swelling and water absorption (%), respectively.

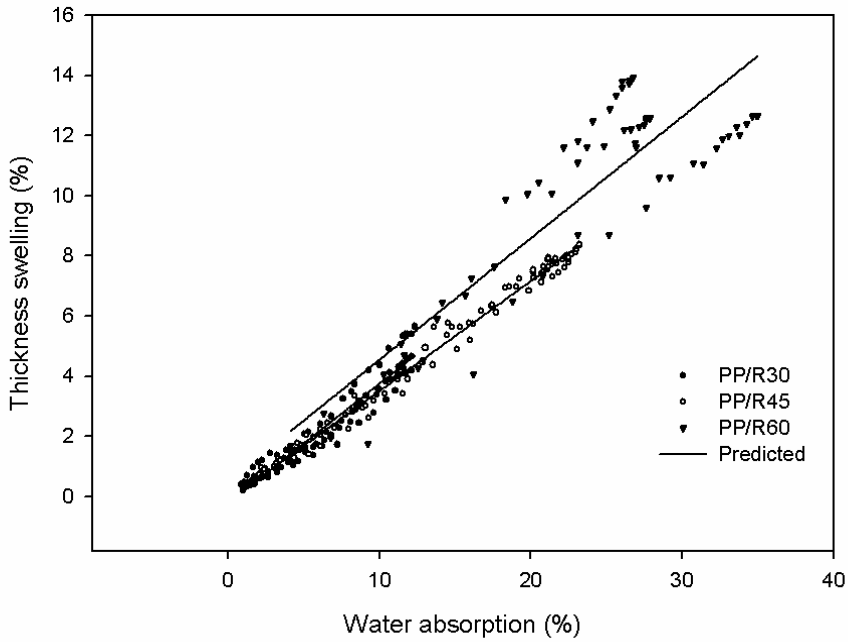

Fig. 3. Relationship between water absorption and thickness swelling of PP/rapeseed composites

Effects of Water Uptake on Flexural Properties

To study the effect of water absorption on the flexural properties, flexural tests were carried out in all the composite panels before and after water absorption. Table 3 shows the flexural strength (*MOR*) and flexural modulus (*MOE*) as a function of filler loading of rapeseed filled PP composites before and after the water uptake. Before the water absorption, a decreasing trend in flexural strength can be seen as the filler content increases. This phenomenon can be attributed to the weakness of lignocelulosic phase in stress transition to the polymer matrix. In contrast to flexural strength, the flexural modulus improved with increasing filler content. This observation is due to the increase in volume fraction of high-modulus lignocelulosic in thermoplastic composites.

In general, the flexural properties of these composites were decreased after the water uptake, due to the effect of the water molecules, which change the structure and properties of the fillers, polypropylene, and the interface between them. Once the water molecules penetrate inside the composite panels, the lignocelulosic fillers tend to swell. The reduction in the flexural strength and modulus values of the composites after water uptake may be due to the inability of the swelled rapeseed flour to carry the stress transferred from the matrix through the disrupted interface as a result of water absorption. This finding is consistent with previous studies. Espert et al. (2004) reported that mechanical properties natural fiber thermoplastic composites are dramatically affected by the water uptake and water-saturated samples present poor mechanical properties. Sain and Panthapulakkal (2007) indicated that long term aging in water decrease the strength properties of the short hemp-glass fiber hybrid polypropylene composites.

Table 3. Effect of the Water Uptake on Flexural Strength and Modulus of Composite Panels

Code	Flexural strength (MPa)		Flexural modulus (MPa)	
	Before water absorption	After water absorption	Before water absorption	After water absorption
PP/R30	15.68	10.19	1915.45	1168.48
PP/R45	14.72	8.83	2024.53	1103.32
PP/R60	11.94	5.85	2193.38	1092.11

CONCLUSIONS

1. The water diffusion coefficient and the swelling rate parameter of the composite panels were clearly dependent upon the filler content.
2. The swelling model presented by Shi and Gardner provided a very good predictor of the hygroscopic swelling process of the composites.
3. A linear relationship was found between water absorption and thickness swelling of the composite panels.
4. The flexural strength decreased as the filler loading increased. This was due to the weakness of the lignocellulosic phase in stress transition to polymer matrix.
5. The flexural modulus improved as the filler loading increased. This was due to the increase in volume fraction of high-modulus lignocellulosic in composite panels.
6. The flexural properties of these composites were decreased after the water uptake.

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