Long-Term Water Uptake Behavior of Natural Fiber/Polypropylene Composites

Mehdi Tajvidi,[1] Saeed Kazemi Najafi,[2] Nazanin Moteei[1]

[1]*Department of Wood and Paper Science and Technology, College of Natural Resources, University of Tehran, Karaj, Iran*
[2]*Department of Wood and Paper Science and Technology, College of Natural Resources and Marine Sciences, University of Tarbiat Modares, Noor, Iran*

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ABSTRACT: Composites of different natural fibers and polypropylene were prepared and their long-term water absorption behaviors were studied. Wood flour, rice hulls, newsprint fibers, and kenaf fibers (at 25 and 50% by weight contents) were mixed with polypropylene and 1 and 2% compatibilizer, respectively. Water absorption tests were carried out on injection-molded specimens at room temperature for 5 weeks. Measurements were made every week and water absorption was calculated. Water diffusion coefficients were also calculated by evaluating the water absorption isotherms. Results indicated a significant difference among different natural fibers, with kenaf fibers and newsprint fibers exhibiting the highest and wood flour and rice hulls the lowest water absorption values, respectively. The difference between 25 and 50% fiber contents for all composite formulations increased at longer immersion times. Water diffusion coefficients of the composites were found to be about 3 orders of magnitude higher than that of pure PP. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2199–2203, 2006

Key words: natural fibers; composites; polypropylene; water absorption; diffusion

INTRODUCTION

Natural fiber thermoplastic composites are becoming more and more commonplace by the development of new production techniques and processing equipment. Automotive, building, and residential applications are the main markets for the products of this industry.[1]

Compared with the traditional synthetic fibers, natural fibers present lower density, less abrasiveness, lower cost, and they are renewable and biodegradable.[2] The main disadvantage of these natural fiber/polymer composites seems to be the incompatibility between the hydrophilic natural fibers and the hydrophobic thermoplastic matrix that makes necessary the use of compatibilizers or coupling agents to improve the adhesion between the fiber and matrix.[3–6]

New applications and end uses of these composites for decking, flooring, and outdoor facilities, for example, and their exposure to atmosphere or contact with aqueous media have made it necessary to evaluate the water uptake characteristics of natural fiber thermoplastic composites. Because of the hygroscopic nature of natural fibers, water uptake of composites containing these fibers as fillers and/or reinforcement can be a limiting parameter as far as the final application of the composite is concerned. Water absorption could lead to a decrease in some of the properties and needs to be considered when selecting applications. It can also lead to a buildup of moisture in the fiber cell wall and in the fiber–matrix interphase region as well. Moisture buildup in the cell wall could result in fiber swelling and concerns regarding dimensional stability of the product. If necessary, the moisture absorbed in the fiber cell wall can be reduced through the acetylation of some of the hydroxyl groups present in the fiber.[7] Poor resistance of the fibers to water absorption can have undesirable effects on mechanical properties and dimensional stability, and in long-term, embrittlement linked to the degradation of the macromolecular skeleton by hydrolysis.[8]

Good wetting of the fiber by the matrix and adequate fiber–matrix bonding can decrease the rate and amount of water absorbed in the interphase region of the composite.[9] Water absorption behavior of natural fiber thermoplastic composites have been studied by a number of researchers and the effectiveness of the compatibilizer in reducing the amount and rate of water absorption has been well-documented.[10–12] Water uptake and water diffusion coefficient also increase with fiber content.[13–16] Mechanisms of water diffusion in natural fiber polypropylene composites have also been studied and the process of water absorption seems to follow the kinetics and mechanisms de-

Correspondence to: M. Tajvidi (mtajvidi@ut.ac.ir).

TABLE I
Composition of Evaluated Formulations (wt %)

Formulation	Fiber content (%)	Resin content (%)	Compatibilizer content (%)
PP	0	100	0
PP-WF-25	25	74	1
PP-WF-50	50	48	2
PP-KF-25	25	74	1
PP-KF-50	50	48	2
PP-RH-25	25	74	1
PP-RH-50	50	48	2
PP-NP-25	25	74	1
PP-NP-50	50	48	2

PP, polypropylene; WF, wood flour; KF, kenaf fiber; RH, rice hulls; NP, newsprint.

scribed by Fick's theory. Mechanical properties are also negatively affected by the absorbed water.[17]

Because of the wide range of natural fillers and fibers (wood and nonwood), study of the effect of fiber type and shape on water absorption behavior of natural fiber thermoplastic composites seems inevitable. The objectives of the present study were to investigate long-term water absorption behavior of various natural fiber polypropylene composites and to study the effect of different natural fiber types and contents on water absorption behavior.

MATERIALS AND METHODS

Materials

Polypropylene, Basell Pro-fax® PD702 homopolymer with a melt flow index of 35 g/10 min (230°C, 2.16 kg) and a density of 0.902 g/cm3, was used as the polymer matrix in this study. Wood flour, kenaf fibers, newsprint, and rice hulls were used as the discontinuous phase (filler and/or reinforcement) in the composites. Wood flour was 40-mesh maple flour and was supplied by American Wood fibers (Schofield, WI). Kenaf fibers were supplied by Kengro (Charleston, MS). Rice hulls were 20–80 mesh ground rice hulls and were supplied by Riceland Foods (Stuttgart, AR). Newsprint fibers were obtained by grinding old newspapers, in our laboratory. MAPP (maleic anhydride polypropylene) was UNITE® MP and was supplied by Aristech Chemical (Pittsburgh, PA).

Composites preparation

Polymer, natural fibers, and the compatibilizer (MAPP) were initially weighed and bagged according to the various fiber contents indicated in Table I. They were then mixed in the proprietary mixing equipment of Teel Global Resources (Baraboo, WI). The compounded materials were then ground using a pilot scale grinder to prepare the granules.

Preparation of the specimens

The granules were then injection molded to produce standard ASTM specimens. Injection molding was performed using a 33 ton Cincinnati Milacron 32-mm reciprocating screw injection molder with an L/D ratio of 20 : 1. Mold temperature was 37.8°C, and barrel and nozzle temperature were set to 187.8°C. Specimens for water absorption testing were cut out of the ASTM specimens, using a table saw. Cut sides of the specimens were finished with no. 0 sandpaper to eliminate any surface roughness that may lead to errors in measurements.

Water absorption tests

Water absorption tests were carried out according to ASTM D-570 specification. Three specimens of each formulation were selected and dried in an oven for 24 h at 105°C. The dried specimens were then weighed to a precision of 0.001 g and were placed in distilled water and kept at room temperature for 24 h. After 24 h, they were removed from the water and the surface water was wiped off using blotting paper and the equilibrium weight value was determined. Results are presented as percent water absorption in relation with the dry weight of the specimens. After weighing the specimens were placed in the water again and kept at room temperature for a week. Weighing was repeated as described above after the 1-week period. The same procedure was followed for 5 weeks at 1-week intervals and water absorption values were determined at the end of each week.

Calculation of water diffusion coefficient

Water absorption values were plotted versus root time/thickness values and the gradient of the linear portion of the curves (m) were determined. Water diffusion coefficients of all formulations were then calculated using the following formula[14]:

$$D = \pi\left[\frac{mh}{4M_\infty}\right]^2\left[1 + \left(\frac{h}{L}\right) + \left(\frac{h}{n}\right)\right]^2 \qquad (1)$$

where D is the water diffusion coefficient corrected for edge effect; m, the gradient of linear portion of the water content against root time/thickness curve; M_∞, the equilibrium moisture content, which is the value of the water absorbed such that there is no further change in the water absorption with time; h, the thickness; L, the length; and n is the width.

Statistical analysis

The collected data have been statistically analyzed in a completely randomized design and Duncan's Multi-

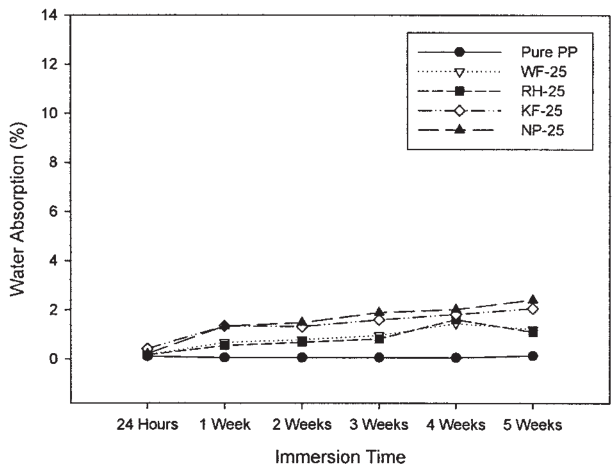

Figure 1 Water absorption curves for PP composites with different natural fibers at 25% fiber content.

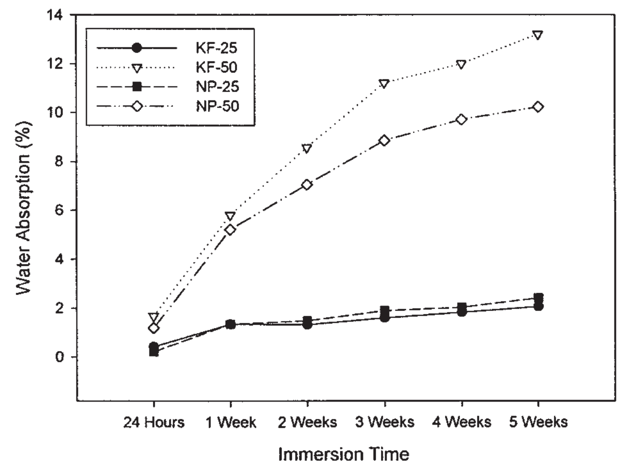

Figure 3 Effect of fiber content on the water absorption of KF/PP and NP/PP composites.

ple Range Test was used for grouping the means. All comparisons have been made at 95% confidence level.

RESULTS AND DISCUSSION

Figures 1 and 2 illustrate the water absorption curves of different composites at 25 and 50% fiber contents, respectively. The curve for pure PP is also presented for comparison. Generally, water absorption increases with immersion time. At 25% fiber content, very little discrepancies can be observed among different fibers. No significant difference was observed among different fibers themselves or between fibers and pure PP at each immersion time. However, statistical analysis has indicated that the water absorption of newsprint composites is significantly higher than that of pure PP. At 50% fiber content, most of the composites are significantly different regarding their water uptake behavior. The composites with kenaf and newsprint fibers exhibit higher water absorption as compared with wood flour and rice hulls. Kenaf fiber composites exhibit the highest water absorption values all over the immersion time studied in this project. The lowest water absorption was observed for rice hulls. All composites are significantly different from each other and pure PP as far as their water uptake is concerned. At 25% fiber content, the maximum water uptake was observed about 2% for newsprint whereas this was about 13% for 50% kenaf fiber composite.

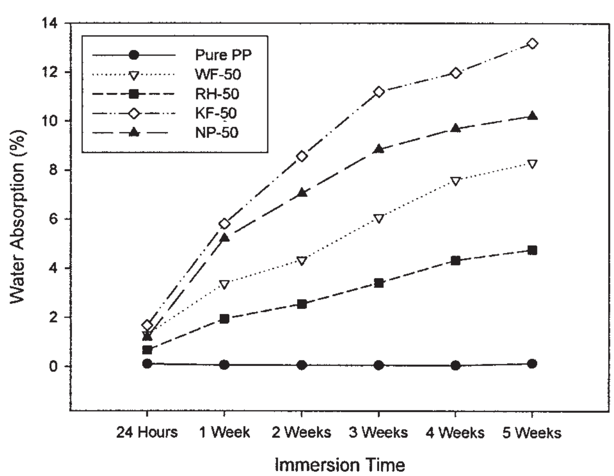

Figure 2 Water absorption curves for PP composites with different natural fibers at 50% fiber content.

The hydrophilic nature of natural fibers is responsible for the water absorption in composites. (The matrix had negligible water absorption as indicated by pure PP curve.) In addition to the different hydrophilic nature of lignocellosics, the shape of fiber (flour or fiber) could affect the water absorption as well.

Chemical composition of natural fibers can explain the differences observed in their water uptake behavior. It appears that the RH/PP has the lowest water absorption. This behavior can be attributed to high amount of extractives and ash and lower amount of cellulose and pentose in rice hulls.[18]

Kenaf fibers are rich in cellulose and hemicelluloses, and they posses low lignin content. Hence, their higher water absorption can be explained by the higher amount of cellulose and pentosan and lower amount of lignin.[18]

One of the major findings of this study was the fact that the water absorption of the composites containing 50% fiber tended to increase even up to 5 weeks immersion and that none of the composites could reach to saturation point. This is very interesting and suggests that the choice of natural fibers, especially at higher fiber contents, should be made with great care if they are to be used in outdoor environments.

Figures 3 and 4 comparably show the water absorption of different composites at 25 and 50% fiber con-

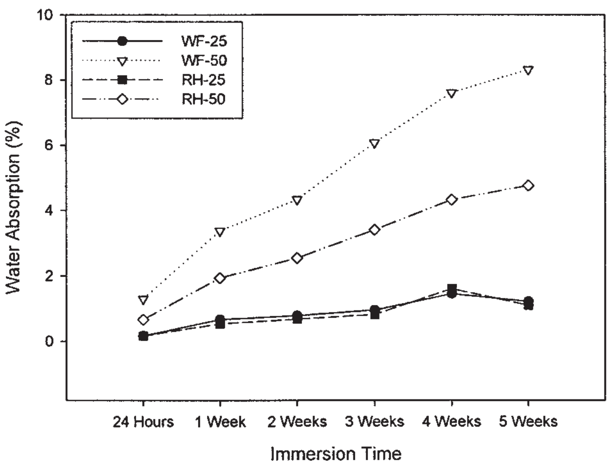

Figure 4 Effect of fiber content on the water absorption of WF/PP and RH/PP composites.

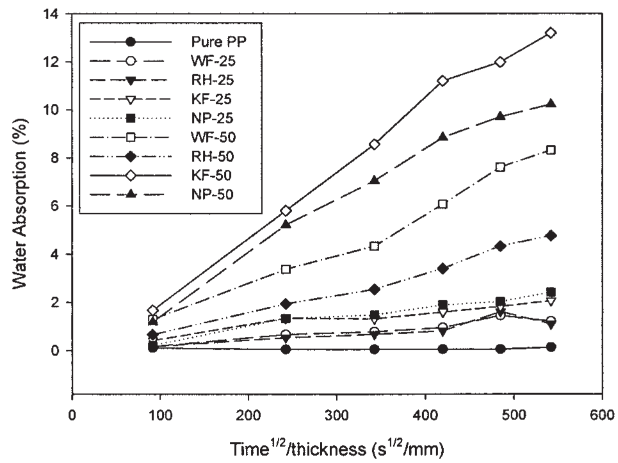

Figure 5 Water absorption isotherms for all composites and pure PP.

tents. As it can be seen, the higher fiber content, the higher water absorption. The difference between water absorption at 25 and 50% fiber content is not the same for all types of fibers, especially at higher immersion times. This difference is higher for kenaf fibers than those of newsprint, wood flour, and rice hulls, respectively.

Figures 3 and 4 also illustrate that the water absorption increases slowly over the time at 25% fiber content. However, at 50% fiber content, the increment rate of water absorption is not the same. For kenaf fibers, water absorption increases very rapidly (Fig. 3) whereas rice hulls present the lowest increment rate (Fig. 4). In fact, for all fibers the water absorption curves of 25 and 50% fiber diverge from each other at longer immersion times. Because of the hydrophilic nature of natural fibers, higher fiber content leads to higher amount of absorbed water.

Water absorption isotherms of the studied composites and pure PP are presented in Figure 5 where composites with 50% fiber content exhibit the highest rate of water absorption. Among various fibers, kenaf fibers resulted in the highest water absorption rate whereas rice hulls composites presented the lowest rate.

The gradients of the linear portion of these curves have been used to calculate the water diffusion coefficient using eq (1). The results are presented in Table II. The lowest water absorption coefficient corresponds to pure PP and all composites exhibit considerably (around 3 orders of magnitude) higher values. An interesting point that could be made is that although higher fiber content has resulted in higher water absorption and higher water absorption rate, water diffusion coefficient is higher for 25% wood flour and rice hulls as compared with the same composites with 50% fiber content. This is due to the form of eq. (1), in which the maximum water absorption is in the denominator, which in turn leads to a lower water diffusion coefficient.

CONCLUSIONS

Long-term water absorption behavior of natural fiber reinforced polypropylene composites were studied in this research and the following conclusions can be drawn from the results and discussions presented above.

1. Fiber type affects the amount of water absorption. RH/PP and KF/PP composites exhibited the minimum and maximum water absorption, respectively. The hydrophilic nature of natural fibers is responsible for the water absorption in such composites.
2. Fiber content had a significant effect on water absorption. Higher contents resulted in higher water absorption. This is due to the fact that the hydrophilic lignocellulosic fraction in composite increases by increasing fiber content.

TABLE II
Maximum Water Absorption and Water Absorption Coefficients for Different Formulations

Formulation	Maximum water absorption (%)	Water diffusion coefficient (mm^2 S^{-1})
PP	0.14	1.398 E −08
PP-WF-25	1.21	1.618 E −05
PP-WF-50	8.32	1.330 E −05
PP-KF-25	2.06	9.391 E −06
PP-KF-50	13.19	1.420 E −05
PP-RH-25	1.10	2.052 E −05
PP-RH-50	4.76	1.350 E −05
PP-NP-25	2.41	1.262 E −05
PP-NP-50	10.22	1.430 E −05

3. The effect of fiber content on water absorption is more pronounced at higher soaking times.
4. At higher fiber contents, composite could not reach to saturation point within 5 weeks immersion in water.
5. Water diffusion coefficients of the composites were about 3 orders of magnitude higher than pure PP.

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