

# Water Absorption Behavior of Acrylonitrile-Butadiene (NBR) Latex Impregnated Jute Nonwoven Fabric Composites

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**ABSTRACT:** Composites were fabricated by impregnating the jute nonwoven fabric in acrylonitrile-butadiene (NBR) latex. The effect of different pickup ratio (dry, wt/wt) of NBR latex to jute nonwoven fabric, viz., 0.5 : 1, 1 : 1.5, 1.5 : 1, 2 : 1, and 2.5 : 1 on the water absorption behavior of the composites were evaluated. Water absorption studies were carried out at different temperatures, viz. 30, 50, and 70°C, based on immersion weight gain method. From the sorption result, the diffusion ( $D$ ) and permeation ( $P$ ) coefficients of water penetrant have been calculated. Significant increase in the diffusion and permeation coefficients was observed with increase in the temperature of sorption experiments. Drastic reductions in diffusion and permeation

coefficients were noticed with increase in the pickup ratio of NBR on to jute nonwoven fabric. Attempts were made to estimate the empirical parameters like  $n$ , which suggests the mode of transport, and  $K$  is a constant that depends on the structural characteristics of the composite in addition to its interaction with water. The temperature dependence of the transport coefficients has been used to estimate the activation energy parameter for diffusion ( $E_D$ ) and permeation processes ( $E_p$ ) from Arrhenius plots. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2045–2050, 2006

**Key words:** jute nonwoven fabric; NBR latex; composite; water absorption; diffusivity

## INTRODUCTION

Unlike metals, the mechanical properties of reinforced composites have been observed to be very sensitive to the presence of moisture because small molecules such as water can easily diffuse into the polymer matrix altering the strength of polymer. Almost all the reinforced composites in service are subjected to the presence of atmospheric moisture at different temperatures and hence, this aspect of the composites has received considerable attention.

The long-range mechanical performance of the polymer composites depends upon their stability in varying environmental conditions. There is a particular need for knowledge of the effect of water on these materials. Water is universally present and capable of diffusing in most materials. The sorption and diffusion of low molecular weight substances such as water into polymers is often sensitive to any change in segment mobility or spatial arrangement of polymer chains.<sup>1</sup> For many applications, knowledge of the water absorption properties is important.

Natural fibers such as jute are potentially hydrophilic because of the presence of hydroxyl (cellulose) groups. This hydrophilicity in turn affects the long-term mechanical properties of the composite when natural fibers are used in the composites. Moisture diffuses into polymers to different degrees depending on a number of molecular and microstructural aspects.<sup>2</sup>

The nature of the fiber dictates the water permeability of an overall performance of composite.<sup>3</sup> All synthetic polymers absorb moisture in a humid atmosphere and when they are immersed in water. Gorrasi et al.<sup>4</sup> explained that the sorption depends on the hydrophilic character of the polymer and the nature of filler. Various parameters such as resin chemical structure, polarity, crosslinking density, and impurities of polymer can make the diffusion process as non-Fickian.<sup>5</sup> Absorbed moisture acts as plasticizer to the matrix and in turn affects the mechanical properties of the composites by breaking the secondary force of attraction in the matrix.<sup>6,7</sup> In a composite, the fiber part and polymer matrix part differs significantly in their independent responses to moisture.

Extensive research studies have been carried out on water permeability in fiber-reinforced polymer composites. Shen and Springer<sup>8</sup> presented a comprehensive moisture absorption analysis in jute-epoxy composites. They showed that a Fickian diffusion model is valid for this type of composite. Rao et al.<sup>9</sup> have de-

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veloped the modified theory for permeable fiber composites using the theory on impermeable fiber composites. They revealed that, in permeable fiber composites, the mechanism of moisture diffusion is controlled by the matrix impregnated fiber phase. Pothan and Thomas<sup>10</sup> have studied on the effect of hybridization of fibers and chemical modification on the water absorption behavior of banana fiber-reinforced polyester composites. They reported that the water diffusion of banana/glass hybrid composites decreases with increase in the glass fiber content. They also found that the chemical modification by silane treatment would reduce the diffusion of the water molecules into the composite. The permeable fiber exhibits a very high degree of moisture absorption, occurring primarily due to a capillary mechanism, resulting from a large free volume of the fibers. However, while considering a resin-impregnated fiber, such as the one present in composite systems, the inherent porosity of the pure fiber is reduced to various degrees depending on the resin to fiber pickup ratio.<sup>9</sup> Generally, in the permeable fiber composites, the diffusivity of pure fiber is very much higher than the composites and the composite have very much higher diffusivity compared to pure resin. All the above studies represent the results of the composites prepared with the resin matrices such as epoxy and polyester, which is chemical reaction, based system. The authors in their earlier research article have reported the effect of different pickup ratio latex based NBR–jute nonwoven<sup>11</sup> on the mechanical and chemical resistance properties of composites. In the present study, the diffusion ( $D$ ), sorption ( $S$ ), and permeation ( $P$ ) coefficients were estimated to study the transport behavior of water into the composites. To understand the type and behavior of transport, the empirical parameters  $n$  and  $K$  were calculated. The activation energy for the process of diffusion ( $E_D$ ) and permeation ( $E_p$ ) were determined using Arrhenius plots.

## EXPERIMENTAL

### Materials

Needle-punched jute nonwoven fabric (150 g/m<sup>2</sup>) having density of 0.1 g/cc and burst strength of 0.60 MPa was procured from Jindal fibers private limited (India). NBR latex having pH 7–8, viscosity of 15 s (B4 cup standard), and solid content of 40% was procured from a local supplier. The acrylonitrile content in the NBR latex was 30%.

### Specimen preparation

Composites were fabricated by impregnating the jute nonwoven fabric in a bath of acrylonitrile–butadiene latex as per the procedure reported elsewhere.<sup>11</sup> A

series of composites were fabricated by maintaining the different pickup ratio of jute nonwoven to NBR latex varying from 1 : 0.5 to 1 : 2.5.<sup>12</sup> The rectangular specimens (25 mm width  $\times$  75 mm length)<sup>9</sup> have been coated along the edges by resin and dried at 105°C until constant weight.

Sorption experiments at 30, 50, and 70°C were performed by immersing the composite specimens in distilled water in the metal-capped bottle maintained at the desired constant temperature ( $\pm 0.5^\circ\text{C}$ ) in a thermostatically controlled oven. At a specified intervals of time, specimens were removed from the containers, surfaces were dried in between smooth filter paper, and were weighed immediately using analytical balance having  $\pm 0.1$  mg resolution. The weighing of the specimens continued until the equilibrium values were reached.

The percentage weight gain,  $Q_t$ , of the immersed composite specimen was calculated as follows:

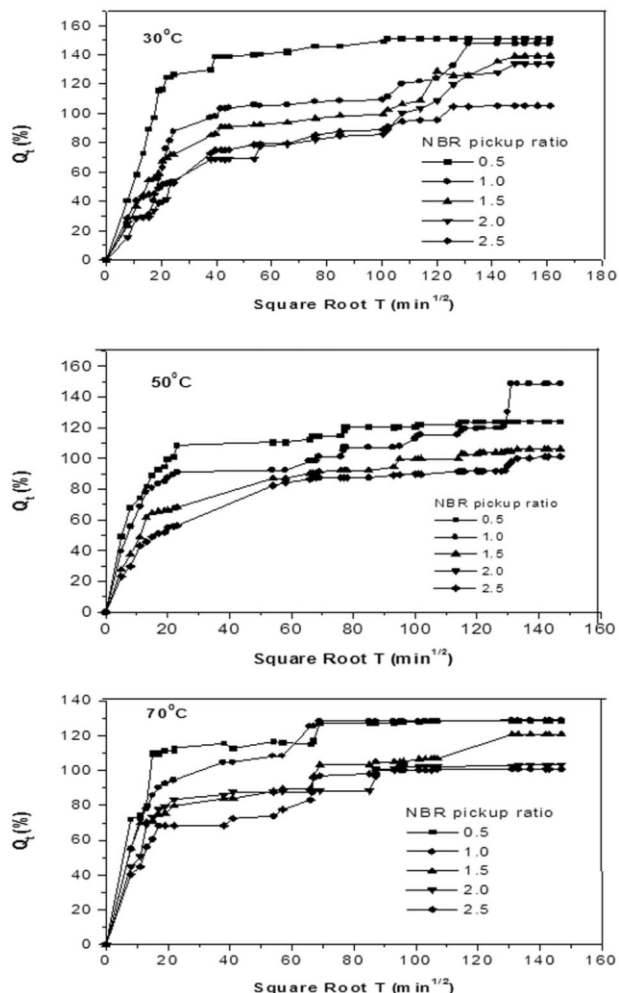
$$Q_t = (M_t - M_i) / M_i \times 100 \quad (1)$$

where  $M_i$  is the initial weight of the composite specimens and  $M_t$  is the weight of the specimen at time  $t$ .

## RESULTS AND DISCUSSION

The percent mass uptake ( $Q_t$ ) of water versus square root of time, for composites with different pickup ratio viz. 1 : 0.5–1 : 2.5 of jute nonwoven fabric to NBR is shown in Figure 1. In all the samples the initial portion of the water absorption curve is linear, after which the mechanism changes. Water diffusion in polymers was found to lead typical phenomena of composite swelling and physical relaxation. The absorption of water by polymer depends mainly on the availability of free nanosized holes in the polymer and the polar sites present in the polymer. There are two states of water molecules present in the polymer: (i) the unbonded molecules in the nano pores of the polymer and (ii) the water molecules that form hydrogen bonds with the polar groups of jute fiber ( $-\text{OH}$ ). The water transport of composites was dictated by the rate of breakage and formation of internal hydrogen bonds with the constituents of the composite. Further, the water in the nanopores may form hydrogen bonds with polymer, blocking the nanopores and reducing further water uptake.

According to Flory's two-stage theory, the swelled polymer chains induce increased elasticity of chain structure and these will inhibits the further absorption of water, which may be observed as the first equilibrium of water uptake (Fig. 1). However, the swelled polymer chain start relaxing with time and subsequently starts increasing in the water absorption. Consequently, the second equilibrium is attained by the decreased elasticity of polymer chains. The penetra-



**Figure 1** Percent mass uptake ( $Q_t$ ) of water by jute-NBR composites at (a) 30, (b) 50, and (c) 70°C.

tion of the water into the matrix causes absorption of water by the fibers and this result in the formation of micro-cavities at the surface of the composite because of differential swelling. The formation of micro-cavities was prominent at 50 and 70°C sorption test temperature compared to 30°C. The absorption of water by the NBR matrix is very low and as the pickup ratio of NBR in composites increases, the ability of the composites to absorb water decreases. The principal water absorption by the composite is from the hydrogen bonding through the —OH group of jute fibers.<sup>13</sup> The differential swelling exist between the matrix and nonwoven fibrous structures leads to the formation of micro-cavities at the surface of the composites and this causes further absorption of water.

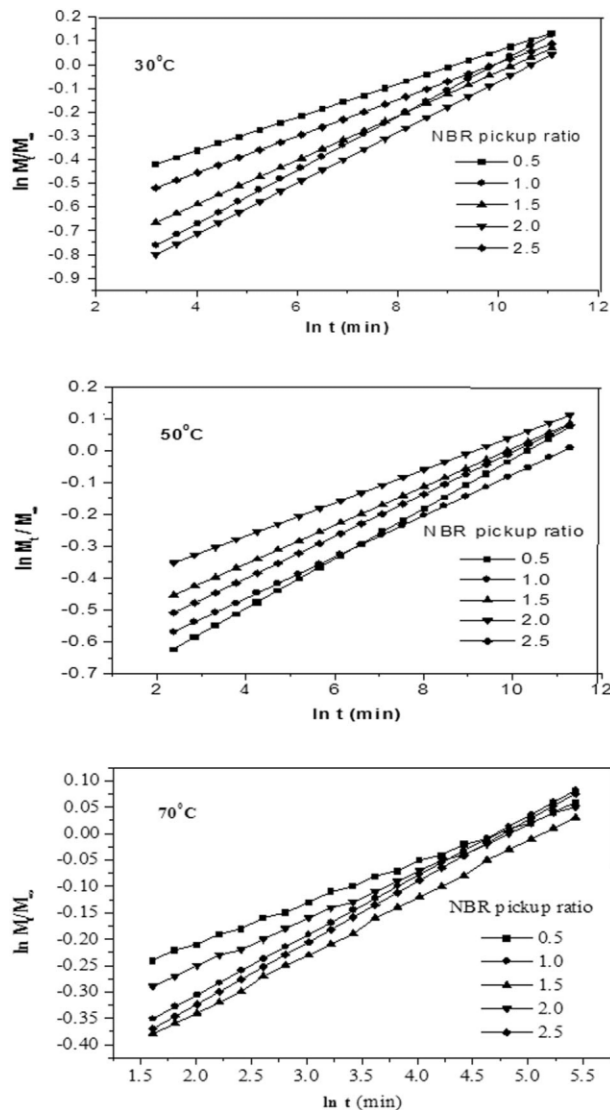
To investigate the type of diffusion mechanism, attempts were made to estimate the values of  $n$  and  $K$  by the following relation:

$$\log(M_t/M_\infty) = \log K + n \log t \quad (2)$$

where  $K$  and  $n$  are empirical parameters,  $M_t$  and  $M_\infty$  are mass uptake values at time  $t$  and at equilibrium.

The magnitude of  $n$  decides the transport mode, for instance, a value of  $n = 0.5$  suggests the Fickian mode and  $n = 1$  the non-Fickian diffusion mode. The value of  $n$  ranging from 0.5 to 1 suggests the presence of anomalous transport mechanism.

To determine  $K$  and  $n$ , plots of  $\log(M_t/M_\infty)$  versus  $\log t$  were plotted and it is shown in Figure 2. The calculated values of the empirical parameters  $n$  and  $K$  for the composite-water systems at different temperatures are given in Table I. The increase of  $K$  with increase in temperature reveals that the interaction of water molecules with the composite is high.  $K$  value did not follow any systematic variation for different NBR pickup ratio. The increased test temperature may lead to the weakening of fiber-matrix adhesion. This poor adhesion leads to create certain free volume at molecular level. In addition to this the chance for water molecules to attract hydrophilic jute fiber be-



**Figure 2** A plot of  $\ln M_t/M_\infty$  versus  $\ln t$  for jute-NBR composites at (a) 30, (b) 50, and (c) 70°C.

TABLE I  
Values of  $n$  and  $K$  for the Jute–NBR Composites at  
Different Temperatures

Temp (°C)	$n$ (+0.0108)	$K$ ( $10^2$ g/g min) (+0.009)
<i>77% fiber, 33% matrix</i>		
30	0.230	2.86
50	0.118	10.36
70	0.231	43.39
<i>50% fiber, 50% matrix</i>		
30	0.127	5.55
50	0.114	11.82
70	0.128	29.33
<i>40% fiber, 60% matrix</i>		
30	0.157	4.93
50	0.114	14.45
70	0.158	27.51
<i>33% fiber, 67% matrix</i>		
30	0.155	4.56
50	0.098	22.10
70	0.154	36.96
<i>21% fiber, 79% matrix</i>		
30	0.129	12.84
50	0.089	16.27
70	0.129	27.64

comes easier. As the test temperature increases, the segmental mobility of the NBR phase in the composite increases and this creates the free volume in the composite and thus the interaction for water molecules with the composite increases. The low value of  $n$  lying in the range 0.089–0.231 clearly shows that the mechanism of water transport deviates from Fickian mode. Generally, the diffusion of water is anomalous in case of natural fiber composites.<sup>14</sup> News<sup>15</sup> and Stamm<sup>16</sup> made a similar observation of this kind in a cellulose system. Pothan and Thomas<sup>10</sup> have reported that the water diffusion in case of banana/glass hybrid composites was found to be dependent on the cellulose fiber content and temperature.

The sorption coefficient of the composite was computed by the following relation;

$$S = M_{\infty}/M_i \quad (3)$$

where,  $M_{\infty}$  and  $M_i$  represent the maximum water uptake and initial composite weight, respectively.

The ability of the water molecules to move along the polymer segments was characterized by diffusion coefficient  $D$ , which is predominantly matrix-dominated parameter and can be calculated from the following equation:

$$D = \pi(h\theta/4M_{\infty})^2 \quad (4)$$

where  $\theta$  is the slope of the linear portion of the sorption curves,  $h$  is the initial thickness of the sample, and  $M_{\infty}$  is the mass uptake at infinite time.

The permeability of the composite specimens to water molecules was related to the diffusion coefficient and equilibrium sorption of the penetrant and it can be expressed by the following equation:

$$P = DS \quad (5)$$

Therefore permeability is the net effect of sorption and diffusion. Table II gives the diffusion ( $D$ ), sorption ( $S$ ), and permeability ( $P$ ) coefficient value of the water-composites with different pickup ratio of NBR at different temperatures. A significant reduction in diffusion coefficient of water into the composites was noticed with increase in the NBR pickup ratio from 0.5 to 2.5 at all test temperature range from 30–70°C. The increased coating thickness of water resistant NBR onto the hydrophilic jute fiber could be the reason for lower  $D$  values with increased NBR pickup ratio. It is also observed that the  $D$  value increased with increase in the test temperature at all pickup ratio of NBR. As known, the diffusion process is a thermally activated process, an increase in temperature was found to increase the diffusion coefficient of the water. The increase in diffusion with increase in the temperature

TABLE II  
Diffusion ( $D$ ), Sorption ( $S$ ), and Permeation ( $P$ )  
Coefficients of Water in Jute–NBR Composites at  
Different Temperatures

Temp (°C)	Diffusion coefficient $D$ ( $10^5$ cm <sup>2</sup> /s)	Sorption coefficient $S$ ( $10^2$ g/g)	Permeability coefficient $P$ ( $10^4$ cm <sup>2</sup> /s)
<i>77% fiber, 33% matrix</i>			
30	6.79	251	1.70
50	9.32	223	2.01
70	17.14	228	3.91
<i>50% fiber, 50% matrix</i>			
30	3.75	247	0.93
50	6.52	248	1.62
70	8.89	228	2.02
<i>40% fiber, 60% matrix</i>			
30	3.18	239	0.76
50	6.39	206	1.32
70	8.33	220	1.83
<i>33% fiber, 67% matrix</i>			
30	2.46	233	0.58
50	4.25	206	0.88
70	6.14	203	1.25
<i>29% fiber, 71% matrix</i>			
30	2.19	192	0.42
50	4.00	201	0.80
70	4.92	200	0.98

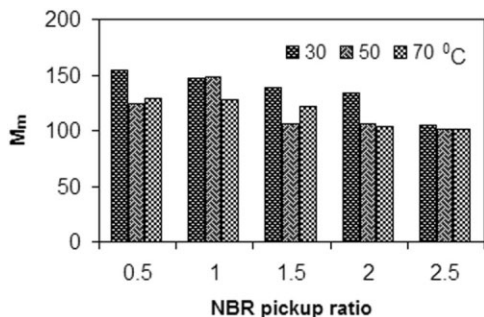


Figure 3 Variation of equilibrium moisture content ( $M_m$ ) with different pickup ratio of NBR at different temperatures.

can be attributed to the development of micro-cracks/voids on the surface and the bulk of the materials.<sup>17</sup> This can also be supported by Henry’s law mode, which states that the sorption proceeds through the creation of new sites or pores in the polymer. The sorption coefficient was reduced with increase in the pickup ratio of NBR in composites. The lower water uptake by the NBR could be the reason for lower sorption coefficients. The sorption coefficient of the composites was reduced from 251 to 192, from 223 to 201, and from 228 to 200 at 30, 50, and 70°C, respectively, for NBR pickup ratio from 0.5 to 2.5. Figure 3 shows the variation in equilibrium water content ( $M_m$ ) of the composites with increase in the pickup ratio of NBR or decrease in the fiber volume fraction. It is observed that the water uptake of the composites decreased with increase in the temperature. The chemical degradation during the sorption process resulting in the leaching of some soluble materials like short-chain hemicellulose, pectin, and so forth from the jute fiber component of the composite may be the reason for the relative lower water uptake at higher temperature.<sup>10</sup>

The activation energy  $E_D$  for the process of diffusion and  $E_p$  for permeation process is estimated from the Arrhenius relation

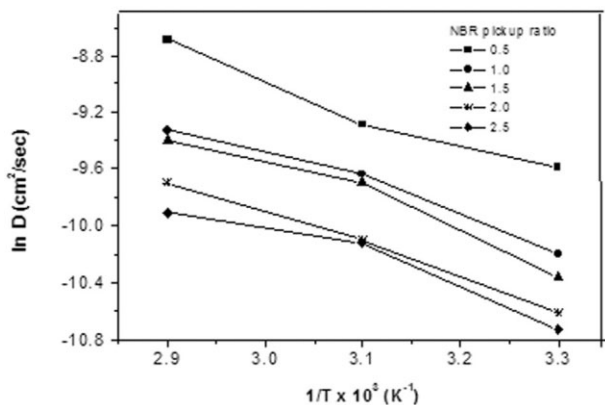


Figure 4 A plot of  $\ln D$  versus  $1/T$  for jute-NBR composites.

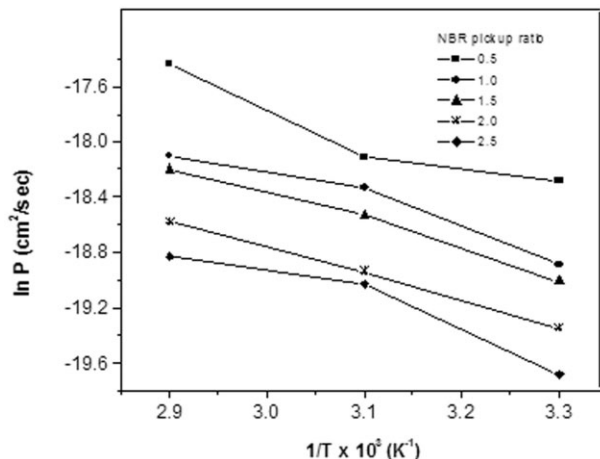


Figure 5 A plot of  $\ln P$  versus  $1/T$  for jute-NBR composites.

$$X = X_0 \exp(-E_a/RT) \tag{6}$$

where  $X_0$  is pre-exponential factor,  $R$  is the molar gas constant,  $T$  is the absolute temperature, and  $X$  is the coefficient ( $D$  for diffusion process and  $P$  for permeation process). The Arrhenius plots of  $\ln D$  and  $\ln P$  versus  $1/T$  are shown in Figures 4 and 5, respectively. The value of  $E_D$  and  $E_p$  lies in the range 3.41–3.99 kJ/mol and 3.12–3.53 kJ/mol, respectively (Table III). There is no systematic variation in  $E_D$  and  $E_p$  values with increase in the pickup ratio of NBR.  $E_D$  values are slightly higher than  $E_p$  values. A common assumption is that the surface layer of the composites reaches saturation instantly on exposure into water and the uptake rates are governed by the rate at which absorbed material diffuses from the surface. The trapped water molecules at the surface hinder the free flow of water into the composites and hence the diffusion process requires more energy. This can also be ex-

TABLE III  
Values of Activation Energy for Diffusion ( $E_D$ ) and Permeation ( $E_p$ ) for Jute-NBR Composites

$E_D$ (kJ/mol)	$E_p$ (kJ/mole)
77% fiber, 33% matrix 3.78	3.49
50% fiber, 50% matrix 3.66	3.28
40% fiber, 60% matrix 3.99	3.37
33% fiber, 67% matrix 3.82	3.12
29% fiber, 71% matrix 3.41	3.53

plained based on the Eyring's hole theory, according to which higher energy is required to "open a hole" in the polymer matrix to accommodate diffusing molecules.

### CONCLUSIONS

The diffusion of water in to jute-NBR composites was found to be dependent on the pickup ratio of NBR and the temperature. The diffusion coefficient ( $D$ ), permeation coefficient ( $P$ ), and sorption coefficient ( $S$ ) were found to decrease with increase in the pickup ratio of NBR. The increase in temperature has increased the  $D$ ,  $P$ , and  $S$  values. The lower value of  $n$  (less than 0.5) clearly revealed that the mechanism of water transport deviates from Fickian mode. The increased  $K$  values with increase in the temperature shows the high interaction of water penetrant with the composites. A drastic improvement in the water resistance behavior of composite was noticed with increase in the pickup ratio of NBR to jute. This may be due to the fact that the increased NBR pickup ratio reduces the amount of hydrophilic jute fiber in the composite.

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