

Effect of Hydrothermal Environment on Moisture Absorption and Mechanical Properties of Wood Flour-Filled Polypropylene Composites

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ABSTRACT: The moisture absorption and mechanical properties of wood flour-filled polypropylene composites in a hydrothermal environment have been studied by immersing the composites in water at 23, 60, and 100°C. The degree of moisture absorption was found to be dependent on the modification of matrix, the weight percentage, mesh size, and surface treatment of wood flours. It increased with increasing the immersion temperature. The tensile strength of all composites with wood flours of different contents, mesh sizes, and surface treatments increased after immersion in water baths of various temperatures, to either greater or lesser extents. The flexural strength and modulus followed a similar trend when immersed in water at ambient temperature. However, the contrary was true for composites when immersed in 60 and 100°C water baths. The impact strength increased after immersion in water at each immersion temperature, and the extent of such increment decreased with increasing the immersion temperature. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2824–2832, 2002

Key words: wood flour; interfaces; polypropylene; moisture absorption; mechanical properties

INTRODUCTION

There is a growing interest in the use of agrowastes and agroforest materials as reinforcing components for thermoplastics because they are renewable, biodegradable, and environmentally friendly. Thermoplastics and their corresponding composites are sensitive to changes in the environment and their mechanical properties may vary considerably with environmental conditions. Variations in temperature and moisture are always encountered by these materials in service.

Their combined effect, known as hydrothermal aging, can be more damaging to the mechanical properties of the composites than to either component alone.¹ Some efforts have been focused on the hydrothermal behavior of thermoplastic composites.^{2–5} The presence of hydroxyl groups in wood flour is available for interaction with water molecules by hydrogen bonding.⁶ In contrast to glass fibers where water adsorption is important only at the surface, wood fibers interact with water not only at the surface but also in the bulk. Therefore, to develop composites with better mechanical properties, it is necessary to impart hydrophobicity to the fibers by suitable chemical treatment.^{7–12}

In the present work, the hydrothermal behaviors of wood flour-reinforced polypropylene (PP) composites were investigated. The effect of hydro-

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thermal aging on the mechanical properties of the composites was also studied.

EXPERIMENTAL

Materials

Polypropylene (type Y1600) was purchased from the Plastics of Shanghai Petrochemical Complex (China). Maleic anhydride grafted polypropylene (MPP) was prepared by the solid method in our laboratory (grafting degree, 1.2%). Wood flour was the mixture of various kinds of discarded sawdust. Coupling agents A-1100 and A-174 were supplied by Shanghai Yaohua Company (China). Antioxidant 1010 and DSTP were the products of Ciba-Geigy Company (Sweden).

Surface Treatment of Wood Flour

All wood flours were heat treated at 120°C for 5 h after being ground to different mesh sizes (20, 40, 80, 120, and 160 meshes). They were then divided into three groups: one group had no surface treatment; the second and the third were placed in a GH-100Y high-speed mixer (Beijing Plastic Machinery Factor, Beijing, China), followed by adding 1 wt % (with respect to wood flour weight) A-1100 and A-174 coupling agent solutions in water, respectively. After being mixed about 5 min, two groups of wood flours were removed and oven dried at 80°C for 1 h. When most water was evaporated, the temperature was raised to 120°C, at which point wood flours were allowed to react with the coupling agents for 30 min.

Preparation of Polypropylene Filled with Wood Flour

Wood flour was mixed with PP and antioxidant, with or without MPP in different weight proportions, then extruded with a GE2.8.30-41 twin-screw extruder (Luxembourg) at a screw speed of 160 rev/min and cut into pellets.

Mechanical Testing

The particles were injection molded with a TTI-80 plastic injection machine (Dong Hua Machinery LTD., Dongguang, China). Then the tensile and flexural properties were measured on a CMT 4204 universal testing machine (Shenzhen SANS Testing Machine Co., LTD., Shenzhen, China) at a crosshead speed of 2 mm/min. The tensile sam-

ples were tested according to ASTM D638, type I specification. The flexural testing followed ASTM D790. The span length between two supporting nodes was 100 mm and a crosshead speed of 2 mm/min was used. Notched charpy impact strength was tested with a WPM-charpy impact tester (VEB Werkstoffprüfmaschinen Lei Pzig, Lei Pzig, Germany) in accordance with ASTM D256-84. At least five specimens were tested for each sample. All mechanical tests were performed at room temperature.

Moisture Absorption of Composite

A water bath with temperature controllers was used for water-immersion tests. The specimens were immersed in water at 23, 60, and 100°C. The specimens were periodically removed from the water bath and the surface water was wiped off. Moisture absorption was determined by weighing the specimens on a balance with a precision of 0.1 mg. The moisture absorption at any time t (M_t) was calculated by

$$M_t = 100(W_t - W_d)/W_d$$

where W_d and W_t refer to the weight of the dry specimen and the wet specimen, respectively.

Scanning Electron Microscopy (SEM)

The tensile-fracture surfaces of the composite samples were studied with a Cambridge Instruments S-250 scanning electron microscope (Cambridge, UK), operated at 15 kV.

RESULTS AND DISCUSSION

Moisture Absorption of Composite

Effect of Wood Flour Content

The moisture absorption of wood flour/PP composites in a hydrothermal environment was studied by varying the weight percentage of wood flour from 10% to 40%. Figure 1 shows that the degree of moisture absorption increased with increasing the wood flour content. Cellulose fiber is the main component in wood flour. Each cellulose fiber is hollow and contains a lumen at its center. There are three main regions where the absorbed water in the composites can reside^{13,14}: the lumen, the cell wall, and the gap and flaw at the interface between fiber and PP. With the increase in wood

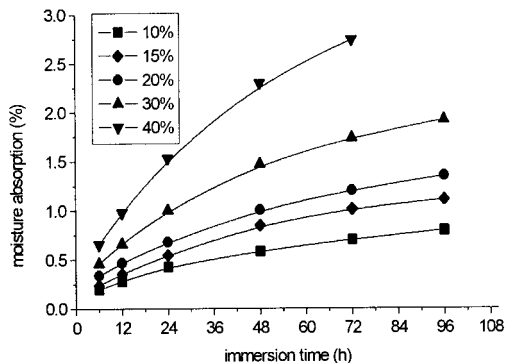


Figure 1 Wood flour content versus degree of moisture absorption. Wood flour mesh size, 40 mesh; interfacial treatment, 1% A-1100 + 5% MPP.

flour content, the gap and flaw at the interface would increase as a result of the poorer dispersion and wettability of wood flour. Consequently, all three regions—the lumen, the cell wall, and the gap and flaw—increased. As a result, the degree of moisture absorption significantly increased with the increase in wood flour content, as expected.

Effect of Wood Flour Mesh Size

Wood flour-filled PP composites were compounded with wood flours of different mesh size and the same PP. Figure 2 shows the relationship between the degree of moisture absorption and the mesh size of the wood flour. The moisture absorption decreased with decreasing the mesh size of the wood flour. The composite using 20-mesh wood flour exhibited a significantly larger difference in moisture absorption from that of the others, although there was no significant differ-

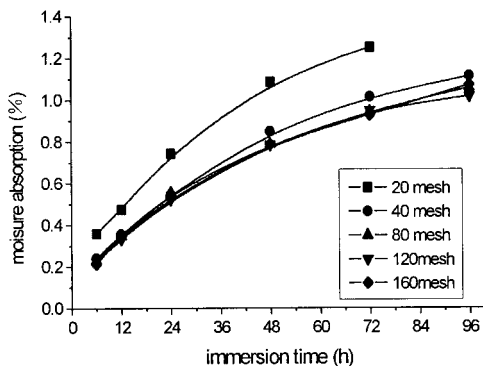


Figure 2 Wood flour mesh size versus degree of moisture absorption. Wood flour content, 15%; interfacial treatment, 1% A-1100 + 5% MPP.

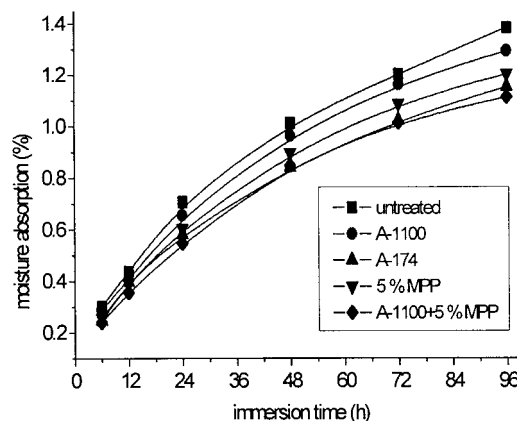


Figure 3 Degree of moisture absorption as a function of interfacial treatment. Wood flour content, 15%; wood flour mesh size, 40 mesh.

ence between composites using 80-, 120-, and 160-mesh wood flours. This might be because the surface areas of 20-mesh wood flour in contact with water were larger at the composite surfaces. Thus, the paths of water entering into the composite’s inner region were more numerous. Wood flour microfibrils of shorter length offer a larger specific surface area in composites than the same weight fraction of microfibrils of greater length. After treatment with A-1100 and MPP, hydrophobicity was imparted to significant portions of the surface of the wood flour, which effectively separated the paths through which water entered from the surface of the composite to the inner region. However, finer particles easily aggregated, which led to poor dispersion of particles in the matrix resin. Consequently, the gaps and flaws at the interface increased. Up to 80-mesh

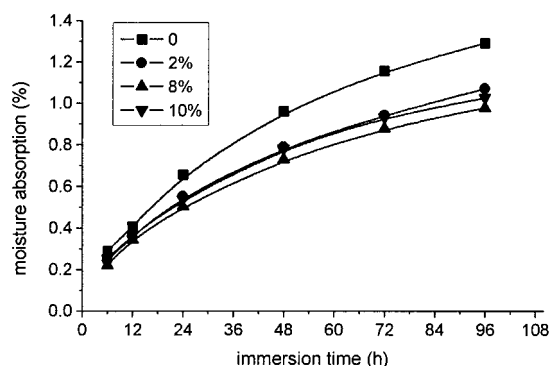


Figure 4 MPP content in matrix versus degree of moisture absorption. Wood flour content, 15%; wood flour mesh size, 40 mesh.

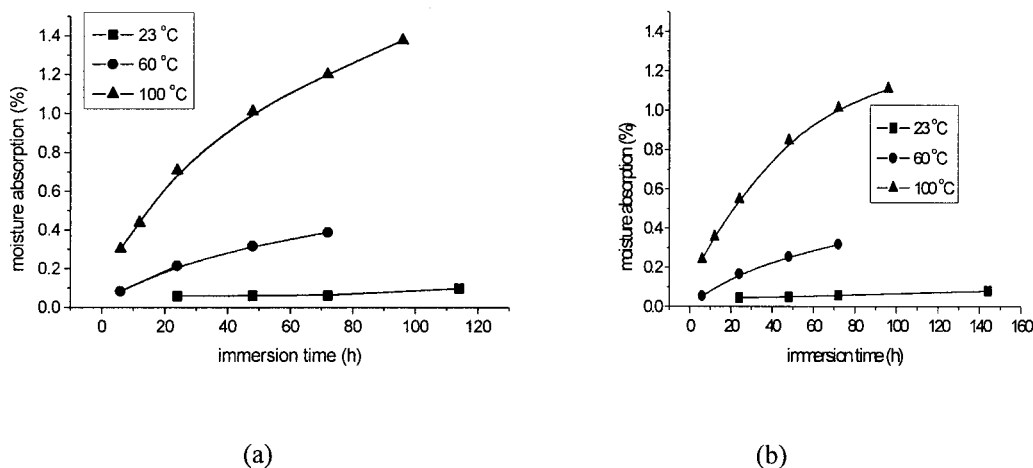


Figure 5 Effect of temperature on degree of moisture absorption: (a) wood flour untreated; (b) wood flour treated with A-1100 and matrix added with MPP. Wood flour content, 15%; wood flour mesh size, 40 mesh.

wood flour size, there was no significant decrease in moisture absorption by a further reduction of wood flour mesh size.

Effect of Interfacial Treatment

Moisture penetration into composites is conducted by three ways: (1) microgaps between polymer chains; (2) gaps and flaws at the interfaces between fiber and polymer because of incomplete wettability and impregnation; and (3) microcracks in the matrix, formed during the compounding process. Because of the presence of hydroxy and other polar groups in various constituents of wood flour, the poor compatibility of hydrophilic wood flour and hydrophobic polypropylene results in a number of gaps and flaws and

weak interfacial adhesion. Thus, it is necessary to impart hydrophobicity to the wood flour by suitable surface treatment.¹⁵ Figure 3 shows the various degrees of moisture absorption by using different treatment methods.

When wood flour was treated with the coupling agent A-1100 [$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)_3$] or A-174 [$\text{CH}_2\text{C}(\text{CH}_3)\text{COO}(\text{CH}_2)_3\text{Si}(\text{OCH}_2\text{CH}_3)_3$], the hydroxy groups could be produced by the hydrolysis of silanes with adsorbed water. They were supposed to link to the cellulose matrix with the formation of strong interactions with the hydroxy groups of cellulose and lignin. The remaining chain of silanes could adhere to the PP with the help of a van der Waals type of weak interaction. In this way, silane made a link between wood flour and PP, which imparted hydrophobicity to the wood flour and improved the interfacial adhesion between wood flour and PP.¹⁶ In addition, the double bonds in A-174 could react with the tertiary carbon of PP in thermal conditions, whereas the hydrogen bonds were formed between the NH_2 groups in A-1100 and water. As a result, the moisture absorption of the composites using A-174 was lower than that using A-1100.

After 5 wt % MPP (with respect to PP) was added into PP, the compatibility between wood flour and PP was improved because the anhydride groups in MPP could form a strong interaction with hydroxy groups in wood flour, whereas the chain entanglement between MPP and PP was formed because of the similar molecular chain structure. It could considerably increase the interfacial bond strength between fiber and matrix.

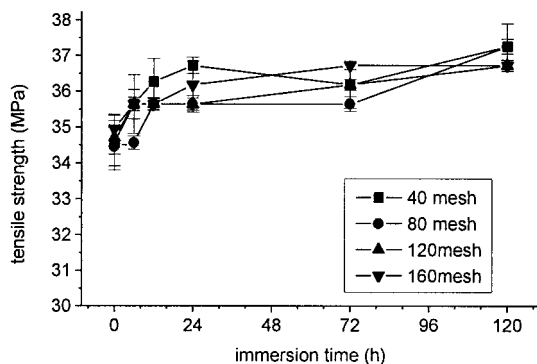


Figure 6 Tensile strength of wood flour-filled PP composites containing wood flours of different mesh sizes. Wood flour content, 15%; interfacial treatment, 1% A-1100 + 5% MPP.

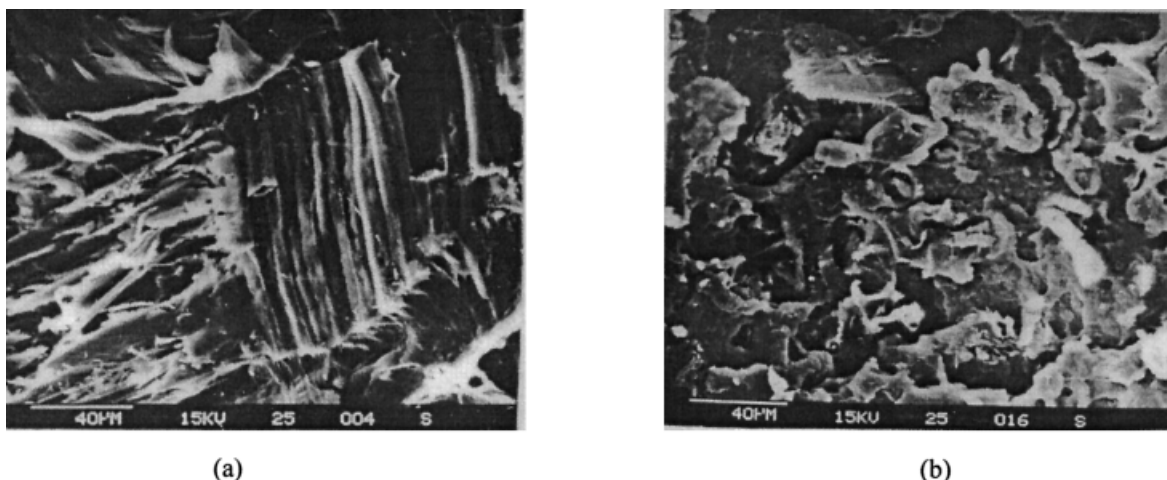


Figure 7 SEM of tensile-fracture surface of wood flour-filled PP: (a) nonimmersed in water; (b) immersed in boiling water for 240 h.

The gaps and flaws at the interface decreased, which reduced the number of paths by which water could penetrate into the composites.

When A-1100 and MPP were used at the same time, the NH_2 groups of A-1100 reacted chemically with the anhydride groups of MPP, which further promoted the interfacial adhesion. Thus the water uptake decreased in the following order: untreated wood flour, A-1100-treated wood flour, 5% MPP-treated wood flour, A-174-treated wood flour, and A-1100 + 5% MPP-treated wood flour.

Figure 4 shows the effect of MPP content in the matrix resin on the moisture absorption of composites. The results indicated that the moisture absorption decreased with MPP addition up to 8% and increased above this level. The compatibility and the interfacial adhesion between wood flour

and PP was increased with increasing the MPP content. However, when the content of MPP was high, some anhydride groups that could not form strong interactions with hydroxy groups in wood flour would strongly hydrolyze to absorbed water. Thus, the moisture absorption of composites using 10% MPP was higher than that using 8% MPP. Chua et al.¹⁷ reported that when a physisorbed layer and a chemisorbed layer are present, more water was absorbed, as indicated by the higher diffusion rate.

Effect of Temperature

The specimens were immersed in 23, 60, and 100°C water baths, respectively. Figure 5 shows the effect of immersion temperature on water uptakes of the untreated wood flour composite and treated wood flour composite, respectively. According to Shen and Springer,^{18,19} the maximum moisture content M_m is insensitive to the temperature but depends on the moisture content of the environment. For a material immersed in liquid, M_m is a constant. From the Shen–Springer equation, the diffusion coefficient could be calculated: it increased with increasing the immersion temperature. It could be seen that the moisture contents of two composites at any time t were strongly affected by the immersion temperature, increasing with the increase in immersion temperature. Moreover, the moisture content of untreated wood flour composite was higher.

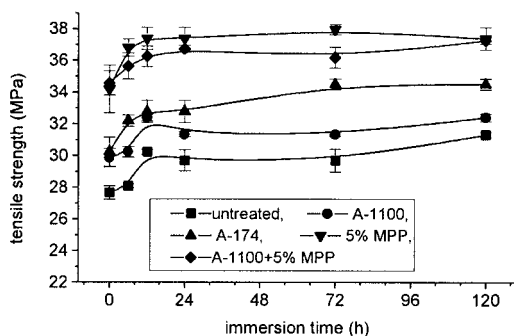


Figure 8 Tensile strength of wood flour-filled PP composites with different interfacial treatments. Wood flour content, 15%; wood flour mesh size, 40 mesh.

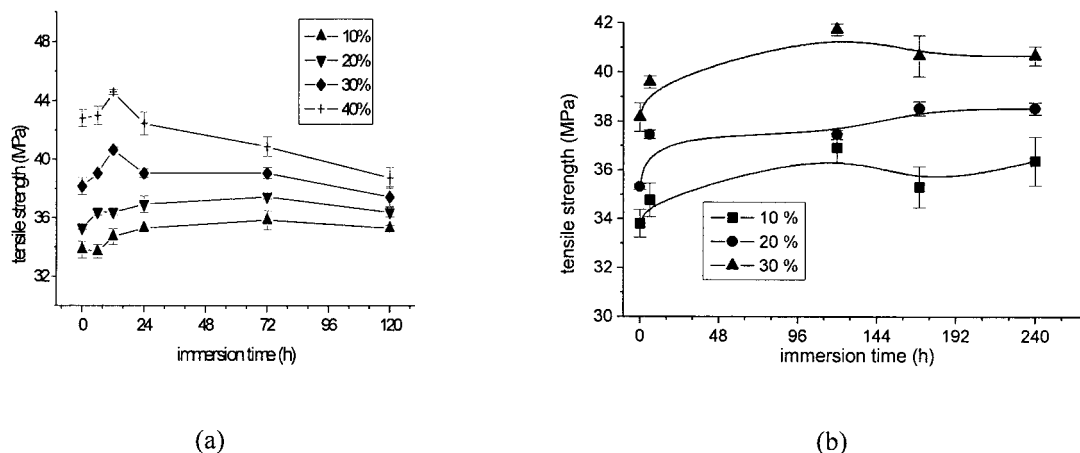


Figure 9 Tensile strength of wood flour-filled PP composites with different contents of wood flour: (a) immersed in 100°C water; (b) immersed in 60°C water. Wood flour content, 15%; interfacial treatment, 1% A-1100 + 5% MPP.

Effect of Hydrothermal Environment on Mechanical Properties

Tensile Strength

Wood flours of different mesh sizes were compounded with PP at the same weight fraction, 15%. Figure 6 shows that the tensile strengths all increased with prolonging the immersion time in boiling water. It was supposed that the additional process of annealing at 100°C increased the degree of crystallinity of PP,^{20,21} which decreased the impact strength but increased the tensile strength of the matrix. After swelling in water, the average increment in size of wood flours led to an increase of interfacial shear strength between the wood flour and the matrix. Moreover, the wet strength of wood fiber might be higher than the

dry strength because the interaction between microfibrils increased after absorbing water. It is evident from Figure 7 that the SEM of the tensile-fracture surface of composites shows the split fracture of wood flour in the composites without being immersed in water.

Figure 8 shows the tensile strength of the composites using different surface treatment methods as a function of exposure time in boiling water. In these composites, the fiber content was 15 wt %. It was interesting to note that all the composites showed an increase in tensile strength with exposure time. It could be seen that the improvement of MPP on the tensile strength in a hydrothermal environment was more significant. When wood flour was treated with 5% MPP, the moisture absorption of the composite was greater than that

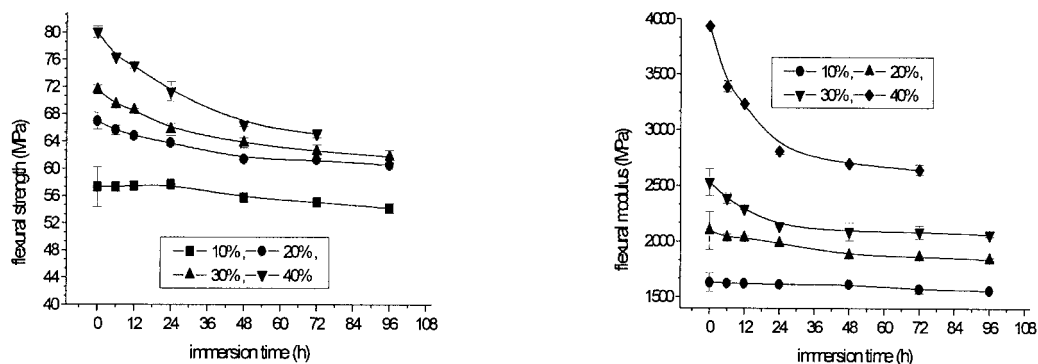


Figure 10 Flexural property of wood flour-filled PP composites with different contents of wood flour. Wood flour mesh size, 40 mesh; interfacial treatment, 1% A-1100 + 5% MPP.

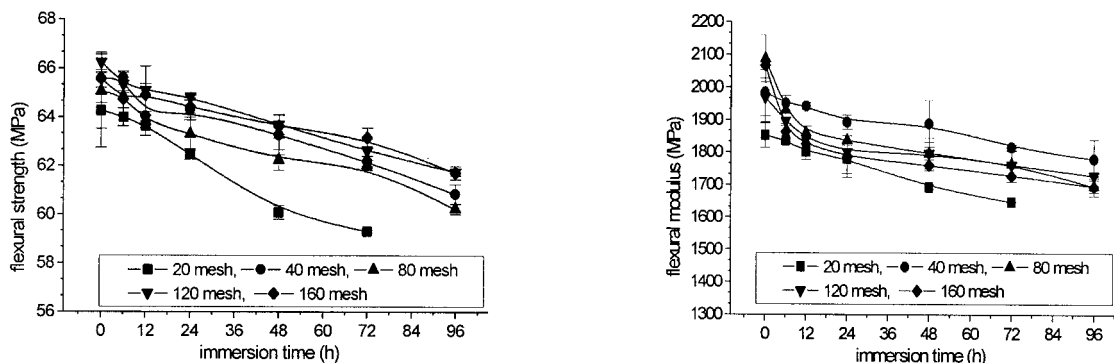


Figure 11 Flexural property of wood flour-filled PP composites containing wood flours of different mesh sizes. Wood flour content, 15%; interfacial treatment, 1% A-1100 + 5% MPP.

using MPP and A-1100 at the same time, which resulted in the higher wood flour strength. On the other hand, the penetration of a large amount of water into the composite led to a reduction in the fiber/matrix adhesion. The interfacial bonding strength of composites using A-1100 was lower than that using MPP because of the excess moisture absorption. Thus, the tensile strength of composites decreased in the following order: MPP-treated wood flour, A-1100 + MPP-treated wood flour, A-174-treated wood flour, A-1100-treated wood flour, and untreated wood flour.

Figure 9(a) and (b) show the tensile strength of composites containing different weight percentage fibers as a function of immersion time in 100 and 60°C water baths, respectively. At high fiber content, the tensile strength increased rapidly then decreased. However, the change in the tensile strength was steady in the case of low fiber content composites and at low temperature. This might be attributed to the fact that the degree of

moisture absorption at time t was dependent on temperature and wood flour content. The proper degree of moisture absorption was beneficial to the tensile strength because of the increment in the wood flour strength, although above this level the tensile strength decreased as a result of the serious reduction in the interfacial bonding strength.

Flexural Property

Figures 10 and 11 show the flexural strength and modulus of composites containing different weight percentages and different mesh sizes of wood flours as a function of immersion time at 100°C water immersion. Both the flexural strength and modulus decreased with prolonging the immersion time. Moreover, the decrease was sharper in the case of high fiber content composites and large-size wood flour composites. The modulus decreased more significantly than the

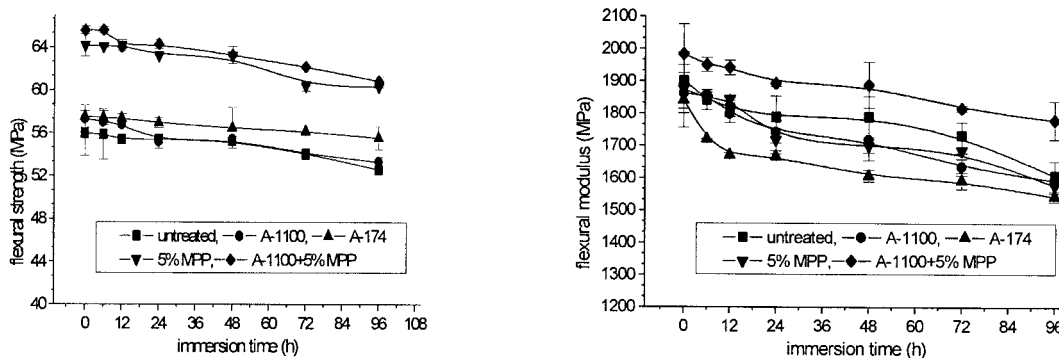


Figure 12 Flexural property of wood flour-filled PP composites with different interfacial treatments. Wood flour content, 15%; wood flour mesh size, 40 mesh.

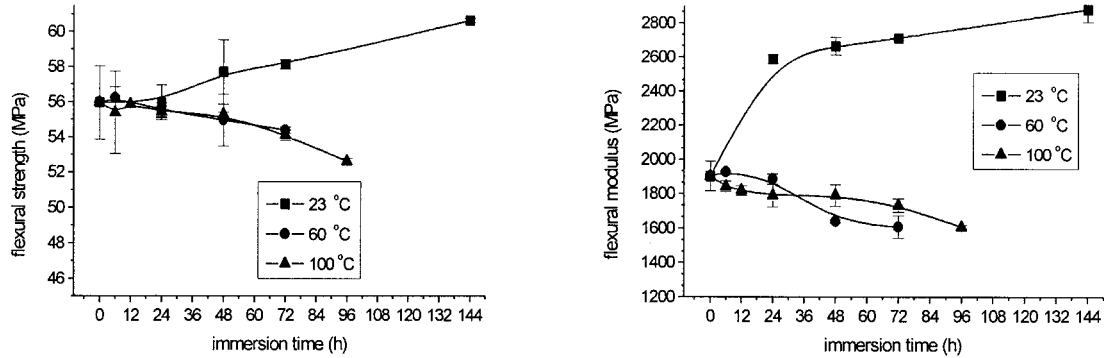


Figure 13 Flexural property of wood flour-filled PP composites immersed in water baths of different temperatures (wood flour untreated).

strength. In fact, because of the excessive moisture absorption the intermolecular hydrogen bonding in the cellulose fiber might be reduced by the formation of intermolecular hydrogen bonding between cellulose molecules and water molecules, thus leading to the deterioration of the modulus. The effect of interfacial adhesion on flexural property was significant, as seen in Figure 12. The stiffness of the cellulose fiber drops considerably after immersion in boiling water because of the softening of the desorbed zones of the cellulose microfibrils.^{22,23} A similar trend was observed at 60°C water immersion. However, the contrast trend was shown at room temperature because the interfacial debonding was less and the interfacial shear strength increased, as can be seen in Figures 13 and 14.

Impact Strength

Table I shows the notched charpy impact strength of composites. At ambient temperature, there was

no recrystallization of matrix. The moisture absorption increased slowly with immersion time. The swelling of wood fibers made it difficult to pull the fibers out of the matrix resin. Moreover, the moisture attack on the interface made the interfacial debonding easy. Thus, the impact strength increased with prolonging the exposure time. At 60 and 100°C water baths, the recrystallization of the matrix led to greater crystallinity, which increased the brittleness of the matrix resin. Thus, the extent of the increment in impact strength decreased with increasing the immersion temperature.

CONCLUSIONS

The degree of moisture absorption increased with the increase in immersion temperature and wood flour content. With the improvement in interfacial adhesion, the water absorption could be de-

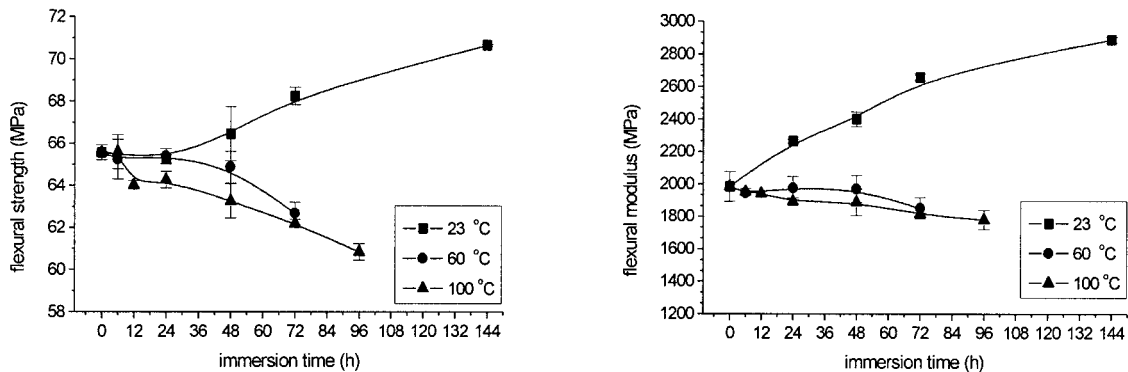


Figure 14 Flexural property of wood flour-filled PP composites immersed in water baths of different temperatures (wood flour treated with A-1100 and matrix added with MPP).

Table I Charpy Impact Strength of Composites Immersed in Water of Different Temperatures

Treatment Condition	Sample		
	A	B	C
	Treatment Method of Wood flour		
	Untreated	A-1100	A-1100
	Matrix Composition		
	PP	PP	PP + 5% MPP
	Notched Charpy Impact Strength (kJ/m ²)		
Nonimmersed	3.29 (0.53)	3.41 (0.52)	3.55 (0.63)
23°C, 6 h	3.42 (0.21)	3.47 (0.10)	3.60 (0.12)
23°C, 12 h	3.95 (0.53)	3.70 (0.11)	4.33 (0.32)
23°C, 420 h	4.60 (0.12)	4.71 (0.12)	4.91 (0.15)
60°C, 6 h	3.89 (0.19)	3.81 (0.44)	3.77 (0.11)
60°C, 120 h	3.64 (0.28)	3.72 (0.10)	3.93 (0.41)
60°C, 170 h	3.59 (0.10)	3.92 (0.20)	3.72 (0.10)
60°C, 240 h	3.80 (0.18)	3.89 (0.16)	3.78 (0.15)
100°C, 6 h	3.35 (0.10)	3.67 (0.13)	3.61 (0.29)
100°C, 12 h	3.43 (0.16)	3.55 (0.12)	3.66 (0.32)
100°C, 24 h	3.64 (0.18)	3.37 (0.09)	3.93 (0.10)
100°C, 72 h	3.36 (0.11)	3.50 (0.19)	3.57 (0.12)
100°C, 120 h	3.47 (0.11)	3.51 (0.06)	3.58 (0.30)
100°C, 240 h	3.66 (0.37)	3.46 (0.24)	3.61 (0.09)

creased. A similar result was obtained by decreasing the mesh size of wood flour, although the extent was limited with further decreases in mesh size.

The mechanical properties changed because of the hydrothermal environment. The tensile strength of all composites with wood flours of different contents, mesh sizes, and surface treatments increased after immersion in water baths of various temperatures, to a greater or lesser extent. The flexural strength and modulus followed a similar trend with immersion in water at ambient temperature; however, the contrary was true for composites when immersed in 60 and 100°C water baths. The impact strength increased after immersion in water at three temperatures, and the extent of such increment de-

creased with increasing the immersion temperature.

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