

Effect of Compatibilizers on Water Absorption Kinetics of Polypropylene/Wood Flour Foamed Composites

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ABSTRACT: Polypropylene (PP)/wood flour foamed composites were prepared by taking PP:wood flour in the ratios of 100 : 0, 90 : 10, 80 : 20, 70 : 30, and 60 : 40 (w/w), with and without compatibilizers like maleic anhydride-treated wood flour and maleic anhydride-grafted PP (PPgMA). The foamed composite samples were employed for water swelling at 27°C, 70°C, and in steam. The absorption of water increased with increase in filler contents for all three-temperature conditions. The maleic anhydride-treated wood flour and PPgMA showed reduction in water swelling, and the best one was in case of the PPgMA-foamed

composites for respective conditions. Diffusion, sorption, and permeation coefficients were determined to study the absorption kinetics. FTIR spectra were also recorded for 30 wt % of filler loading for all the composites, which showed the effect of compatibilizers on reduction in water absorption in foamed PP/wood flour composites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2530–2537, 2006

Key words: PP; PPgMA; wood flour; water absorption; diffusion kinetics; FTIR

INTRODUCTION

In our earlier research work,^{1–3} we have studied the effect on absorption of steam and water at different temperatures on composites of Novalac and Polystyrene with banana, agave, and hemp fibers. The absorption of steam is more than any other temperatures because of higher penetration of steam into the composites. The common mechanism for sorption of water is diffusion of water molecules into the composites through capillary action in lignocellulosic phase that propagates microcracks in interface. The adsorption and desorption of water in wood is accompanied by volume change. In fact, change in volume or shape may occur because of the development of moisture gradient and stresses.⁴ Agarwal and Brotmann⁵ studied and found that water molecules act as a plasticizer by influencing the fiber, matrix, and interface simultaneously and disturb the mechanical integrity of the composite system. Many authors^{6,7} have studied about the fiber/resin debonding, which is initiated by the development of osmotic pressure pockets at the surface of fibers due to the leaching of water-soluble substances from the fibers. The absorption of water in composites depends on many factors such as temperature, fiber volume fraction, orientation of reinforcement, fiber nature (that is permeable or impermeable),

area of exposed surface (cellular structure), diffusivity, reaction between water and the matrix, and surface protection.^{8,9} The moisture absorption and mechanical properties of wood flour/polypropylene (PP) composites in hydrothermal environment were studied by Lin et al.¹⁰ Similar approach, i.e., incorporation of fiber in Novalac resin, was also studied by other investigators.^{1,2,11,12} Tajvidi and Ebrahimi¹³ reported that as the filler content increased, the water uptake also increased. Statistical test performed indicated that there was a significant difference between various filler contents. The difference between 15 and 25% filler content was significant; but the difference between these two percentages and 35% filler content was much more pronounced. It was caused by the filler agglomeration that might have happened during mixing, which can lead to extra voids in the texture and also caused some surface roughness in the case of higher filler content. Karmakar et al.¹⁴ reported that the absolute water contents after the maximum absorption time remain the same in the case of jute fiber-reinforced PP composites, although the rate of water absorption depends upon the fiber orientation in the composites. Moisture diffusion into the polymer depends on molecular and microstructural aspects such as polarity, the extent of crystallinity, thermoplasticity, and the presence of residual hardeners or other water attractive species.¹⁵ Maggana and Pissis¹⁶ studied the absorption and diffusion of water in epoxy system. Lignocellulose natural fibers are highly hydrophilic due to the presence of OH groups in it. The incorporation of these fibers into the matrix increases the water uptake of the compos-

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ites by forming the hydrogen bond between water and hydroxyl groups of cellulose, hemicellulose, and lignin.^{1,17} However, lignin is a component with the least amount of water absorption due to 3D configuration and OH inaccessibility. Therefore, most of the water is absorbed by hemicelluloses and cellulose.

In present work, detailed investigation of water sorption behavior of PP/wood flour foamed composites have been done. The effect of surface treatment on water sorption kinetics of the composites has been studied. The studies have been carried out by varying the percentage of wood flour in PP matrix and water sorption of these composites at different temperatures. The diffusion coefficient, sorption coefficient, permeability coefficient, and the kinetic parameter of water diffusion of the composites have been determined.

EXPERIMENTAL

Materials

Polypropylene (PP) grade 310367 (REPOL) MFI (8.94 × g/10 min), density 0.92 g/mL from Reliance Industries (India) was used for this study. Different chemicals such as maleic anhydride and dicumyl peroxide (DCP) of commercial grade were procured from s-d Fine Chemicals (Mumbai, India) for the synthesis of maleated PP. Azo di carbamide was procured from High Polymer Labs (New Delhi).

Material preparation

Maleated PP was prepared by solution process. PP was dissolved in xylene in the ratio of 1 : 50 (w/v), and then, the initiator (DCP) 1 phr of PP was added with continuous stirring. After 1 min, maleic anhydride (2 phr of PP) was added into it to give a highly viscous mass, and then, the nonsolvent (acetone) was added into it. The maleated PP was separated out, which has 1.09% acid functionality. Its 5% amount by weight of neat wood flour was taken for preparation of composites of different weight percentage of filler.

Filler preparation

Teakwood flour was obtained from the sawmill. Initially, it was dried in an oven at 60°C till constant weight and then ground in flourmill up to 75 μm size. Esterification was done by maleic anhydride treatment. The details of esterification are given elsewhere¹¹

Compounding and processing

Compounding of the materials was carried out in the Data Processing Plasticorder Model (PL-2003) with a single screw extruder attachment. The mixing was

carried out by keeping the temperatures of the feed zone, compression zone, and metering zone as 160, 170, and 180°C, respectively, at 30 rpm screw speed. The compounded materials were extruded through a strand die, and the extrudates were pelletized. The loading of wood flour was varied from 0 to 40% by weight of filler. Then, the pelletized material was mixed with 1 phr of azo di carbamide, and the foamed square sheets of 10 × 10 × 0.66 cm³ were taken out in injection molding machine. Three different types of wood flour/polymer foamed composites were prepared: untreated wood flour (UWF), maleic anhydride-treated wood flour (MWF), and PPgMA/wood flour (MPP).

FTIR characterization

A Shimadzu model 8400 FTIR spectrophotometer was used to obtain the FTIR spectra of treated and untreated composites. For each sample, 45 scans were recorded from 4000 to 500 cm⁻¹ at a resolution of 5 cm⁻¹ in the absorption mode. Samples of the material surface, finely divided, were ground and dispersed in a matrix of KBr and further ground to a fine mixture in a mortar, before pressing to form KBr pellet for analysis.

Water absorption

Rectangular specimens having 5.0 cm length, 1.0 cm breadth, and 0.66 cm thickness were cut from the composite sheets. Initially, samples were weighed and immersed in water bath containing distilled water for a duration of 0–150 h. The temperature of water was maintained at 70°C, and loss of water due to evaporation was compensated by continuous addition of water. The specimens were removed from the distilled water at a regular interval of time, wiped with filter paper to remove water from surface, and weighed. The samples were re-immersed in distilled water to permit the continuation of the water sorption until saturation established. The studies were carried out at 27 and 70°C, respectively, for the calculation of mole of water uptake by the foamed composites. The mole of water uptake (Q_t) by 100 g of polymer composite was plotted against square root of time. The Q_t value can be calculated using the following equation.

$$Q_t = \frac{M_c(w)/M_r(w)}{M_l(s)} \times 100 \quad (1)$$

Where Q_t is the mole of water uptake by 100 g of polymer composites, $M_c(w)$ is the mass of water at a given time, $M_r(w)$ is the relative molecular mass of water, and $M_l(s)$ is the initial mass of the sample. At equilibrium, Q_t is equal to Q_∞ , which is mole of water

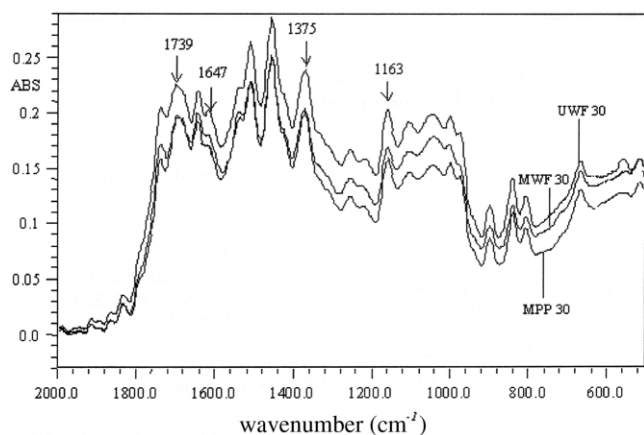


Figure 1 FTIR spectra of MPP, MWF, and UWF composites at 30 wt % filler loading between 500 and 2000 cm^{-1} region.

uptake by 100 g of polymer composites at infinite time.

Steam absorption

Rectangular specimens having 5.0 cm length, 1.0 cm breadth, and 0.66 cm thickness were cut from the composites. Initially, samples were weighed, tied with thread, and hanged over the steam bath for duration of 0–150 h. Relative humidity of the system was measured by hygrometer and found 100%. At a regular interval of time, the specimens were taken out from the steam. The steam (water molecules) from the surface was removed by filter paper and weighed. Loss of water due to evaporation was compensated by continuous addition of water. All the measurements were carried out within 30–40 s. The mole of water uptake (Q_t) by 100 g of polymer was plotted against square root of time and was calculated from eq. (1).

RESULTS AND DISCUSSION

FTIR spectroscopy analysis of wood flour foamed composites

Figure 1 shows the FTIR spectra of composites containing 30% lignocellulose of wood flour. The bands observed at 1375 cm^{-1} are due to structural changes mainly conformational in characters generated by the interaction between the two phases.¹⁸ The band at 1647 cm^{-1} corresponds to the water absorbance due to hydrophilic character of the wood flour.¹⁹ The highest absorbance value corresponds to the untreated wood flour foamed composites, which is due to the hydrophilic nature of the wood flour; and less absorbance is recorded in MWF- and MPP-foamed composites, which is due to the formation of hydrophobic groups at the interface by the compatibilizer. At 1739 cm^{-1} , the absorbance spectrum is due to the carbonyl link-

ages mainly ester linkages ($\text{C}=\text{O}$), or carbonyl stretching vibration of carbonyl groups in hemicellulose, lignin, and also ester in lignin and extractives.²⁰ The said peak for MPP-foamed composites is bigger compared with MWF-foamed composites, while UWF composites do not show sharp peak. This means that MPP and MWF composites have more ester linkages than UWF composites. The peak observed near 1163 cm^{-1} is due to the ether linkage formation to some extent in all the composites.¹⁸

Effect of filler loading on absorption of water in composites

Mole of water uptake of untreated wood flour-filled PP composites as a function of immersion time and at different temperatures is given in Figures 2–4. From these figures, it is clear that as the weight percent of filler content increases, the mole of water uptake also increases. This is due to the fact that with increase in the wood flour, the number of free OH groups of cellulose also increases, which in turn makes the composites more hydrophilic. These free OH groups come in contact with water at different temperatures and form hydrogen bonding, which results in weight gain in the composites. Initially, the water absorption is more, and after that, the increment is rather less.

The effect of filler loading on the Q_∞ values for composites at different temperatures is given in Table I. From Table I, it is clear that as the filler loading and temperature increase, the Q_∞ also increases. This is due to the fact that as the temperature increases, the activity of water molecules also increases. But, in the case of steam absorption, Q_∞ value is more in comparison with others. This is due to the higher penetration of

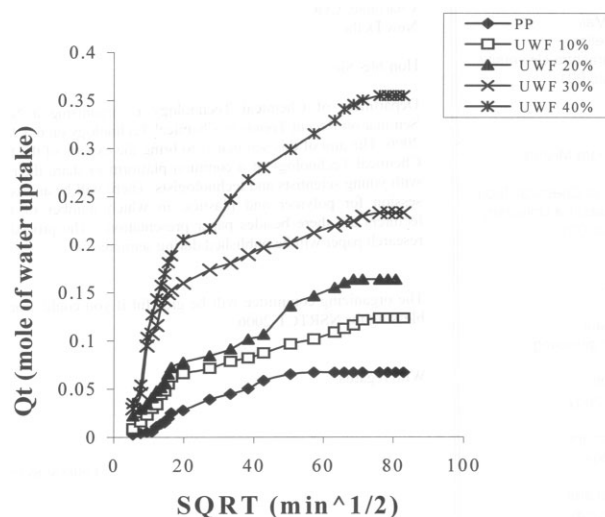


Figure 2 Mole of water uptake as a function of square root of immersion time for UWF at 27°C.

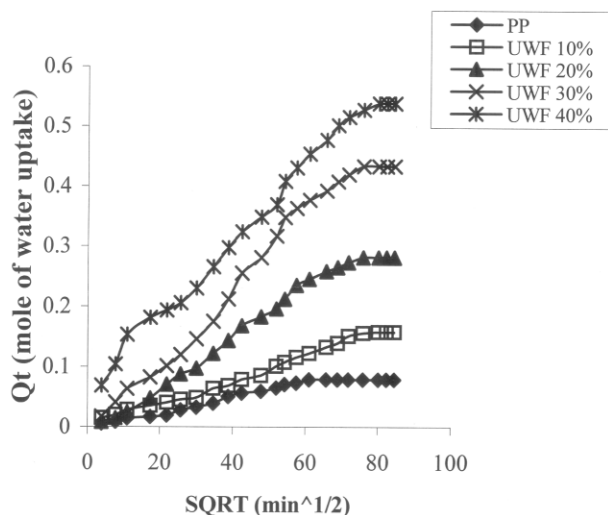


Figure 3 Mole of water uptake as a function of square root of immersion time for UWF at 70°C.

steam in the cell wall that inserts inside the intermolecular structure of the cellulosic part.

Effect of surface modification of wood flour on absorption of water

The main purpose of surface modification by maleic anhydride is to convert the hydrophilic cellulose into hydrophobic. This occurs because of the ester linkages or the bond formation with the maleic anhydride.^{3,21} Figures 5–7 depict the effect of chemical treatment on the water absorption characteristics of wood flour/PP composites with different percentages of filler loading

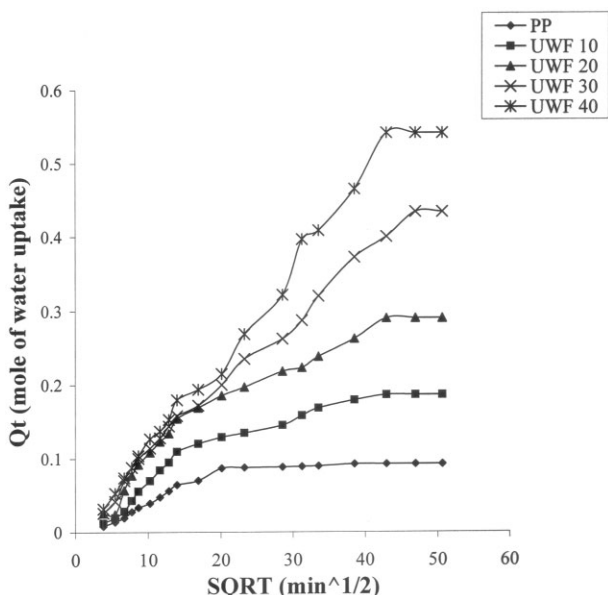


Figure 4 Mole of water uptake as a function of square root of time for UWF in steam.

TABLE I
 Q_{∞} Value of Untreated Wood Flour-Filled PP Foamed (UWF) Composites at Different Filler Loading and at Different Temperatures as well as Steam

Wood flour loading (%)	Temperature (°C)	Q_{∞} (mol)
10	27	0.1235
	70	0.1578
	Steam	0.1866
20	27	0.165
	70	0.282
	Steam	0.2904
30	27	0.2335
	70	0.4341
	Steam	0.4344
40	27	0.3556
	70	0.539
	Steam	0.5425
Virgin PP	27	0.0673
	70	0.079
	Steam	0.0925

as well as at different temperatures. It is clear that the mole of water uptake at equilibrium increases with increase in the percentage of wood flour (Table II). But, the increment is rather less, compared with that in untreated foamed composites. This decrement is due to the improved filler/matrix adhesion by the formation of either hydrogen bond or chemical bond that reduces the moisture which results in filler matrix debonding. It is also clear from Table II that as the temperature increases, the mole of water uptake at equilibrium also increases. This favors the fact that at higher temperature the activity of molecules increases, which results in higher water absorption. But, in case

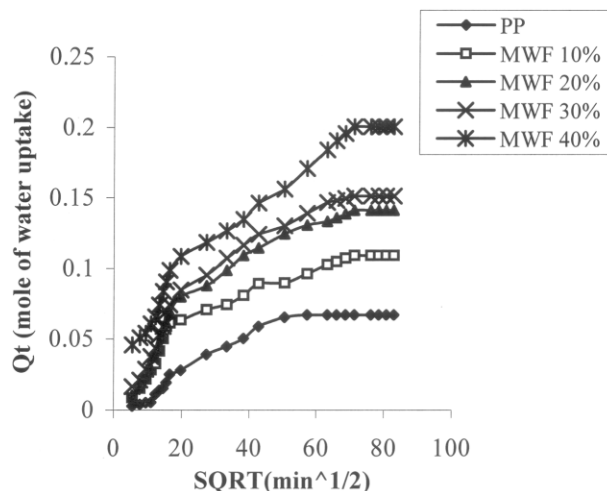


Figure 5 Mole of water uptake as a function of square root of immersion time for MWF at 27°C.

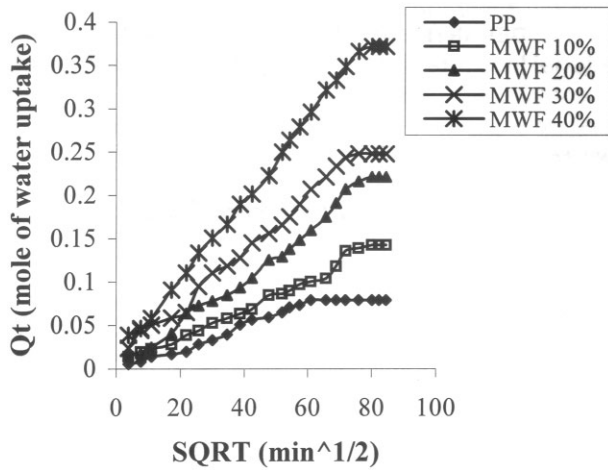


Figure 6 Mole of water uptake as a function of square root of immersion time for MWF at 70°C.

of steam, the penetrability is more, and therefore, the Q_{∞} is more unlike at different temperatures.

Mole of water uptake of PPgMA/wood flour-filled PP composites increases with increase in temperature and wood flour contents, but it is less compared with other composites (Figs. 8–10). The enhanced bonding in MPP composites is due to the capability to cover the more surface area during compounding, which results in more ester linkages between the hydroxyl groups of wood flour and the anhydride part of PPgMA. This causes a reduction in interfacial tension and an increase in interfacial adhesion between PP and filler. It

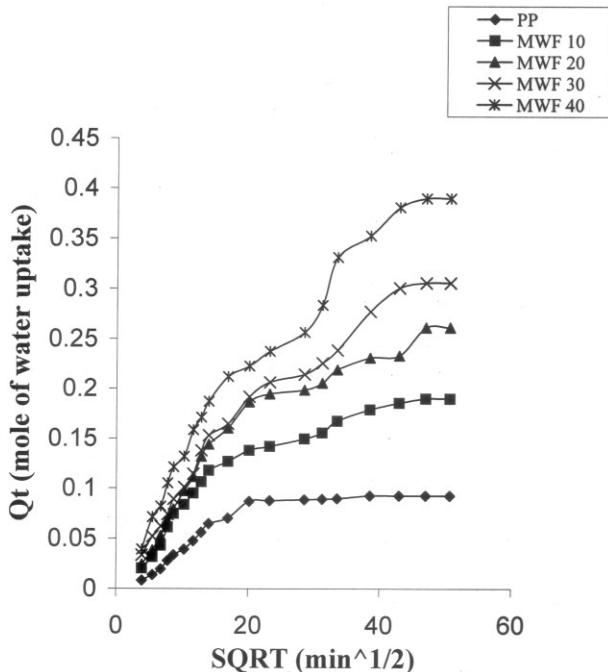


Figure 7 Mole of water uptake as a function of square root of time for MWF in steam.

TABLE II
 Q_{∞} Value of Treated Wood Flour-Filled PP Foamed (MWF) Composites at Different Filler Loading and at Different Temperatures as well as Steam

Wood flour loading (%)	Temperature (°C)	Q_{∞} (mol)
10	27	0.1093
	70	0.1429
	Steam	0.190
20	27	0.1414
	70	0.2212
	Steam	0.2615
30	27	0.1514
	70	0.248
	Steam	0.3059
40	27	0.2007
	70	0.3719
	Steam	0.3902
Virgin PP	27	0.0673
	70	0.0791
	Steam	0.0925

is also noticed that the crystallinity of treated wood polymer composites is greater than that of the untreated composites. The crystalline regions are impermeable to the penetrant; therefore, the absorption of water is less in treated composites. Because of this fact, the water absorption at equilibrium is rather less than that of UWF and MWF-foamed composites (Table III).

Kinetics of water absorption

To study the mechanism of water sorption of wood flour foamed composites, the value of n and k were calculated from the given equation.²²

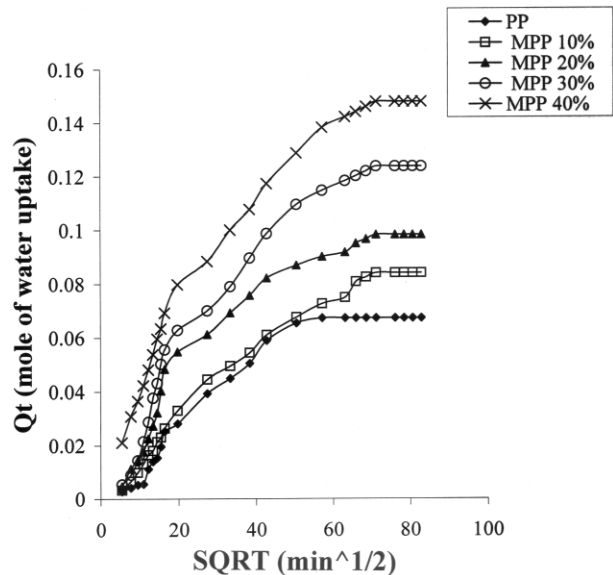


Figure 8 Mole of water uptake as a function of square root of immersion time for MPP at 27°C.

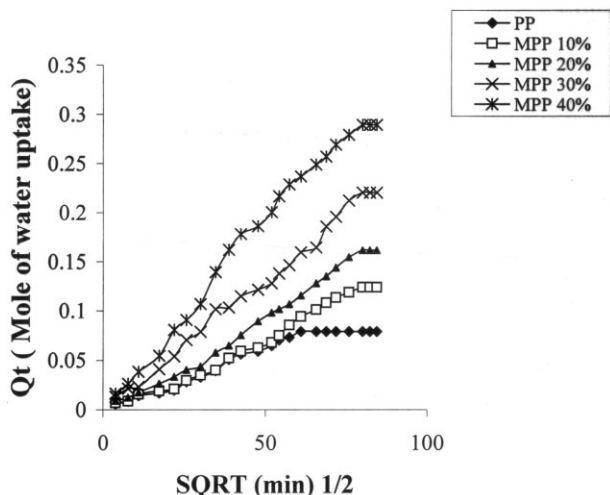


Figure 9 Mole of water uptake as a function of square root of immersion time for MPP at 70°C.

$$\log\left(\frac{Q_t}{Q_\infty}\right) = \log k + n \log t \quad (2)$$

Where Q_∞ is the mole of water uptake at equilibrium, Q_t is the mole of water uptake at time t , and k and n are constants.

The constant k indicates the interaction between polymer and water, and n is the diffusion exponent, which tells about the mode of diffusion. The values of n and k were calculated with the help of linear regression method. When $n = 1/2$, diffusion obeys the Fick's law; this occurs when the segmental mobility of the polymeric chains is faster than the rate of diffusion of water molecules. When $n = 1$, the mechanism is non-Fickian; this occurs when water diffusion rates are

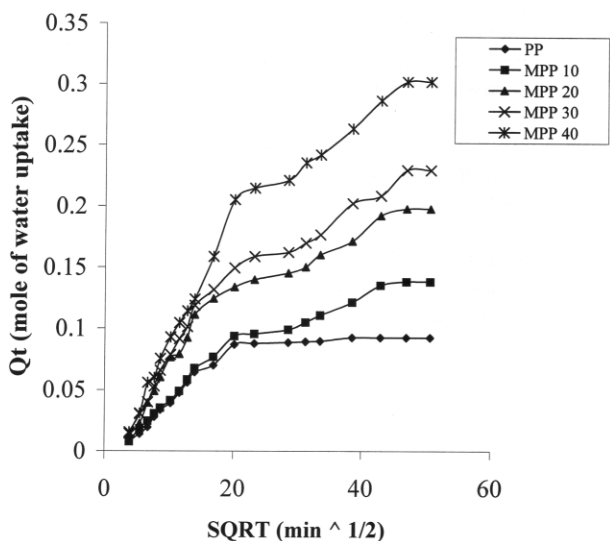


Figure 10 Mole of water uptake as a function of square root of time for MPP in steam.

TABLE III
 Q_∞ Value of Compatibilized (PPgMA) Wood Flour-Filled PP Foamed (MPP) Composites at Different Filler Loading and at Different Temperatures as well as Steam

Wood flour loading (%)	Temperature (°C)	Q_∞ (mol)
10	27	0.0841
	70	0.1242
	Steam	0.1383
20	27	0.0983
	70	0.1613
	Steam	0.1979
30	27	0.1238
	70	0.2201
	Steam	0.2296
40	27	0.148
	70	0.289
	Steam	0.302
Virgin PP	27	0.0673
	70	0.079
	Steam	0.0925

much faster than segmental mobility of the polymeric chains. When n lies between 0.5 and 1, the diffusion is anomalous. This is the case when permeant mobility and polymer segmental relaxation rates are almost equal. It is clear from Table IV that when the value of n approaches 0.5, the system obeys the Fickian behavior, i.e., the water absorption increases linearly with square root of time and then gradually approaches equilibrium.

The diffusion coefficient (D) of the wood flour foamed composites can be calculated from following equation²³:

$$D = \pi \left[\frac{h\theta}{4Q_\infty} \right]^2 \quad (3)$$

where θ is the slope, which can be calculated from the graph between the Q_t and $t^{1/2}$, and h is the initial thickness of the sample. The value of D has been given in Table V. It is clear from Table V that as the temperature increases, the diffusion coefficient increases. The diffusion coefficient characterizes the ability of the solvent to move along with the polymer segment. As the temperature increases, the activity within the polymer molecules enhances, which helps the water molecules to diffuse in to the composites through the fillers and the voids present in it due to foaming. However, the trend of diffusion coefficient is not regular with increase in filler contents in composites.^{24,25} It is because the diffusion in wood polymer composites occurs through different mechanisms being the different natures of the polymer and wood filler. Hence, variation in diffusion is observed. Moreover,

TABLE IV
Values of n and k for Wood Flour/PP Foamed Composites at Different Filler Loading and after Treatment

Composites	n			k		
	27°C	70°C	Steam	27°C	70°C	Steam
Virgin PP	0.499	0.4946	0.4505	0.0166	0.0169	0.0448
UWF						
10	0.3901	0.4277	0.4776	0.0374	0.0235	0.0336
20	0.3592	0.50	0.4568	0.0472	0.0150	0.0369
30	0.2635	0.4401	0.462	0.1121	0.0248	0.0335
40	0.327	0.3451	0.50	0.0644	0.0500	0.0252
MWF						
10	0.3729	0.4177	0.4084	0.0449	0.0248	0.0549
20	0.4177	0.4833	0.4395	0.0311	0.0143	0.0415
30	0.375	0.4065	0.426	0.0440	0.0303	0.0432
40	0.2897	0.4335	0.4173	0.0834	0.0246	0.0457
MPP						
10	0.4441	0.4757	0.50	0.245	0.165	0.255
20	0.4551	0.53	0.4825	0.0231	0.0095	0.0315
30	0.486	0.4932	0.484	0.0179	0.0138	0.0299
40	0.3335	0.4147	0.4988	0.0606	0.0322	0.0261

the time taken for the absorption of water will be less in cellular structure in comparison with normal wood polymer composites.

The sorption coefficient (S) is a phenomenon, which occurs because of diffusibility as well as the sorption of water molecule by the fillers that shown in the following equation.²³

$$S = \frac{M_\alpha}{M_p} \quad (4)$$

Where M_p is the mass of the initial polymer sample, M_α is the mass of the solvent taken at equilibrium swelling wherein water molecule activity is 1. The values of S have been quoted in Table V for MPP,

MWF, and UWF composites. From the values, it is clear that as the weight percentage of wood flour increases, the sorption coefficient also increases, and the values at 40 wt % filler loading of MPP, MWF, and UWF composites are 0.054, 0.070, and 0.0976 g/g, respectively. Thus, these values decrease with increment in modification of the filler surfaces. MPP and MWF show less sorption coefficient unlike UWF composites. This is due to the bond formation during the processing, which is an obstacle to the water molecules to penetrate deep in to the composites. It is also clear from the data that the sorption coefficient enhances with enhancement of temperature. This is due to the weakening of the filler matrix interface, which reflects in increase in water absorp-

TABLE V
Values of D , S , and P for Wood Flour/PP Foamed Composites at Different Filler Loading and after Treatment

Composites	D (10^{-9} m ² /min)			S (g/g)			P (10^{-9} m ² /min)		
	27°C	70°C	Steam	27°C	70°C	Steam	27°C	70°C	Steam
Virgin PP	1.529	1.372	3.237	0.011	0.014	0.016	0.017	0.019	0.051
UWF									
10	0.947	1.373	3.545	0.022	0.028	0.034	0.021	0.038	0.119
20	1.142	1.552	3.179	0.030	0.050	0.052	0.033	0.078	0.164
30	0.566	1.747	3.508	0.042	0.078	0.0784	0.024	0.136	0.273
40	0.828	1.095	3.977	0.064	0.097	0.098	0.053	0.106	0.388
MWF									
10	1.030	1.211	2.738	0.019	0.026	0.034	0.020	0.031	0.094
20	1.094	1.371	2.881	0.025	0.040	0.047	0.028	0.054	0.135
30	1.078	1.251	3.180	0.027	0.043	0.055	0.029	0.054	0.174
40	0.849	1.252	3.075	0.0363	0.067	0.070	0.031	0.083	0.215
MPP									
10	1.209	1.419	3.504	0.015	0.022	0.025	0.018	0.031	0.086
20	1.274	1.449	3.151	0.018	0.029	0.035	0.022	0.042	0.110
30	1.255	1.286	3.139	0.022	0.040	0.041	0.028	0.050	0.128
40	0.999	1.326	3.375	0.026	0.052	0.054	0.0265	0.068	0.182

tion by the composites. The sorption coefficient is minimum in virgin PP.

The solution diffusion model for permeability coefficient (P) can be mathematically expressed as follows:²⁶

$$P = D \times S \quad (5)$$

Table V shows that the permeability coefficient increases with increase in temperature. This is due to the higher penetrability of water molecules in the composites especially in wood flour. But the compatibilizer decreases the permeability of water in the wood flour foamed composites because of its reaction with the OH groups of wood flour that are responsible for water absorption by forming the hydrogen bonds with water molecules. Thus, this effect is more pronounced in the case of steam.

CONCLUSIONS

The reduction in peak at 1647 cm^{-1} in MWF and MPP in comparison with UWF shows the elimination of hydrophobic characteristics of the composites, which is much prominent in MPP. The increment in peak intensity at 1739 cm^{-1} for MPP in comparison with MWF and UWF shows the greater degree of esterification in MPP. The greater hydrophobic characteristic of MPP than MWF and UWF has also observed by water absorption at 27°C , 70°C and in steam. The kinetics of water absorption of wood flour foamed composites shows that the n value approaches to 0.5, which obeys the Fickian behavior. The mole of water uptake of MPP-foamed composites is minimum compared with that of MWF and UWF composites; this is due to the varying degree of reaction of maleic anhydride as compatibilizer. The diffusion coefficient as well as the permeability coefficient increase with increase in temperature, whereas the sorption coefficient increases with increase in the weight percentage of filler loading and decreases with the surface treatment that increases the hydrophobicity.

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