Long-Term Water Uptake Behavior of Lignocellulosic-High Density Polyethylene Composites

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ABSTRACT: Composites of different lignocellulosic materials and high-density polyethylene were prepared and their long-term water absorption behaviors were studied. Wood flour, rice hulls, newsprint fibers, and kenaf fibers were mixed with the polymer at 25 and 50 wt % fiber contents and 1 and 2% compatibilizer, respectively. Water absorption tests were carried out on injection-molded specimens at room temperature for five weeks. 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. Very little difference was observed between kenaf fiber and newsprint composites and between rice hulls and wood flour composites regarding their water uptake behavior. The difference between 25 and 50% fiber contents for all composite formulations increased at longer immersion times, especially for the composites with higher water absorption. Kenaf fiber composites containing 50% kenaf fibers exhibited the highest water diffusion coefficient. A strong correlation was found between the water absorption and holocellulose content of the composites. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3907–3911, 2006

Key words: natural fibers; composites; high-density polyethylene; water absorption

INTRODUCTION

Natural fiber thermoplastic composites are a relatively new family of composite materials. In such composites, a natural fiber/filler (such as kenaf fiber, wood fiber, hemp, sisal etc.) is mixed with a thermoplastic (e.g., polyethylene, polypropylene, PVC etc.) to produce the composite. 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.

Among different thermoplastics currently used for the production of natural fiber plastic composites, polyethylene is the most frequently used one, thanks to its lower melting point, wide availability, and lower cost.[1] Compared with the traditional synthetic fibers, natural fibers possess lower density, less abrasiveness, lower cost, and they are renewable and biodegradable. Moreover, their mechanical performance can be compared to that of synthetic fibers nowadays used and they have good thermal properties.[2] The fact that they are fibers obtained directly from natural resources makes them even more attractive in terms of sustainability and environmental concerns. However, the main disadvantage of these 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 and to decrease their potential moisture absorption.[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 has 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 is one of the important characteristics of natural fiber polymer composites that determine their end use applications. It could lead to a decrease in some of the properties and needs to be considered when selecting applications. Water absorption in lignocellulosic-based composites could cause a buildup of moisture in the fiber cell wall and also in the fiber–matrix interphase region. Moisture buildup in the cell wall could result in

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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] However, this requires additional costs. 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 authors 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.[17]

In a previous study, long-term water absorption behavior of polypropylene (PP)-based natural fiber composites has been studied.[18] The investigation of long-term water absorption behavior of various natural fiber high-density polyethylene composites and the study of the effect of different natural fiber types and contents on their water absorption is the main focus of the present study.

MATERIALS AND METHODS

Materials

High-density polyethylene (HDPE) was Chevron HiD® 9035 with a melt flow index of 40 g/10 min (190°C, 2.16 kg) and a density of 0.952 g/cm^3. 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. The average kenaf fiber length in the composites was microscopically measured to be 1.168 mm with a standard deviation of 0.42 mm. 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 the laboratory. They had an average length of 1.1 mm. MAPE (Maleic anhydride polyethylene) was Fusabond® C modified polyethylene (product MB-100D) and was supplied by DuPont Industrial Corporation.

Composites preparation

Polymer, natural fibers and the compatibilizer (MAPE) 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.

TABLE I
Composition of Evaluated Formulations (wt %)

Formulation	Specimen	Fiber content (%)	Resin content (%)	Compatibilizer content (%)
1	PE	0	100	0
2	PE-WF-25	25	74	1
3	PE-WF-50	50	48	2
6	PE-KF-25	25	74	1
7	PE-KF-50	50	48	2
8	PE-RH-25	25	74	1
9	PE-RH-50	50	48	2
10	PE-NP-25	25	74	1
11	PE-NP-50	50	48	2

PE, high-density polyethylene; WF, wood flour; KF, kenaf fiber; RH, rice hulls; NP, newsprint.

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 93.3°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, which 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 after 24 h soaking in water at room temperature. 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 up to five weeks. Weighing was repeated as described above at 1-week intervals.

Water absorption values were plotted versus root time/thickness values and the gradient of the linear portion of the curves (m) were determined. These were

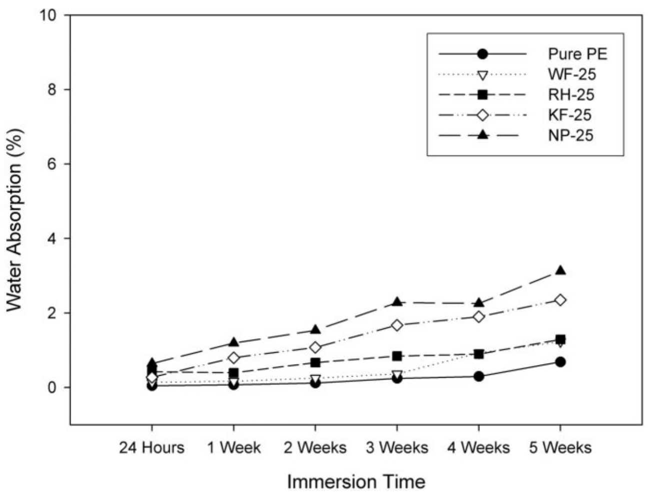

Figure 1 Water absorption curves for PE composites with different natural fibers at 25% fiber content.

only used as an index for comparing the water absorption rate over time in different composites because no equilibrium was reached after 5-weeks immersion in water. Hence the values of water diffusion coefficients could not be calculated.

Determination of the chemical composition of the lignocellulosics

Acid-insoluble lignin, α-cellulose, pentosans, and ash content of the lignocellulosics were determined according to ASTM D-1106, D-1103, and D-1102 specifications, respectively.

Statistical analysis

The collected data have been statistically analyzed in a completely randomized design and Duncan's multiple range test was used for grouping the means. All comparisons have been made at 95% confidence level.

RESULTS AND DISCUSSION

Water absorption curves of different composites at 25 and 50% fiber contents, are illustrated in Figures 1 and 2, respectively. The curve for pure PE is also presented for comparison. As it is clearly seen, generally water absorption increases with immersion time. At 25% fiber content, very little discrepancies can be observed among different fibers. Statistical analysis proved that after 24 h immersion in water, only newsprint composite exhibited a significant difference from pure PE whereas the water absorption of other composites was not significantly different from each other or pure PE. After one week, no significant difference was observed between the water absorption of rice hulls and wood flour or between newsprint and kenaf fiber composites. Composites containing newsprint fibers also had a water absorption value significantly different from those of rice hulls and wood flour composites as well as pure PE. The same behavior was observed after 3, 4, and 5 weeks of immersion with newsprint fibers being significantly different from other fibers. At 50% fiber content, the composites with kenaf and newsprint fibers exhibited higher water absorption as compared with wood flour and rice hulls. While the water absorption of newsprint and kenaf fiber composites was not significantly different, these two composites were significantly different from rice hulls and wood flour composites. This was true for all immersion times. At 50% fiber content, all composites were significantly different from pure PE as far as their water uptake was concerned. At 25% fiber content, the maximum (5 weeks) water uptake was observed to be about 3% for newsprint composites whereas this was about 9% for 50% kenaf fiber and newsprint composites.

Figures 3 and 4 comparatively show the water absorption of different composites at 25 and 50% fiber contents. As it can be seen, the higher the fiber content, the higher the water absorption. The difference between water absorption at 25 and 50% fiber content was not the same for all types of fibers especially at higher immersion times. This difference for kenaf fibers was higher than those of newsprint, wood flour, and rice hulls, respectively.

Figures 3 and 4 also illustrate that the water absorption increased slowly over the time at 25% fiber content. However, at 50% fiber content, the increment rate of water absorption was not the same. For kenaf and newsprint fibers, water absorption increased very rapidly (Fig. 3) while rice hulls and wood flour presented the lowest increment rate (Fig. 4). In fact, for all fibers the water absorption curves of 25 and 50% fiber di-

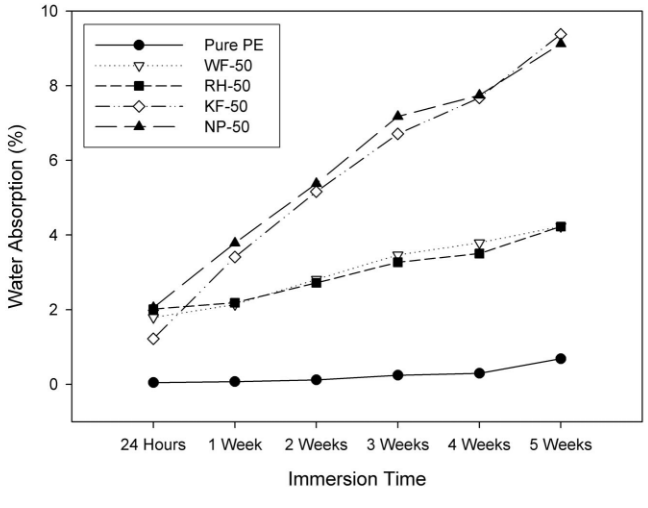

Figure 2 Water absorption curves for PE composites with different natural fibers at 50% fiber content.

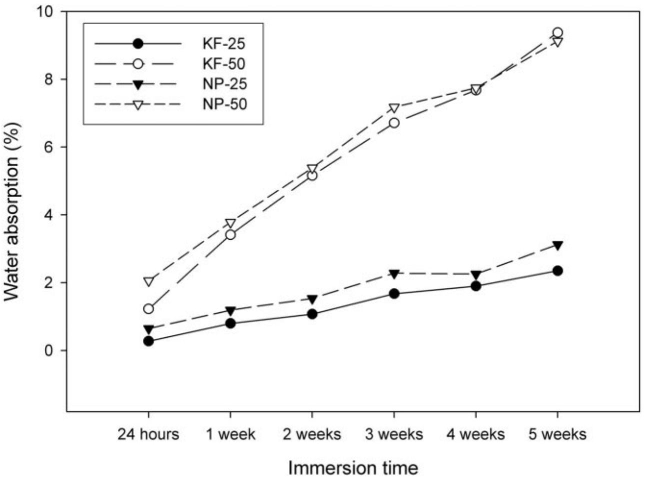

Figure 3 Water absorption curves for KF/PE and NP/PE composites at 25 and 50% fiber contents.

verged 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.

The hydrophilic nature of natural fibers is responsible for the water absorption in composites (The matrix had negligible water absorption as indicated by pure PE curve). In addition to the different hydrophilic nature of lignocellulosics, 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. Table II presents the chemical compositions of different fibers/fillers used in the studied composites.

TABLE II
Chemical Composition of Different Natural Fibers Used in the Studied Composites

Lignocellulosic type	α-Cellulose (%)	Lignin (%)	Pentosans (%)	Ash (%)
Kenaf fiber	34	10.5	22	0.1
Wood flour	45	22	17	0.2
Newsprint	45	28	10	0.2
Rice hulls	28	12.5	21	17

It appears that the RH/PE composite exhibited the lowest water absorption. This behavior can be attributed to high amount of and ash and lower amount of cellulose in rice hulls. Kenaf fibers are rich in cellulose and pentosans and they posses low lignin content. Hence, their higher water absorption can be explained by the higher amount of cellulose and pentosans and lower amount of lignin. Newsprint fibers have a rougher surface due to the refining process performed on them, which could be a reason for their higher water absorption.

Of all constituents making up the composites, cellulose and hemicelluloses are the ones with the highest water absorption.[19] In an attempt to evaluate the effect of these portions of the composites on their maximum (5 weeks) water absorption, the total amount of holocellulose (cellulose plus hemicelluloses) in each composite formulation was calculated and plotted against water absorption. The result is presented in Figure 5 where a relatively significant relationship can be observed. The coefficient of determination (R^2) was calculated to be equal to 0.58. An R^2 of 0.58 means that 58% of the variations in water absorption can be explained by variations of holocellulose content.

Water absorption isotherms of the studied composites and pure PE are presented in Figure 6 where composites with 50% fiber content exhibit the highest rate of water absorption. Among various fibers, kenaf

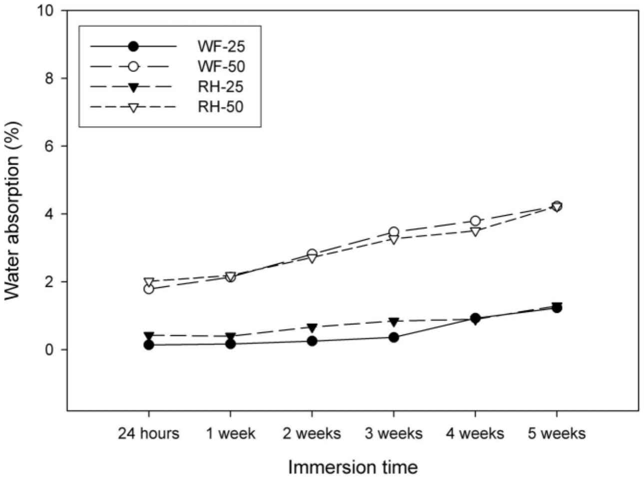

Figure 4 Water absorption curves for WF/PE and RH/PE composites at 25 and 50% fiber contents.

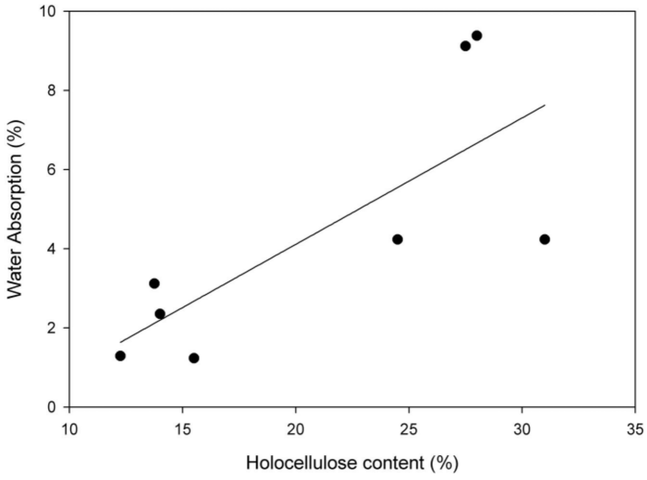

Figure 5 Correlation between holocellulose content and maximum water absorption of different composites.

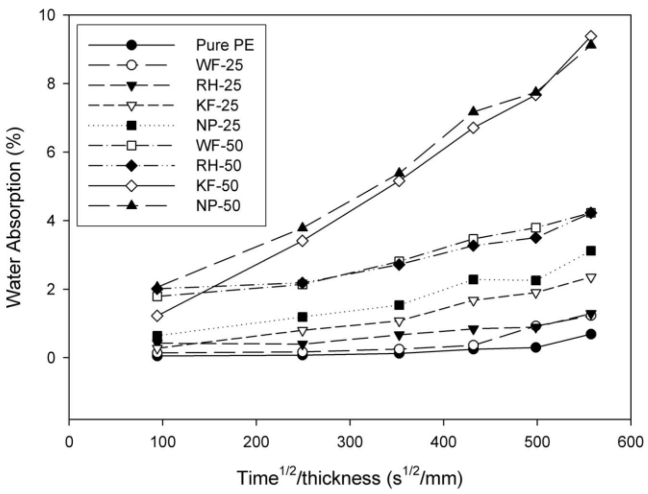

Figure 6 Water absorption isotherms for all composites and pure PE.

fibers and newsprint resulted in the highest water absorption rates whereas rice hulls and wood flour composites presented the lowest rate. As mentioned earlier, none of the composites reached equilibrium after 5-weeks immersion in water. Such a phenomenon has also been reported by Stark et al.[20] where injection-molded specimens continued to absorb water even after 12-weeks immersion. This can be due to the fact that injection-molded specimens have a thin plastic coating all around them, which results in lower water absorption at a slower pace.

CONCLUSIONS

Long-term water absorption behavior of lignocellulosic-reinforced HDPE composites was studied in this research and the following conclusions can be drawn from the results and discussions presented above.

- Fiber type affects the amount of water absorption. RH/PE and WF/PE composites exhibited minimum and KF/PE and NP/PE exhibited maximum water absorptions, respectively. The hydrophilic nature of natural fibers and shape of filler (flour or fiber) are responsible for the water absorption in such composites.
- 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.
- The effect of fiber content on water absorption is more pronounced at higher soaking times.
- A strong correlation was observed between the total fraction of cellulose and hemicelluloses in the composites and their water absorption.
- None of the studied composites reached an equilibrium water content after 5-weeks immersion in water. Hence, water diffusion coefficients could not be calculated. However, water uptake rate was highest for kenaf fiber and newsprint composites containing 50% fiber.

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