EVALUATION ON THE EFFECT OF WOOD FLOUR AND COUPLING AGENT CONTENT ON THE HYGROSCOPIC THICKNESS SWELLING RATE OF POLYPROPYLENE COMPOSITES

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The effect of wood flour and coupling agent content on the hygroscopic thickness swelling rate of polypropylene composites was investigated in this study. To meet this objective, the wood flour was compounded with polypropylene and coupling agent in an internal mixer; then the samples were fabricated by injection molding. The concentration was varied from 40 to 60% for wood flour and from 0 to 4% for coupling agent. A swelling model developed by Shi and Gardner (2006) was used to study the thickness swelling process of polypropylene/wood flour composites, from which the parameter K_{SR} can be used to quantify the swelling rate. The results indicated that the swelling model provided a good prediction of the hygroscopic thickness swelling process of polypropylene-wood flour composites immersed in water. The minimum thickness swelling values were observed in composites made of 40% wood flour and 4% of PP-g-MA. Thickness swelling of the composite increased with immersion time, reaching a certain value at saturation point, after which the composites water content remained constant. Also, a good linear relationship was fit between K_{SR} and coupling agent contents. When the coupling agent content increased, K_{SR} linearly decreased. The maximum tensile modulus was achieved with 60% wood flour and 4% of PP-g-MA. The SEM revealed a positive effect of coupling agent on interfacial bonding between sawdust flour and polymer matrix.

Keywords: Hygroscopic thickness swelling rate; Swelling model; Wood flour; Coupling agent; Polypropylene

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INTRODUCTION

Wood is a hygroscopic and hydrophilic material that can absorb or desorb water depending on the relative humidity (RH) and temperature of surroundings. Wood is also subject to dimensional changes when its moisture content fluctuates below the fiber saturation point (FSP). Wood composites, such as fiberboard and particleboard, are processed from woody materials in the shape of fibers, flakes, shavings, and many other types of wood elements bonded with synthetic resin-adhesives consolidated under high pressure and often with high temperature. The internal stress induced in the composites during hot pressing tends to result in greater thickness swelling of the wood composites compared to normal wood after exposure to moisture (Cooper 1996; Shi and Gardner

1999). Wood composites swell at a rate defined by temperature, moisture, etc. Thickness swelling of wood composites is a serious and complex phenomenon because it can have a deleterious effect on other mechanical and physical properties of the board (Shi and Gardner 1999).

It has been shown that the water absorption of wood fiber/polymer composites typically between 0.7 and 3% by weight after 24 hours of immersion. This can be compared to water absorption by wood, such as pressure-treated lumber, which absorbs about 24% water by weight after 24 hours of immersion. When immersed into water for a much longer time, commercial wood plastic composites (WPCs) materials absorb up to 20 to 30% of water, whereas wood picks up more than 100% by weight (Oksman and Sain 2008). In comparing the hygroscopic thickness swelling of different wood composites, the different test durations of water immersion or water vapor exposure will provide different results because of swelling rate differences (Clemons et al. 1992).

Wood-based composites are often subjected to the environment where the moisture conditions change rapidly. In addition to the total amount of hygroscopic thickness swelling, the thickness swelling rate of composites is also an important parameter that can influence the durability of the composites. For example, composites with a higher swelling rate are likely to be subjected to fatigue when the relative humidity fluctuates because of the more rapid rate of change in the induced internal stress of the composites. Thus, water absorption is one of the most important characteristics of wood plastic composites exposed to environmental conditions that determine their end use applications. Therefore, as a limiting parameter, water absorption has to be taken into account in the design of wood plastic composites for final applications (Shi and Gardner 1999; Clemons et al. 1992; Cooper 1996). Generally, water absorption in wood plastic composites is governed by two significant mechanisms: the hygroscopic nature of natural fillers/fibers and the penetration of water into the composites (diffusivity) via gaps and flaws at the interfaces between fibers and plastics (Ellis 1994; Mantanis et al. 1994; Shi and Gardner 2006).

Considering the role of filler concentration and coupling agent treatment in wood plastic composites manufacturing and its application in aqueous media, the objectives of this study was to investigate the effect of wood flour and coupling agent content on the rate of hygroscopic thickness swelling of polypropylene composites.

EXPERIMENTAL

Materials

Polypropylene, V30S (MFI=18 g/10min, density=0.92g/cm^3) was supplied by Arak Petrochemical Co. (Iran). Beech wood-flour (WF) which was used as the reinforcing material was supplied from Cellulose Aria Co. (Iran); the average size of wood flour particles was about 425 µm. Maleic anhydride grafted polypropylene (PP-g-MA) provided by Solvay with trade name of Priex 20070 (MFI=64 gr/10min, grafted maleic anhydride 1 Wt. %) was used as coupling agent.

Composite Preparation

Before preparation of samples, wood flour was dried in an oven at 65 ± 2 °C for 24 hours. Then polypropylene (PP), wood flour and coupling were weighed and bagged according to formulations given in Table 1. The mixing was carried out with a Haake internal mixer (HBI System 90, USA). First the PP was fed to the mixing chamber; after it was melted, the coupling agent was added. At the fifth minute, wood flour was added, and the total mixing time was 13 min. The compounded materials were then ground using a pilot-scale grinder (Wieser, WGLS 200/200 Model). The resulting granules were dried at 105 °C for 4 hours. Test specimens were prepared by injection molding (Eman machine, Iran). The specimens were stored under controlled conditions (50% relative humidity and 23 °C) for at least 40 hours prior to testing.

Table 1. Composition of the Studied Formulations

Sample Code	Wood flour Content (%)	Polypropylene Content (%)	Coupling Agent Content (%)
40W60P	40	60	0
40W60P2M	40	60	2
40W60P4M	40	60	4
50W50P	50	50	0
50W50P2M	50	50	2
50W50P4M	50	50	4
60W40P	60	40	0
60W40P2M	60	40	2
60W40P4M	60	40	4

Measurements

Thickness swelling tests were carried out according to ASTM D 7031. Specimens with a dimension of 20 × 20 × 20 mm were cut for the hygroscopic thickness swelling measurements. Four replicates were used for each sample code. To ensure the same moisture content for the specimens before each test, all the specimens were oven-dried at 102 ± 3 °C. The thickness of dried specimens was measured to a precision of 0.001 mm. The specimens were then placed in distilled water and kept at room temperature. For each measurement, specimens were removed from the water, and the surface water was wiped off using blotting paper. Thicknesses of the specimens were measured at different times during the long-time immersion. The measurements were terminated after the equilibrium thicknesses of the specimens were reached. The values of the thickness swelling in percentage were calculated using the Equation 1,

$$TS\,(t) = \frac{T\,(t) - T_0}{T_0} \times 100 \qquad (1)$$

where $TS(t)$ is the thickness swelling at time t, T_o is the initial thickness of specimens, and $T(t)$ is the thickness at time t.

Equation 1 was applied to the thickness swelling data for all composites. We noticed that Shi and Gardner (2006) tried to quantify the thickness swelling rate of wood plastic composites for more convenient comparisons. They developed a swelling model describing the hygroscopic swelling process of wood based composites. In this model, a swelling rate parameter K_{SR}, as determined using the test data, can be used to quantify the swelling rate. The swelling model is expressed in the following equation,

$$TS(t) = \left(\frac{T_\infty}{T_0 + (T_\infty - T_0)e^{-K_{SR}t}} - 1\right) \times 100 \tag{2}$$

where $TS(t)$ is the thickness swelling at time t. T_o and T_∞ are initial and equilibrium board thickness, respectively. K_{SR} is a constant referred to as the initial (or intrinsic) relative swelling rate. The values of K_{SR} in Equation 1 depend on how fast the composites swell, and also on their equilibrium thickness swelling.

Non-linear curve fitting was used to find the swelling rate parameter K_{SR} that provided the best fit between the equation and the data. This algorithm seeks the parameter values that minimize the sum of the squared differences between the observed and predicted values of the dependent variable, as seen in Equation 3,

$$SS = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \tag{3}$$

where SS is the sum of squared difference, and y_i and $\hat{y}_i$ are the observed and predicted values of the dependent variable, respectively.

RESULTS AND DISCUSSION

A thickness swelling curve is illustrated in Fig. 1, where the percentage of thickness swelling is plotted against time for all samples. As can be clearly seen in this example, thickness swelling generally increased with immersion time, reaching a certain value at a saturation point, beyond which no more water was absorbed and the composites thickness swelling content remained constant. The time to reach the saturation point was not the same for all formulations. The 40W60P4M and 60W40P samples showed minimum (3.26 %) and maximum (3.92 %) thickness swelling, respectively.

The hydrophilic nature of wood flour causes the thickness swelling in wood plastic composites manufactured (the plastics have negligible water absorption). Figure 1 shows that the thickness swelling of composites increased with increase of wood flour loadings. It is well established that the thickness swelling in natural fibers (lignocellulosic plant fiber) under fiber saturation point is mainly due to their hydroxyl groups on cellulose or hemi-cellulose that can react with water and increase gap between the cellulose chains. The absorption of water by non-polar polymers that contain fillers depends on the nature of the filling material. In the case of cellulosic fibers, which are hydrophilic, an increase in water sorption can be expected. Because polypropylene is hydrophobic and the wood flour is hydrophilic, the absorption of water depends solely on the fibers. As the wood flour loading increases, the cellulose content increases, which in turn results in the absorption of more water (Ellis 1994; Mantanis et al. 1994; Shi and Gardner 2006; Mishra et al. 2004; Yang et al. 2005; Adhikary et al. 2008).

When wood-plastic composites are exposed to moisture, the swelling wood fiber can cause local yielding of the plastics due to swelling stress, fracture of wood particles due restrained swelling, and interfacial breakdown. Initially, there is adhesion between the wood particles and matrix in a dry WPC. As the wood particle absorbs moisture, it swells. This creates stress in the matrix, leading to the formation of microcracks. It also creates stress in the wood particles, causing damage. After drying composites, there is no longer adhesion at the matrix and wood particles interface. Cracks formed in the plastics and the interfacial gap contributes to penetration of water into the composite at a later exposure (Oksman and Sain 2008).

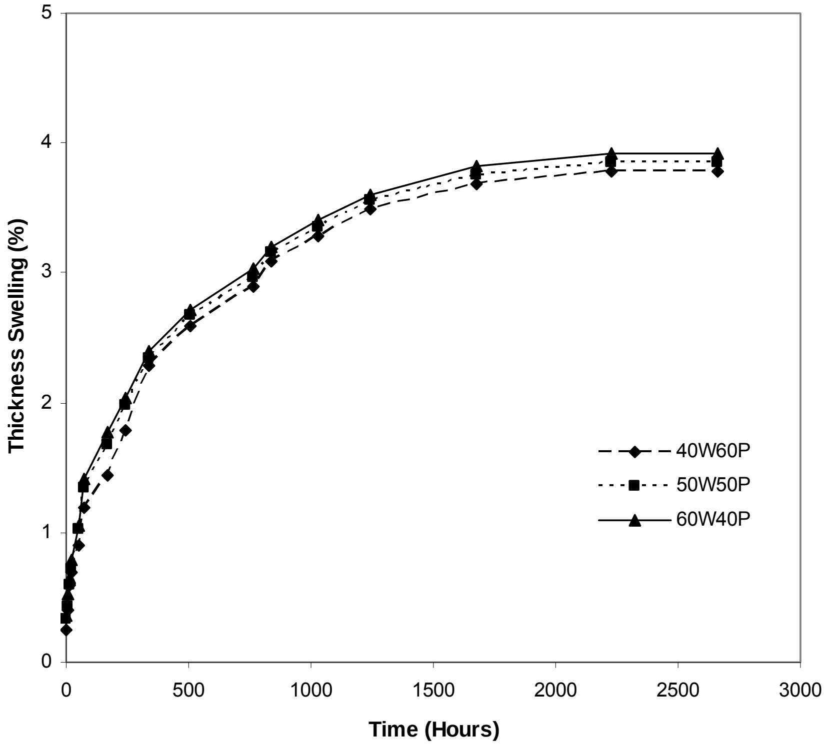

Fig. 1. Effect of wood flour content on thickness swelling of the composites

Figure 2 shows that the thickness swelling decreased with the addition of coupling agent. This means that the interfacial region influences the water uptake of the composite. Because uncompatibilized wood flour composite has weak fiber/matrix adhesion, the interface is enhanced in the presence of the coupling agent. Generally it is necessary to use compatibilizers or coupling agents in order to improve the polymer/fiber bonding and in turn to enhance water resistance. The coupling agent chemically bonds with the OH groups in the wood flour and limits water absorption by the composites. As a result, it is important to use coupling agents to improve the quality of adhesion between plastics and fibers, to reduce the gaps in interfacial region, and to block the hydrophilic groups (Kokta et al. 1990; Raj and Kokta 1989; Yang et al. 2005).

According to a review of the literature the incompatibility between phases results in a poor interfacial adhesion between hydrophilic wood and the hydrophobic polymer matrix, which results in poor adhesion and therefore in poor ability to transfer stress from the matrix to the fiber, reducing the composite properties (Raj and Kokta 1989; Gauthier et al. 1998; George et al. 2001; Yang et al. 2005; Ghasemi and Kord 2009). So, the use of coupling agents improves the quality of adhesion between polymer and wood flour to reduce the gaps in interfacial region and to block the hydrophilic groups.

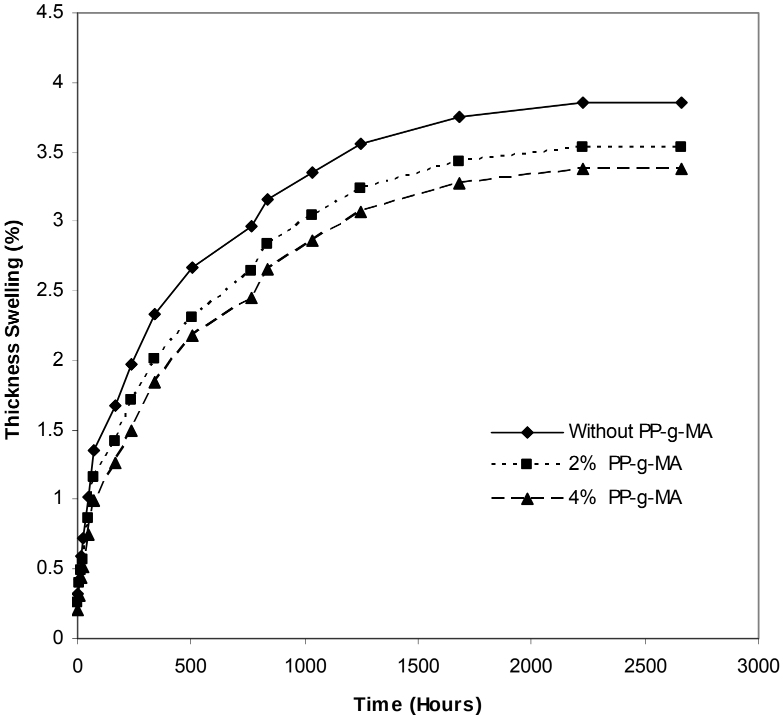

Fig. 2. Effect of coupling agent content on thickness swelling of the composites

The swelling rate parameter K_{SR} of composites is given in Table 2. It can be seen that the composites containing 60W40P exhibited higher K_{SR} than those containing coupling agent.

It is important to note that in the swelling model K_{SR} was obtained considering the whole thickness process until it was equilibrated; i.e. it was dependent not only on the initial rate of swell but also on the equilibrium thickness swelling of the composites (Shi and Gardner 2006).

For composites containing PP with higher equilibrium thickness swelling, there was less time to reach the equilibrium thickness, as well. This can explain the very high K_{SR} value determined in this case. Figure 3 shows that the K_{SR} of the composites was influenced by wood flour and coupling agent content. The minimum K_{SR} values were observed in composites made of 40% wood flour and 4% of PP-g-MA.

Table 2. Thickness Swelling Values and Swelling Rate Parameters for All Formulations

Sample Code	W_∞	T_0 (mm)	T_∞ (mm)	TS (%)	K_{SR} ($\times 10^{-3} h^{-1}$)
40W60P	14.3204	10.1267	10.4567	3.7847	0.0044
40W60P2M	14.0547	10.0933	10.3914	3.4860	0.0033
40W60P4M	13.7526	9.7933	10.1233	3.2686	0.0029
50W50P	15.1012	10.1933	10.5167	3.8515	0.0055
50W50P2M	14.5301	10.0467	10.4133	3.5318	0.0042
50W50P4M	14.0801	9.8533	10.1967	3.3739	0.0036
60W40P	16.2964	10.2133	10.5933	3.9238	0.0061
60W40P2M	15.4861	10.1	10.4333	3.6875	0.0049
60W40P4M	14.6171	10.0067	10.4567	3.4346	0.0037

W_∞, equilibrium water absorption; T_0, initial thickness; T_∞, equilibrium thickness; TS(∞), equilibrium thickness swelling; K_{SR}, Swelling rate parameter;

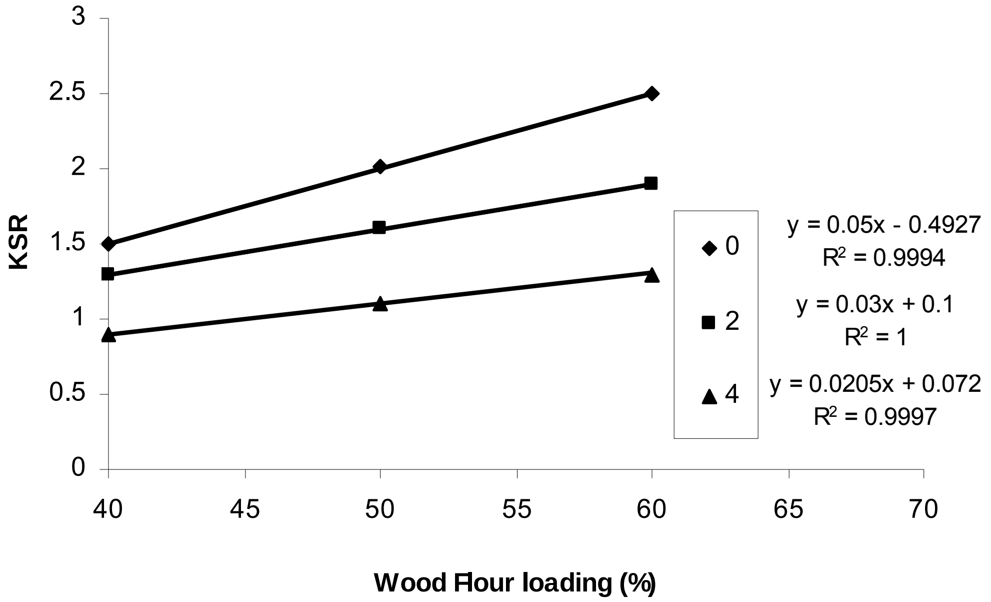

Fig. 3. Effect of wood flour and coupling agent content on K_{SR} of the composites

Also the thickness swelling curve of composites was predicted by non-linear curve fitting. It was found that the swelling model fit the experimental data well for all samples (the R^2 values for all the model fits were above 0.75). For example, it can be seen from Figs. 4 and 5 that the model provided better prediction for the initial portion of the thickness swelling process of composites containing different levels of wood flour and coupling agent. This phenomenon can be related to lower inner de-bonding or damage that could have occurred at higher swelling rates (higher water uptake). This could eventually lead to changes in the thickness swelling process and induce some error in the swelling model prediction. A good linear relationship was fit between K_{SR} and coupling agent contents in Fig. 4, and when the coupling agent content increased, K_{SR} linearly decreased.

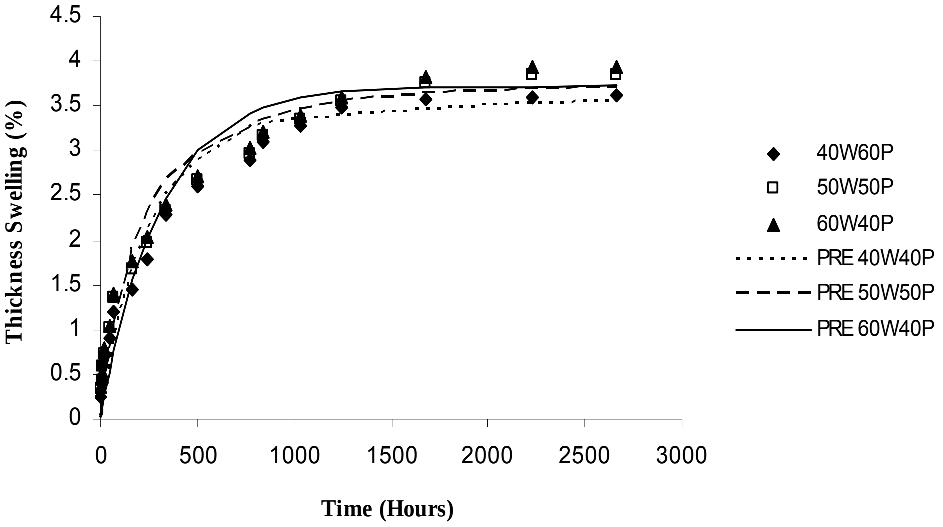

Fig. 4. Experimental and prediction models for thickness swelling of composites at different levels of wood flour

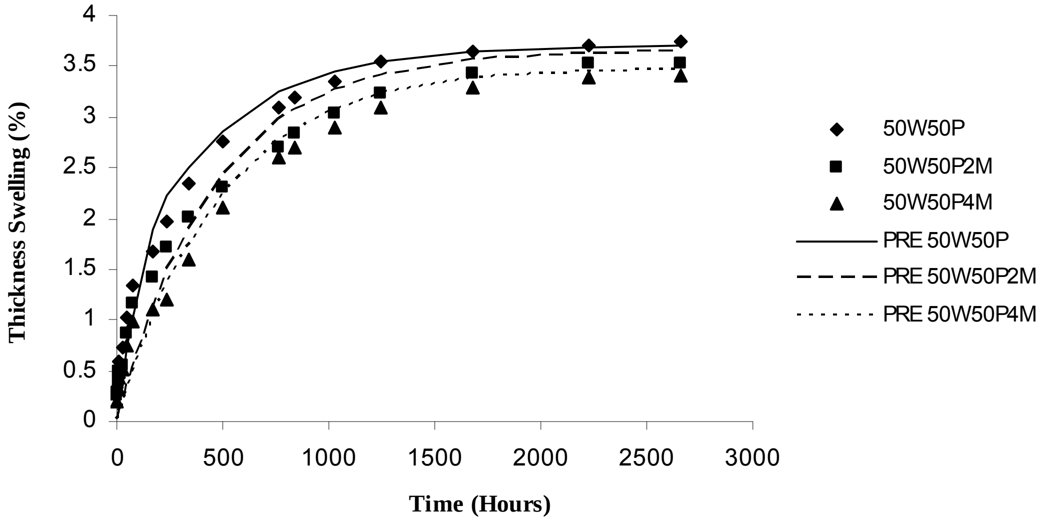

Fig 5. Experimental and prediction models for thickness swelling of composites at different levels of coupling agent

Tensile modulus of composites was evaluated to confirm the positive effect of wood flour and coupling agent (Fig. 6). As can be seen, the tensile modulus of composites increased with increase of wood flour loading. It is well established that the presence of the fillers had reduced the ductility of the composites and increased their stiffness**.** This is true for WPCs in which fillers added to a polymer restrains the movement of its chains, thereby increasing its modulus (Rowell et al. 1997; Yang et al. 2005; Oksman and Sain 2008). Figure 6 also shows that the modulus of composites increased with increase of coupling agent. It is well established that presence of the PP-g-MA as coupling agent enhances the interface adhesion between wood flour and pp matrix and brings better encapsulation of wood particles by the plastic (Raj and Kokta 1989; Gauthier et al. 1998; George et al. 2001; Yang et al. 2005; Ghasemi and Kord 2009).

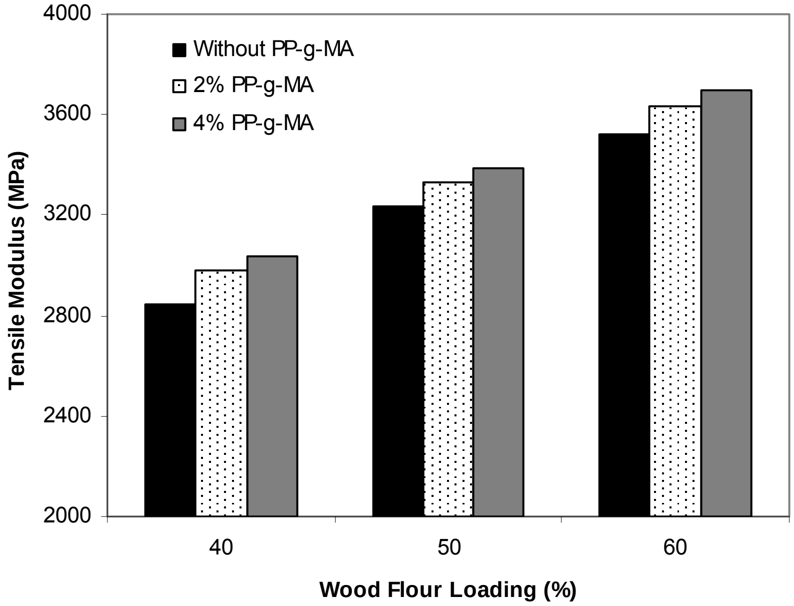

Fig. 6. Effect of wood flour and coupling agent content on tensile modulus of the composites

SEM micrographs show the fracture surfaces of the composites at different loadings of coupling agent are shown in Fig. 7. In the case of the composite without PP-g-MA, few wood flour particles are to be seen at the fracture surfaces, with the main component being matrix polymer, and some cavities are to be seen where the wood flour has been pulled-out. The presence of these cavities means that the interfacial bonding between the wood flour and the matrix polymer is poor and weak. In the case of the composite made with PP-g-MA, the interfacial bonding between the wood flour and the matrix polymer is strong, and the fracture occurred not at the interface but at the wood flour itself.

CONCLUSIONS

From the research work herein, the following conclusions can be drawn:

1. The swelling model was found to be a good predictor of the hygroscopic thickness swelling process of polypropylene-wood flour composites immersed in water.
2. The minimum thickness swelling values were observed in PP composites made with 40% wood flour and 4% of PP-g-MA.
3. Thickness swelling of the composite increased with immersion time, reaching a certain value at saturation point, beyond which the composites water content remained constant.

4. The swelling rate parameter K_{SR} of the composites was influenced by wood flour and coupling agent content. When the coupling agent content increased, K_{SR} linearly decreased.
5. The maximum tensile modulus was achieved with 60% wood flour and 4% of PP-g-MA.
6. The SEM micrographs revealed well-dispersed fillers on the fracture surfaces of the test samples fabricated using PP-g-MA as the coupling agent.

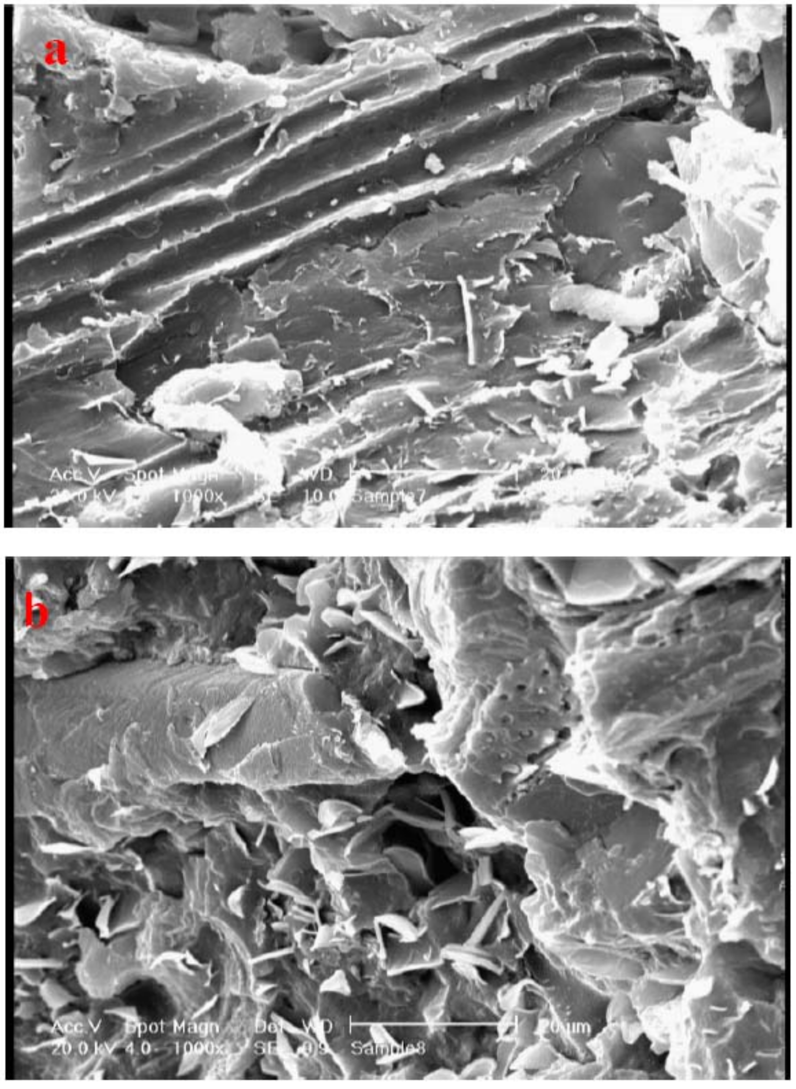

Fig. 7. SEM micrograph of the fracture surfaces in polypropylene/wood flour composite (a) without PP-g-MA (b) with 2% PP-g-MA

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