

Esterification Effect of Maleic Anhydride on Swelling Properties of Natural Fiber/High Density Polyethylene Composites

J. B. Naik,¹ S. Mishra²

¹Department of Chemical Technology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431 004, India

²Department of Chemical Technology, North Maharashtra University, Jalgaon 425 001, India

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ABSTRACT: The natural fibers (banana, hemp, and sisal) and high density polyethylene were taken for the preparation of natural fiber/polymer composites in different ratios of 40 : 60 and 45 : 55 (w/w). These fibers were esterified with maleic anhydride (MA) and the effect of esterification of MA was studied on swelling properties in terms of absorption of water, at ambient temperature, and steam. It was found that the steam penetrates more within lesser period of time than water at ambient temperature. Untreated fiber composites show more absorption of steam and water in comparison to MA-treated fiber composites. The more absorption of water was found in hemp fiber

composites and less in sisal fiber composites. Steam absorption in MA-treated and untreated fiber composites are higher than the water absorption in respective fiber composites. The natural fiber/polymer composites containing low amount of fibers show less absorption of steam and water at ambient temperature than the composites containing more amount of fibers in respective fiber composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 2571–2574, 2007

Key words: natural fiber polymer composites; HDPE; banana; hemp; sisal; fibers; absorption; steam; water; maleic anhydride

INTRODUCTION

The natural fibers such as jute, flax, and kenaf used as reinforcing fibers are able to satisfy economical as well as ecological interests, while their low cost and high performance are able to fulfill the economic interest of industries. One of the physical properties of these natural fibers is their hydrophilic characteristic. The hydrophilic lignocellulosic fibers do not adhere well to the hydrophobic thermoplastics used as matrix materials.^{1–3} The adsorption and desorption of water in wood is accompanied by volume changes. In fact, changes in volume or shape may occur because of the development of the moisture gradients and stresses.⁴ Normal wood/polymer composite contains polymer only in void spaces and little, if any, in the cell walls and the result is the lowering in rate of water vapor diffusion into the cell walls.⁵

Caesar et al.⁶ studied the swelling of medium density fiber (MDF) board from oil palm fiber by varying the amount of fiber. George and Ramakrishnan⁷ have also studied the swelling properties of rice husk particleboard and found that the swelling property decreases with increase in density of particleboard.

Okubayashi et al.⁸ studied the kinetics of dynamic water vapor sorption and desorption on viscose, modal, cotton, wool, and polyester fibers. He found that, according to the parallel exponential kinetics (PEK) model, the total equilibrium moisture regain in all the materials decreases with increasing temperature.

In our earlier work, we have studied^{9–12} the effect of absorption of steam and water at ambient temperature on natural fiber/polymer composites with and without treatment of maleic anhydride (MA). In those studies, it was found that the steam penetration is more than the water in respective fiber composites. In the present work, MA is used as a compatibilizer for HDPE/natural fibers (banana, hemp, and sisal) composites and the absorption of steam and water at ambient temperature is studied on MA-treated and untreated natural fibers/HDPE composites.

EXPERIMENTAL

Preparation of natural fiber/polymer composites

Banana, hemp, and sisal fibers were obtained from the raw material by the process of retting.⁹ The fibers obtained were washed with water and dried in sunlight. These fibers further dried in oven and cut into 2.0–2.5 mm in length. These fibers were esterified by 2% maleic anhydride (MA) in xylene keeping fiber solvent ratio 1 : 20 (w/v). The soaking of MA was

Correspondence to: J. B. Naik (jitunaik@japs.com).

allowed for 18 h at 65°C. The fibers were filtered out and dried in oven at 60°C till constant weight of fibers. PILENE HDPE PF 4577F is used for the preparation of natural fibers/polymer composites. This sample was obtained from National Organic Chemicals (NOCIL), Mumbai. Selected fiber and HDPE (40 : 60 and 45 : 55, w/w) were mixed on a two-roll mill at (165 ± 5)°C for about 10 min. The mixture of fiber and resin was then cooled and molded to 2-mm thick sheets in a compression-molding machine. The molding was carried out at (165 ± 5)°C for 4 min, employing pressure in the sequence of 4.8, 9.8, 14.7, and 19.6 MPa with a duration of 1 min each. The mold was then cooled under pressure by circulating cold water and the molded sheet was ejected from the mold after releasing the pressure.

Swelling properties

Water absorption

The samples (20 × 10 × 2 mm³ size) were taken for absorption of water for 2–30 h. First the initial weights of samples were taken and the samples were immersed in a beaker containing distilled water. The percentage absorption of water was calculated at different periods of time, using following equation

$$\% \text{ Water absorption} = \frac{W_i - W_n}{W_n} \times 100$$

where W_n , weight of sample before water absorption; n , time (h), 0, 2, 6, 12, 18, 24 respectively; W_i , weight of sample after water absorption; and (time) $i = 2, 6, 12, 18, 24, 30$ respectively.

Steam absorption

The samples (20 × 10 × 2 mm³ size) were taken for absorption of steam for 2–30 h. First the initial weights of samples were taken and the samples were tied with thread and hanged over the steam bath. At every respective period of time, the samples were taken out from the steam. The steam from the surface of sample was removed by blotting paper and then weight of sample was taken for finding the percentage absorption of steam, using following equation

$$\% \text{ Steam absorption} = \frac{W_i - W_n}{W_n} \times 100$$

where W_n , weight of sample before steam absorption; $n =$ time (h), 0, 2, 6, 12, 18, 24 respectively; W_i , weight of sample after steam absorption; and (time) $i = 2, 6, 12, 18, 24, 30$ respectively.

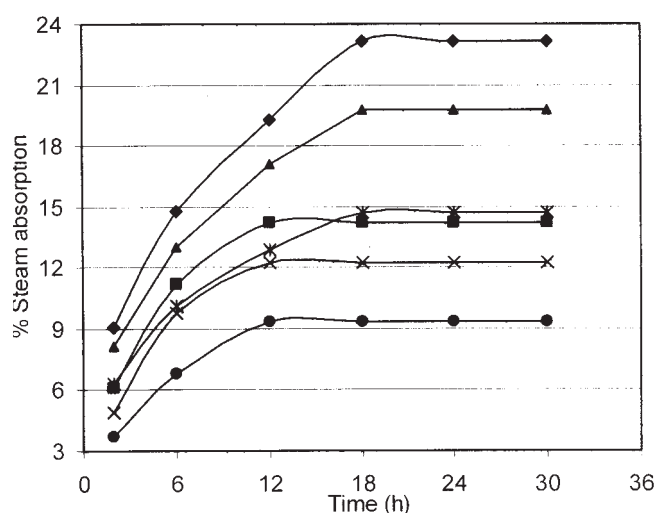


Figure 1 Effect of absorption of steam on hemp, banana, and sisal fiber/high density polyethylene (HDPE) composites (45 : 55, w/w) with and without treatment of maleic anhydride. ♦ untreated hemp fiber; ■ maleic anhydride-treated hemp fiber; ▲ untreated banana fiber; × maleic anhydride-treated banana fiber; * untreated sisal fiber; ● maleic anhydride-treated sisal fiber.

RESULTS AND DISCUSSION

Absorption of steam by MA-treated and untreated fiber/HDPE composites (45 : 55, w/w)

Figure 1 shows the results of absorption of steam in MA-treated and untreated banana, hemp, and sisal fiber (45 : 55, w/w) composites. More absorption of steam is obtained in untreated hemp fiber composite and lesser absorption in MA-treated sisal fiber composite. The absorption of steam increases with increase in time up to 18 h in untreated fiber composites. The absorption of steam becomes constant after 18 h. Banana, hemp, and sisal fiber, treated with MA, are employed for steam absorption for the same period of time. The absorption of steam increases with increase in time up to 12 h in all these fiber composites and absorption becomes constant after respective period of time. The MA-treated fiber composites show very less absorption of steam with respect to untreated fiber composites, except untreated sisal fiber composite, which shows lesser absorption of steam than the MA-treated hemp fiber composite.

On comparison with untreated and MA-treated hemp fiber composites, the absorption of steam at 2 h in untreated fiber is 3% more than the MA-treated fiber composite. Further, the difference in absorption of steam increases with increase in time and more difference is obtained at 18 h. In the same way, absorption of steam increases with increase in time for MA-treated and untreated banana fiber composites. However, the same difference is observed at

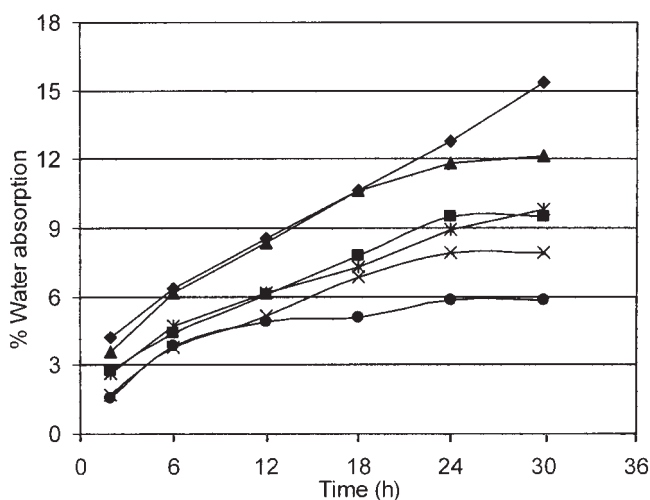


Figure 2 Effect of absorption of water at ambient temperature in hemp, banana, and sisal fiber/high density polyethylene (HDPE) composites (45 : 55, w/w) with and without treatment of maleic anhydride. ◆ untreated hemp fiber; ■ maleic anhydride-treated hemp fiber; ▲ untreated banana fiber; × maleic anhydride-treated banana fiber; * untreated sisal fiber; ● maleic anhydride-treated sisal fiber.

2 h like hemp fiber composite and further this difference increases up to 10.0% and becomes constant after 18 h. Like banana and hemp fiber, the untreated and MA-treated sisal fiber composites show the wide difference in absorption of steam at 2 h and further the difference in absorption of steam increases up to 5.0% and becomes constant.

Absorption of water at ambient temperature by MA-treated and untreated fiber/HDPE composites (45 : 55, w/w)

The HDPE and banana fiber (45/55, w/w) composite is taken for the study of absorption of water for 2–30 h at ambient temperature. It is observed from Figure 2 that the absorption of water increases with increase in time in banana fiber composite. Now, we consider the results of rate of absorption of water at ambient temperature in banana, hemp, and sisal fiber/HDPE composites at different times. The low value (3.6%) of absorption of water in untreated banana fiber composite is recorded at 2 h and high value (12.2%) of absorption of water is observed at 30 h. The rate of absorption of water is high at 2 and 6 h, and it decreases thereafter. The rate of absorption is more or less equal from 12 to 24 h. The MA-treated banana fiber/HDPE composite is taken for water absorption for the same period of time. About 1.7% absorption of water is observed at 2 h and a high value of 7.9% is recorded at 24 h. Beyond 24 h the absorption becomes constant. The rate of absorption of water in MA-treated banana fiber composite is constant from 6 to 30 h.

Figure 2 illustrates the results of hemp fiber/HDPE composites with and without treatment of MA. Like banana fiber, the absorption of water at ambient temperature increases with increase in time in MA-treated and untreated hemp fiber composites. On comparing the absorption of water in MA-treated and untreated fiber composites, it is observed that at 2 h the difference in absorption of water is very less and this difference increases with increase in absorption of water up to 30 h. It is also observed that the rate of water absorption in MA-treated hemp fiber composite is more or less equal from 6 to 12 h and 18 to 24 h. Like banana and hemp fiber, the sisal fiber is also treated with and without MA and further composites made from this fiber are employed for water absorption from 2 to 30 h. From the results, it is found that the untreated sisal fiber composite shows more absorption than MA-treated sisal fiber composite. Untreated sisal fiber shows more rate of water absorption at 2 h, while MA-treated shows more rate of water absorption at 6 h.

Absorption of steam by MA-treated and untreated fiber/HDPE composites (40 : 60, w/w)

Figure 3 shows the results of absorption of steam in untreated and MA-treated banana, hemp, and sisal fiber/HDPE (40 : 60, w/w) composites. The absorption of steam increases with increase in time up to 12 h in all these fiber composites; beyond this period of time, no absorption of steam is found. The MA-treated fiber composites show very less absorption of steam with respect to untreated fiber composites,

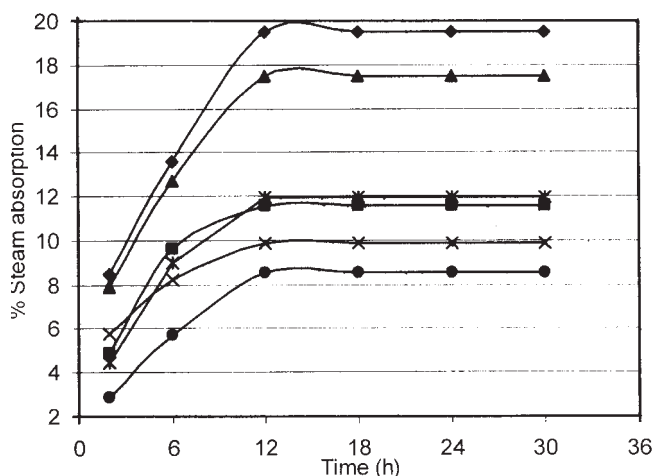


Figure 3 Effect of absorption of steam on hemp, banana, and sisal fiber/high density polyethylene (HDPE) composites (40 : 60, w/w) with and without treatment of maleic anhydride. ◆ untreated hemp fiber; ■ maleic anhydride-treated hemp fiber; ▲ untreated banana fiber; × maleic anhydride-treated banana fiber; * untreated sisal fiber; ● maleic anhydride-treated sisal fiber.

except untreated sisal fiber composite, which shows lesser absorption of steam at 2 h than the MA-treated hemp and banana fiber composites. On comparison of untreated and MA-treated natural fiber composites, it is observed that the absorption of steam in untreated banana and hemp fiber composites is twice that of the MA-treated respective fiber composites.

Absorption of water at ambient temperature by MA-treated and untreated fiber/HDPE composites (40 : 60, w/w)

The results of water absorption in composites of banana, hemp, and sisal fiber with HDPE (40 : 60, w/w) exhibit that the untreated sisal fiber composite absorbs less amount of water among the untreated and MA-treated respective fiber composites for the period of 2–30 h at ambient temperature (Fig. 4). It is also observed that the absorption of water in MA-treated banana and hemp fiber composites is more or less equal from 2 to 18 h, while untreated and MA-treated sisal fiber composites show equal amount of water absorption at 6 h.

Absorption of water is much less in comparison with absorption of steam, because water cannot penetrate the resin matrix as much as steam can. The absorption of water by different fiber-based composites is largely dependent on the availability of free —OH groups on the surface of the reinforcing fiber. On MA treatment, some of these —OH groups are esterified, and, due to that, the absorption of water

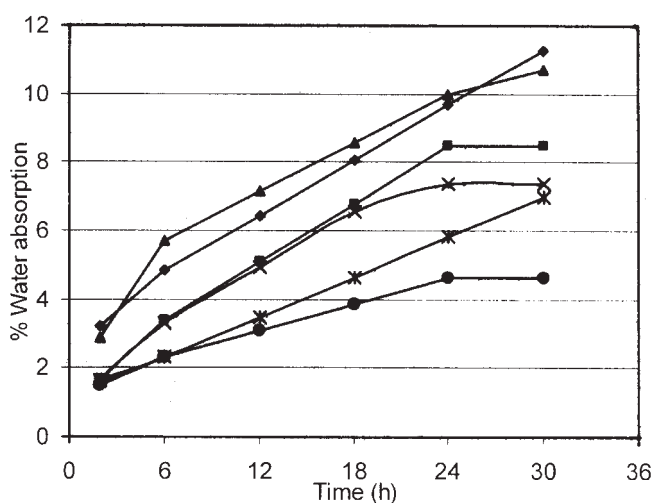


Figure 4 Effect of absorption of water at ambient temperature in hemp, banana, and sisal fiber/high density polyethylene (HDPE) composites (40 : 60, w/w) with and without treatment of maleic anhydride. ◆ untreated hemp fiber; ■ maleic anhydride-treated hemp fiber; ▲ untreated banana fiber; × maleic anhydride-treated banana fiber; * untreated sisal fiber; ● maleic anhydride-treated sisal fiber.

gets restricted. The difference in absorption of water between treated and untreated fiber composites are due to blocking of —OH groups to a good measure by esterification on treatment with MA. The detailed mechanism has already been established in our earlier work^{9,10} that the MA esterifies the free —OH groups present in fibers, due to that the absorption of water and steam declines. The HDPE is hydrophobic in nature and the fibers, containing —OH groups, are prone to moisture absorption by formation of hydrogen bonding between water molecules and cellulose. It has been observed from the results that the —COOH groups do not get esterified as the acid value is recorded in all MA-treated fibers, while no acid value is observed in untreated respective fibers. Thus fibers become nonpolar in nature and form the bond with HDPE.

CONCLUSIONS

The following conclusions can be drawn from this study:

1. The absorption of water and steam increases with increase in time in all fibers composites.
2. The MA-treated fibers composites show lesser absorption of steam and water at ambient temperature than the respective untreated fibers composites.
3. The more absorption of steam and water at ambient temperature is observed in untreated hemp fiber composite, while less absorption of steam and water at ambient temperature is observed in MA-treated sisal fiber composite.
4. The natural fiber polymer composites containing low amount of fibers show less absorption of steam and water at ambient temperature than the composites containing more amount of natural fibers in respective fibers composites.

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