Effect of Bark Flour Content on the Hygroscopic Characteristics of Wood–Polypropylene Composites

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ABSTRACT: The effects of the bark content on the water absorption and thickness swelling of wood–plastic composites prepared from polypropylene, wood flour, and bark flour were studied. Samples were made with a laboratory twin-screw extruder. The results showed that among composites free of maleic anhydride polypropylene, those composites containing a higher bark flour content exhibited lower water absorption and lower thickness swelling. Maleic anhydride polypropylene reduced water absorption and thickness swelling in composites containing wood flour and a lower content of bark flour but had no influence on the hygroscopic properties of composites made with higher bark contents. Adding maleic anhydride polypropylene had no effect on the water diffusion coefficients and swelling rate parameters of composites made with a higher bark flour content. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3116–3120, 2008

Key words: composites; poly(propylene) (PP); swelling

INTRODUCTION

Wood–plastic composites (WPCs) are a relatively new family of composite materials. In such composites, a natural fiber/filler (e.g., kenaf fiber, wood flour, hemp, or sisal) is mixed with a thermoplastic [e.g., polyethylene, polypropylene, or poly(vinyl chloride)] to produce a WPC. WPCs are becoming more and more commonplace with the development of new production techniques and processing equipment.

The enforcement of new and stricter environmental policies has forced industries to search for new materials that can substitute for traditional composite materials consisting of a plastic matrix and inorganic fillers as reinforcements. Inorganic fibers present several disadvantages, such as their nonbiodegradability, the abrasion that they cause in the processing equipment, and the health problems that they cause in workers due to the skin irritation occurring during processing and handling. Compared to traditional synthetic fillers, natural fillers/fibers present lower density, less abrasiveness, and lower cost, and they are renewable and biodegradable.[1,2]

Using the residual materials of wood industries to manufacture WPCs is a major task for researchers. One of these residuals is bark, which is produced in high quantities in wood industries. The collection and disposal of this large amount of waste material present some problems and costs for wood industries. In addition, small-diameter round wood has a considerable amount of bark, which can influence WPC properties.

The environmental and disposal problems created by the accumulation of considerable volumes of bark in the forest industry and the increasingly scarce supply of wood and fiber resources are forcing the industry to seriously consider all possible utilization of bark as a raw material, particularly in the form of higher value products.[3] Various researchers have investigated the use of bark as a raw material in the production of wood-based panels such as particleboard, hardboard, and medium-density fiberboard.[3–6] The results have shown that the mechanical properties, such as the modulus of elasticity, bending strength, and internal bond, decrease with increasing bark content. The thickness swelling and water absorption of medium-density fiberboard panels are not greatly affected by the bark fiber content.[3] Bark has large amounts of extractives, which are the principal physical and chemical contributors to surface inactivation and hence to poor wettability by adhesives.[7]

Industrial sawdust collected from major woodworking facilities often contains considerable

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amounts of bark, the separation of which is not economically feasible. Because of chemical and structural differences between wood flour and bark flour, it is necessary to study the effects of the bark content on the physical and mechanical properties of WPCs.

New applications and end uses of WPCs and their exposure to the atmosphere or contact with aqueous media have made it necessary to evaluate the hygroscopic characteristics of WPCs. Therefore, as limiting parameters, hygroscopic characteristics have to be taken into account in the design of WPCs for final applications. Considerable research has been conducted on the water absorption of WPCs made of virgin and/or recycled plastics,[8–10] and a number of attempts have been made to reduce the water absorption of WPCs through the use of compatibilizers and modification.[11,12] A few studies have also been conducted on the thickness swelling of WPCs.[13–15]

The potential of using large amounts of bark as a raw material for WPCs and the effects of the bark content on panel properties are still unclear. The aim of this research was to study the effects of the bark content on the long-term hygroscopic characteristics of WPCs and to evaluate the compatibilizer performance.

EXPERIMENTAL

Plastic

Thermoplastic polypropylene homopolymer (grade PI0800) was supplied by Bandar Imam Petrochemical Co. (BIPC) (Mahshahr, Iran) in the form of pellets with a melt flow index of 3.1 g/10 min.

Filler

Beech wood flour and beech bark flour were used as lignocellulosic fillers. They were obtained separately through the grinding of small pieces of beech wood and bark. The mesh size of the flour was +60/−40. Wood and bark of Iranian beech (*Fagus orientalis*) were prepared from the Research Forest of the Natural Resources Faculty of Tarbiat Modares University (Noor, Iran).

Compatibilizer

Maleic anhydride polypropylene (MAPP) as a coupling agent was supplied by Malajchoob Factory (Gorgan, Iran).

Sample preparation

Oven-dried beech wood flour and beech bark flour with a moisture content of less than 3%, polypropylene, and MAPP were weighed for each formulation according to Table I and were physically mixed in a laboratory mixer for 10 min.

TABLE I
Compositions of the Evaluated Formulations

Formulation code	Wood flour content (wt %)	Bark content (wt %)	PP	MAPP
WP	60	0	40	0
WPM	60	0	38	2
W5BP	55	5	40	0
W5BPM	55	5	38	2
W10BP	50	10	40	0
W10BPM	50	10	38	2
W20BP	40	20	40	0
W20BPM	40	20	38	2

The mixtures were then extruded with a model WPC-4815 laboratory twin-screw extruder (Borna Pars Mehr Co., Iran) to produce strips with a nominal thickness and width of 10 and 70 mm, respectively. The extruder had eight temperature zones, with six zones on the barrel and two zones on the mold. The specimens for water absorption and thickness swelling testing were cut from these strips with 2.5 × 2.5 × 1 cm^2 dimensions.

Water absorption and thickness swelling

Water absorption tests were carried out according to ASTM D 7031-04 specifications.[16] Five specimens of each formulation were selected and dried in an oven for 24 h at 102 ± 3°C. The weight and thickness of the dried specimens were measured to a precision of 0.001 g and 0.001 mm, respectively. 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 with blotting paper. The weights and thicknesses of the specimens were measured at different time intervals during the long period of immersion. The measurements were terminated after the equilibrium thicknesses of the specimens were reached. The values of the water absorption as percentages were calculated with the following equation:

$$\mathrm{WA}(t) = \frac{W(t) - W_0}{W_0} \times 100 \tag{1}$$

where WA(t) is the water absorption (%) at time t, W_0 is the oven-dried weight, and $W(t)$ is the weight of the specimen at a given immersion time t.

Also, the values of the thickness swelling as percentages were calculated with Eq. (2):

$$\mathrm{TS}(t) = \frac{T(t) - T_0}{T_0} \times 100 \tag{2}$$

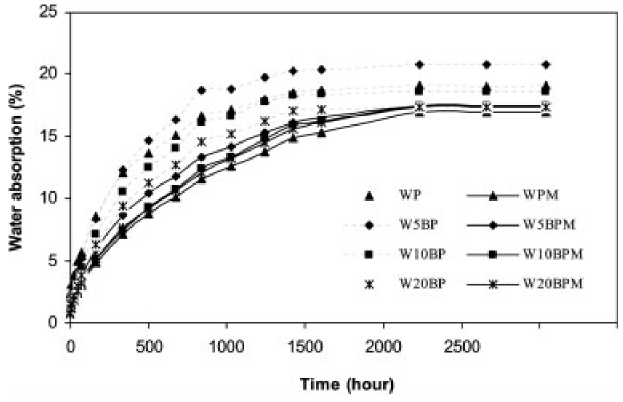

Figure 1 Water absorption curves for all formulations.

where TS(t) is the thickness swelling (%) at time t, T_0 is the initial thickness of the specimen, and $T(t)$ is the thickness at time t.

RESULTS AND DISCUSSION

Water absorption

Water absorption curves of different composites are illustrated in Figure 1, in which the percentage of water absorbed is plotted against the time for all samples. As can be clearly seen, water absorption generally increased with the immersion time, reaching a certain value at a saturation point at which no more water was absorbed and the composite water content leveled off.

Figure 1 shows that in WPCs without MAPP, there was no regular change in water absorption with the addition of bark or an increase in the bark content. The maximum water absorption of the composites was not the same for all formulations. The W20BP and W5BP composites showed minimum (17.4%) and maximum (20.7%) water absorptions, respectively.

Generally, when lignocellulosic materials are used as flour, they have similar influences on WPCs without compatibilizers. The slight differences in water absorption can be related to the chemical structures of the fillers. In this case, bark has less hygroscopic material (especially cellulose; Table II). This can explain why the composites containing large amounts of bark absorbed a little less water.

Figure 1 also shows that the composites containing MAPP exhibited lower water absorption than those made without MAPP. Adding MAPP reduced the maximum water absorption by about 15% in composites without bark and by about 5% in those with bark (Table III). When the bark content was increased to 20%, there was no difference between the water absorption of the composites without MAPP and the water absorption of those made with MAPP.

Generally, it is necessary to use compatibilizers or coupling agents to improve the filler/fiber bonding and in turn to enhance the water resistance. The compatibilizing agents have a positive effect on water absorption. The strong interfacial bonding between the filler and polymer matrix caused by the compatibilizing agents (MAPP chemically bonds with the OH groups in the lignocellulosic filler) limits the water absorption of the composites. In conclusion, it seems necessary to use coupling agents to improve the quality of adhesion between plastics and fibers to reduce the gaps in the interfacial region and to block the hydrophilic groups. Thus, it can be concluded that a larger amount of bark influences MAPP performance in such a way that it cannot cause good bonding between polypropylene and the filler. Bark flour has less cellulose, more lignin, and more extractives than wood flour (Table II).

Large amounts of extractives in bark flour cause a decrease in the polarity on the surface of the filler and a decrease in the wettability, so they limit MAPP performance. Saputra et al.[17] showed that extractives form a weak boundary layer in pine flour and that the removal of this layer by extraction improves the shear strength between the PP matrix and the extracted wood filler.

An analysis of the diffusion mechanism and kinetics was performed on the basis of Fick's theory, and the experimental values were fitted to Eq. (3) according to the method described by Espert et al.[9] and Kazemi Najafi et al.:[10]

$$\log\left(\frac{M_t}{M_\infty}\right) = \log(k) + n\log(t) \qquad (3)$$

where M_t is the water absorption at time t, M_∞ is the water absorption at the saturation point, and k and n are constants.

TABLE II
Chemical Compositions of the Wood and Bark of Beech

	Extractive (%)						
	Alcohol/acetone	NaOH (1%)	Hot water	Cellulose (%)	Lignin (%)	Hemicellulose (%)	Ash (%)
Wood	2	<1	<0.5	34	21	25	0.8
Bark	8	37	13	26	37	35	12

TABLE III
Water Diffusion, Maximum Water Absorption, and n and k Coefficients for All Formulations

Formulation code	Maximum water absorption (%)	n	k (h^2)	Water diffusion coefficient ($\times 10^{-12}$ m^2/s)
WP	19.1	0.41	0.055	4.29
WPM	16.9	0.50	0.038	2.97
W5BP	20.7	0.50	0.031	5.46
W5BPM	17.8	0.49	0.027	3.77
W10BP	18.6	0.49	0.031	4.85
W10BPM	17.4	0.48	0.026	3.12
W20BP	17.4	0.50	0.028	4.73
W20BPM	17.3	0.48	0.026	3.07

The n values were similar for all formulations and close to the value of $n = 0.5$ (Table III). Therefore, it can be concluded that the water absorption of all formulations approached the Fickian diffusion case. The diffusion coefficient is the most important parameter of Fick's model and shows the ability of water molecules to penetrate composite structures.

Table III shows the water diffusion coefficients for all formulations. The water diffusion coefficients decreased with the application of MAPP. The composites without bark and containing MAPP exhibited the lowest diffusion coefficients.

Thickness swelling

Thickness swelling curves of different composites are illustrated in Figure 2, in which the percentage of thickness swelling is plotted against the time for all samples. Similar to water absorption, thickness swelling increased with the immersion time, reaching a certain value at which no more thickness swelling occurred.

When the bark content was increased to 20%, the thickness swelling relatively decreased. The maximum thickness swelling and initial thickness swelling rates (the slope of the swelling curve at the initial stage) of composites containing 20% beech bark flour were less than those of composites made with less beech bark flour (among composites without MAPP). As mentioned before, the lower thickness swelling in composites containing higher amounts of beech bark flour can be related to the lower amounts of hygroscopic materials in the cell walls of the bark filler.

Figure 2 also shows that the thickness swelling decreased with the addition of MAPP. Among the composites containing MAPP, the composites without bark exhibited the lowest maximum thickness swelling. Similarly to the water absorption results, when the bark content was increased to 20%, there was no difference between the thickness swelling of the composites without MAPP and that of the composites made with MAPP. This means that the interface region influenced the thickness swelling of the composites. Because the uncompatibilized wood flour composite had weak fiber/matrix adhesion, the presence of bark did not affect the thickness swelling. In the presence of the compatibilizer, the interface was enhanced, and the addition of bark flour (with lower compatibility due to extractives) had a greater impact.

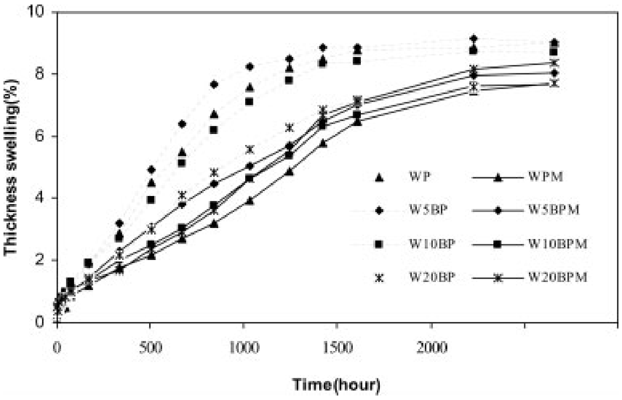

Figure 2 Thickness swelling curves for all formulations.

For more convenient comparisons, the thickness swelling rates of the composites were quantified by the model described and developed by Shi and Gardner.[18] In this model, a swelling rate parameter (K_{SR}), determined with the test data, can be used to quantify the swelling rate. The swelling model can be expressed as follows:

$$\mathrm{TS}(t) = \left(\frac{T_\infty}{T_0 + (T_\infty - T_0)e^{-K_{SR}t}} - 1 \right) \times 100 \qquad (4)$$

where T_∞ is the equilibrium board thickness. K_{SR} is a constant called the initial (or intrinsic) relative swelling rate. The values of K_{SR} in Eq. (4) depend on how fast the composites swell and also on their equilibrium thickness swelling.

The K_{SR} values of the composites are given in Table IV. The composites made with 20% bark content had the lowest K_{SR} values, and adding MAPP had no influence on this parameter. However, in other

TABLE IV
Thickness Swelling (TS) and K_{SR} Values for All Formulations

Formulation code	T_0 (mm)	T_∞ (mm)	TS (%)	K_{SR} ($\times 10^{-3}$ h^{-1})
WP	9.91	10.78	9.0	1.8
WPM	9.89	10.65	7.7	0.9
W5BP	10.10	11.02	9.0	1.91
W5BPM	9.92	10.71	8.0	1.11
W10BP	9.95	10.82	8.7	2.00
W10BPM	9.9	10.66	7.7	1.00
W20BP	9.97	10.74	7.7	1.11
W20BPM	9.91	10.74	8.1	1.00

formulations, adding MAPP led to a significant decrease (up to 50%) in K_{SR}.

CONCLUSIONS

The effects of the bark content on the water absorption and thickness swelling of WPCs prepared from polypropylene and wood flour were studied in this research. Among composites free of MAPP, those containing higher bark flour contents exhibited lower water absorption and lower thickness swelling because of the lower hygroscopicity of bark flour. MAPP reduced water absorption and thickness swelling in composites containing wood flour and lower contents of bark flour because of the enhancement of the fiber/plastic interface, but it had no influence on the hygroscopic properties of composites made with higher bark contents. Adding MAPP had no effect on the water diffusion coefficients and K_{SR} values of composites made with higher bark flour contents. Therefore, it can be said that at higher bark contents, although the compatibilizer improves the water resistance by limiting maximum water absorption, it has little effect on the rate at which water is absorbed. The bark content appears not to be a limiting factor as far as the physical properties of the composite material are concerned.

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