

# Moisture Absorption Phenomenon in Permeable Fiber Polymer Composites

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## Synopsis

Studies were conducted on the moisture absorption characteristics of jute fiber composites based on polyester and epoxy resin systems, under constant humidity ( $\phi$ ) and ambient temperature ( $T$ ) conditions. The initial slope of the moisture absorption curve (a direct measure of the composite diffusivity) increased with increased superficial fiber volume fraction ( $V_f$ ), where as the time ( $t_m'$ ), needed to reach the equilibrium moisture absorption value showed a reversed trend. This behavior is just a reverse to that observed<sup>1</sup> in case of composites with practically impermeable fibers (e.g., glass and graphite) in the same resin matrices. The theoretical expressions governing moisture diffusion phenomenon in impermeable fiber composites were modified and analyzed for the case of composites containing a permeable fiber. The experimental data obtained on the latter were then discussed in relation to the modified theory. The meaning of a correct fiber volume fraction ( $V_f'$ ) as applicable to permeable fiber composites was defined.

## INTRODUCTION

Moisture absorption in polymer composites occurs primarily by a "Fickian" diffusion mechanism. Shen and Springer<sup>1</sup> presented expressions for calculating the equilibrium moisture content ( $M_m$ ) and the composite diffusion coefficient ( $D_c$ ) as functions of relative humidity ( $\phi$ ) and fiber volume fraction ( $V_f$ ), respectively, for unidirectional graphite-epoxy composites. They showed that the composite diffusivity decreased and the  $t_m$  value increased with increased fiber volume. Romanenkov and Machavariani<sup>2</sup> reported calculation of  $D_c$  values for glass-fiber composites from a knowledge of the equilibrium moisture absorption data. Mehta and co-workers<sup>3</sup> studied the sorption and diffusion of water in glass-ribbon-reinforced composite specimens and reported that the presence of impermeable fillers in the resin matrix increased the effective diffusion path length and also decreased the polymeric chain mobility in the filler's proximity.

All the above studies represent results on single fiber volume fractions in general and limit the diffusion mechanism to impermeable fiber composites in particular.

In this paper, data are presented on composites containing a highly permeable fiber (jute) in polyester and epoxy matrices with varied superficial fiber volume fraction ( $V_f$ ) under constant humidity and ambient temperature conditions. Data on the effect of  $V_f$  on the composite diffusivity are also reported. Moisture absorption characteristics of the constituent phases have also been obtained for a comprehensive analysis of the overall diffusion problem in such composites.

Further, the existing theory with respect to impermeable fiber composites has been modified for the case of permeable fiber composites. The experimental data are discussed in relation to this modified theory.

Finally, a ternary diagram is used to picture the moisture absorption situation in such composites under equilibrium conditions, treating such moisture as a third stable phase of the highly saturated composite.

## THEORETICAL CONSIDERATIONS

### Practically Impermeable Fiber Composites

The diffusion coefficient  $D_c$  of an unidirectional composite (Fig. 1) can be calculated<sup>1</sup> in terms of the constituent properties as

$$D_c = D_{11} \cos^2 \alpha + D_{22} \sin^2 \alpha \quad (1)$$

where

$$D_{11} = (1 - V_f)D_r + V_f D_f \quad (2)$$

and

$$D_{22} = (1 - 2 \sqrt{V_f/\pi}) D_r + \frac{D_r}{B_D} \left\{ \pi - \frac{4}{\sqrt{1 - B_D^2 V_f/\pi}} \times \tan^{-1} \left[ \frac{\sqrt{1 - (B_D^2 V_f)/\pi}}{1 + \sqrt{(B_D^2 V_f)/\pi}} \right] \right\} \quad (3)$$

Here  $D_{11}$  and  $D_{22}$  are the composite diffusivities along and across the fiber respectively,  $\alpha$  is the fiber orientation angle with respect to a reference axis,  $D_r$  and  $D_f$  are, respectively, the diffusivities of the resin and the fiber, and  $B_D = 2(D_r/D_f - 1)$ . Thus for impermeable fiber composites, since  $D_r \gg D_f$ , eqs. (2) and (3) can be rewritten as

$$D_{11} = (1 - V_f) D_r \quad (4)$$

$$D_{22} = (1 - 2 \sqrt{V_f/\pi}) D_r \quad (5)$$

Hence, eq. (1) becomes

$$D_c = D_r(1 - V_f) \left[ \cos^2 \alpha + \frac{(1 - 2 \sqrt{V_f/\pi})}{(1 - V_f)} \sin^2 \alpha \right] \quad (6)$$

indicating that  $D_c$  decreases as  $V_f$  increases at a constant  $\alpha$  value.

This behavior is to be expected since Mehta observed that in impermeable fiber composites, as  $V_f$  increased, the diffusion path was distorted and hence

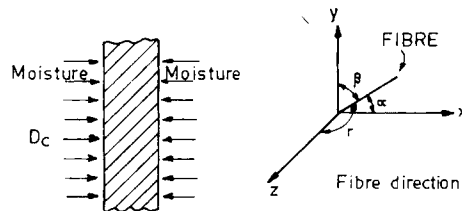


Fig. 1. Schematic of fiber orientation and diffusion direction.

lengthened and that the polymer chain mobility was decreased in the filler's proximity.

Shen and Springer<sup>1</sup> further presented an expression for unidirectional graphite-epoxy specimens, viz.,

$$t_m = \frac{0.67 S^2}{D_x} \quad (7)$$

where  $t_m$  is the time needed to obtain equilibrium conditions,  $S$  is twice the specimen thickness, and  $D_x$  the composite diffusivity in the reference co-ordinate direction. Equation (7) indicates that  $t_m$  increases as  $D_x$  decreases. This coupled with eq. (6), suggests that  $t_m$  increases as  $V_f$  increases, which is true since, as  $V_f$  increases, the diffusion process becomes more retarded, as pointed out earlier.

### Permeable Fiber Composites: Analysis of the Moisture Absorption Phenomenon

A totally different picture emerges in the case of moisture absorption in permeable fiber composites.

Permeable fibers are defined here as those that themselves absorb moisture to a much larger extent than the resin itself, in which they are incorporated. Such fibers are also noted to absorb the resin to considerable extent. Thus a comprehensive analysis of the relative magnitudes of the moisture diffusivities of the pure fiber ( $D_f$ ) resin impregnated fiber ( $D_f'$ ) and the related composite ( $D_c'$ ) becomes important for developing a suitable theory for the moisture absorption mechanism with respect to permeable fiber composites.

A pure 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 a composite system, the inherent porosity of the pure fiber is reduced to various degrees depending upon the level of the fiber impregnation in the resin, under typical curing conditions. The original free volume of the fiber is thus occupied by the resin during the composite fabrication stage itself. The following cases can arise under these conditions.

*Case (i):* Resin partly filling the fiber-free volume as well as covering its permeable surface before the composite sets, so that the basic capillary mechanism of moisture absorption is made less probable and brings the mechanism closer to a diffusion type though not strictly Fickian. In the process, the diffusion coefficient of the original fiber ( $D_f$ ) is modified ( $D_f'$ ), since the fiber is impregnated with a less permeable medium, i.e., the resin, so that

$$D_f > D_f'$$

*Case (ii):* Resin occupying the fiber-free volume mostly and the permeable surface partly, prior to resin-gelling (or setting) stage, which is equivalent to considering a fiber with negligible free volume as compared to its original value, but with a still permeable surface so that

$$D_f \gg D_f' \gg D_r$$

*Case (iii):* Resin filling all the fiber-free volume as well as its surface prior

to gelling, so that it is nearly equivalent to considering a practically impermeable fiber in a resin matrix. Thus,

$$D_f \gg D_f' \geq D_r$$

The most appropriate of the above three cases is the one which is largely governed by typical curing conditions.

## EXPERIMENTAL

Unidirectional untreated (pure) jute fiber composite laminates in polyester (GP grade with MEKP catalyst and Cobalt naphthenate accelerator system) and epoxy [Ciba Geigy (I) LY 556 Grade with HY 951 hardener system] resin matrices have been fabricated using a filament winding technique. They are cured at room temperature for 24 h under 40 psi laminating pressure, followed by a post cure at 100°C for 1 h. The specimens (Fig. 2) cut from these laminates have been coated along the edges and dried at 100°C to constant weight. A typical drying curve is shown in (Fig. 3).

The dried specimens are immersed in water maintained at room temperature ( $25 \pm 2^\circ\text{C}$ ). The specimens are periodically taken out of water and their surface moisture is carefully dried off using a low absorbing filter cloth. The weight measurements are made using a single pan balance with a high degree of accuracy. These measurements have also been carried out on pure resin specimens as well as on pure jute fiber specimens.

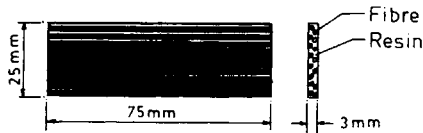


Fig. 2. Unidirectional jute-epoxy specimen.

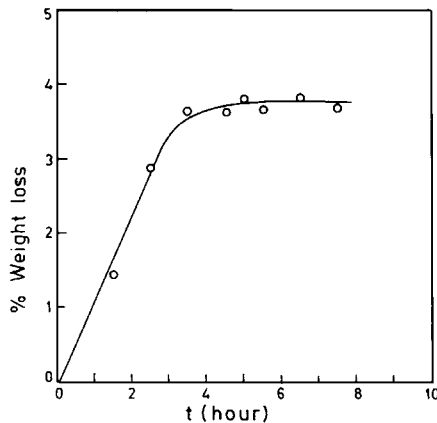


Fig. 3. Drying curve for unidirectional jute-epoxy composite ( $V_f = 0.6$ ).

## RESULTS AND DISCUSSIONS

Figure 4 indicates that the equilibrium resin absorption value of a jute-epoxy curing system (120% by weight) is much higher than that for an uncatalyzed system. This may be expected since the viscosity of the resin in the catalyzed state is reduced due to an associated exotherm, as compared to the viscosity of an uncatalyzed resin.

Figure 5 shows that the equilibrium moisture absorption value ( $M_m$ ) of a pure jute fiber immersed in water is as high as 160% by weight, a value much higher than its equilibrium resin absorption value under curing conditions.

Thus these figures clearly indicate that the fiber does not get as much saturated with a catalyzed resin as with the moisture, considering that the densities of water and a less viscous resin are very close, viz., 1.0 and 1.1, respectively.

Further, Figures 6-8 show that the equilibrium moisture absorption value for pure resin specimens and the jute-resin composites ( $V_f = 0.64$ ), respectively, are 0.65% and 20% by weight, whereas that for a pure jute fiber, as already noted,

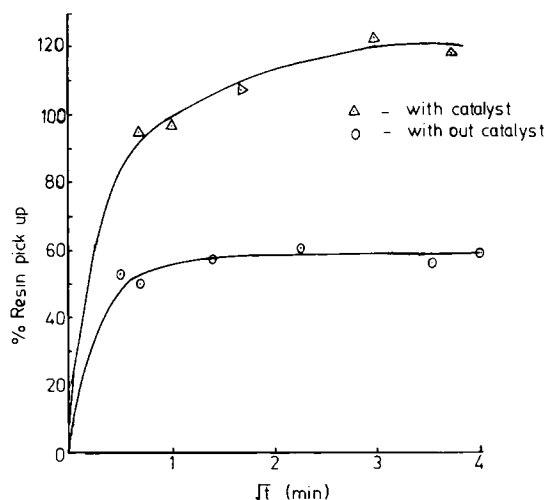


Fig. 4. % Resin absorption vs.  $\sqrt{t}$  for jute-epoxy composite.

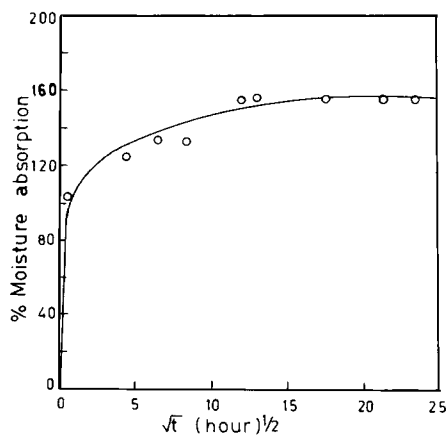


Fig. 5. Moisture absorption curve for untreated jute fiber.

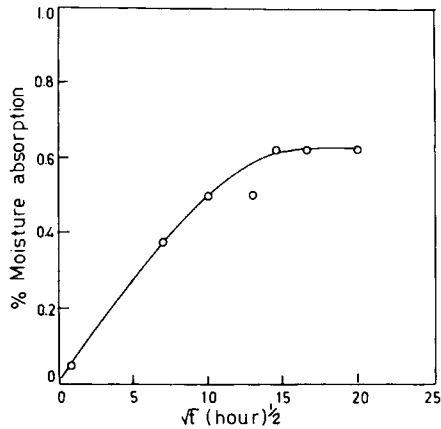


Fig. 6. Moisture absorption curve for polyester resin.

is as high as 160%. These values point out that moisture diffusion coefficient is the highest in pure jute fiber, lower in its composite, and the least in pure resin.

Thus it may be concluded that, in a cured composite, the originally permeable fiber does not get totally saturated with the resin, but absorbs a sufficient amount of resin (before the onset of a gel state) to drastically reduce the equilibrium moisture absorption level of a pure fiber (160%) to a lower value (20%) when made into a composite. This value of 20% is, however, much higher than that for the pure resin, viz., 0.65%.

Finally referring to Table I, it can be seen that the initial slopes of the moisture absorption curves for pure resin, jute-resin composite, and pure jute fiber are 0.05, 1.33, and very high, respectively. The initial slopes being direct measures of the diffusion coefficient, it can be concluded that

$$D_f \gg D_f' \gg D_r$$

thus establishing that case (ii) is the most appropriate one under typical curing conditions considered for the permeable fiber composite. From the above

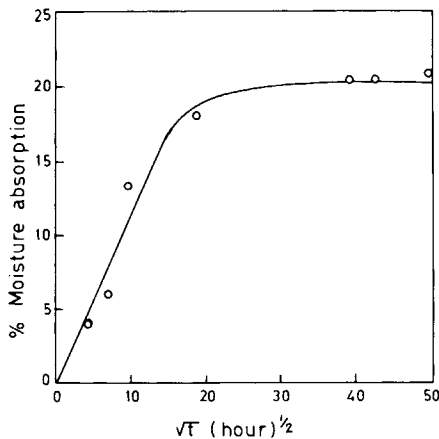


Fig. 7. Moisture absorption curve for jute-polyester composite ( $V_f = 0.64$ ).

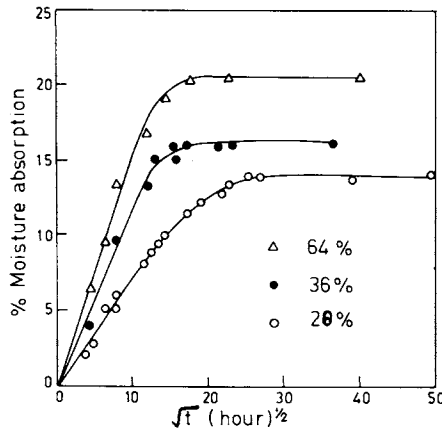


Fig. 8. Moisture absorption curve for jute-epoxy composite for different fiber vol. %.

analysis, it is clear that in permeable fiber composites, it is the volume fraction of a resin impregnated fiber ( $V_f'$ ) that is significant and not the superficial fiber volume fraction  $V_f$  an important parameter for composites with practically impermeable fibers.

Neglecting  $D_r$ , the resin diffusivity in view of its least order of magnitude, eqs. (2) and (3) can be rewritten as

$$D_{11}' = V_f' D_f' \tag{8}$$

$$D_{22}' = F_p \tag{9}$$

where  $F_p$  is the term introduced to account for the transverse fiber diffusivity constituting,  $K_p$ , such that,  $F_p$  can be rewritten as

$$F_p = (K_p D_f') V_f' \tag{10}$$

$(K_p D_f')$  represents the diffusivity transverse to the fiber. Here  $D_f'$  is more or less constant, since it signifies the diffusivity of a resin-saturated fiber prior to gelling conditions in a curing composite.

Thus from eqs. (8) and (10) it is possible to calculate the composite diffusivity  $D_c'$ , in terms of eq. (1), so that

$$D_c' = D_{11}' \cos^2\alpha + D_{22}' \sin^2\alpha \tag{11}$$

or

$$\begin{aligned} D_c' &= V_f' D_f' \cos^2\alpha + K_p V_f' D_f' \sin^2\alpha \\ &= V_f' D_f' (\cos^2\alpha + K_p \sin^2\alpha) \end{aligned} \tag{12}$$

TABLE I  
Moisture Absorption Characteristics of Fiber, Resin, and Composite

	Jute epoxy composite (vol. %)			Pure fiber	Jute polyester composite (64%)	Pure polyester resin
	26%	36%	64%			
% $M_m$	13.5	16.0	20.0	160.0	20.0	0.65
$t_m'$	625.0	400.0	320.0	280.0	260.0	225.00
Slope of initial linear plot	0.66	1.14	1.33	very high	1.3	0.05

Equation (12) is of the same form as eq. (6), derived earlier for the impermeable fiber composites. The value of  $K_p$  for the permeable fiber composites, however, cannot be determined as easily as it can be for the impermeable fiber composites.

$D_c'$  should therefore be determined by a separate method. Assuming a Fickian behavior for the permeable fiber composite considered (which is reasonable when void-free specimens are fabricated and all the fibers are resin-saturated prior to curing), an equation for  $D_c'$  can be derived as follows, starting with McKay's<sup>4</sup> equation:

$$\frac{M_m - M_t}{M_m} = F_s = \frac{4}{l} \left( \frac{D_c' t}{\pi} \right)^{1/2} \quad (13)$$

Rewriting eq. (13) for two different instants of exposure ( $t_1$  and  $t_2$ )

$$\frac{M_m - M_{t_1}}{M_m} = \frac{4}{l} \left( \frac{D_c' t_1}{\pi} \right)^{1/2} \quad (13a)$$

and

$$\frac{M_m - M_{t_2}}{M_m} = \frac{4}{l} \left( \frac{D_c' t_2}{\pi} \right)^{1/2} \quad (13b)$$

subtracting eq. (13b) from eq. (13a) and rearranging for  $D_c'$

$$D_c' = \pi \left( \frac{l}{4 M_m} \right)^2 \left( \frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}} \right)^2 \quad (14)$$

Thus  $D_c'$  can be computed from eq. (14) from a knowledge of the moisture absorption data ( $M - VS - \sqrt{t}$ ), since  $M_m$  is the saturation moisture content and  $[(M_2 - M_1)/(\sqrt{t_2} - \sqrt{t_1})]$  is the slope of the linear portion of the moisture absorption curve for the composite and  $l$ , the specimen thickness.

Therefore the  $D_c'$  value obtained from eq. (14) can be used in eq. (12) to compute the  $K_p$  factor for the permeable fiber composite. Also the value of  $D_f'$  can also be determined by using eq. (14) and  $V_f'$  can be determined experimentally from a knowledge of the resin saturation limit of the permeable fiber.

However, while the diffusivity reduces with increased fiber volume fractions [eq. (6)] in an impermeable fiber composite, it increases with increased fiber volume fractions in a permeable fiber composite [eq. (12)]. This is expected since the overall diffusivity of a composite containing partially permeable fibers (resin-saturated) should increase as its fiber volume fraction increases. Equation (7) may be rewritten for the case of permeable fiber composites as

$$t_m' \propto S^2/D_c' \quad (15)$$

Therefore, as  $D_c'$  increases with  $V_f'$  as noted through eq. (12),  $t_m'$  varies inversely as  $V_f'$  through eq. (15). Thus as the volume fraction of the partially permeable fiber increases, the time needed to reach equilibrium moisture absorption level decreases, since then the overall composite permeability increases. Figures 7 and 8 indicate that the  $M_m$  values for jute-polyester and jute-epoxy composites (both of the same superficial volume fraction, viz., 0.64) are about the same, viz., 20%. This clearly shows that the moisture absorption characteristic in a permeable fiber composite is practically fiber-controlled and that the resin has a



highly retarding effect on the moisture penetration into the composite. This is just a reverse of the effect noticed in composites of practically impermeable fibers. Figure 8 shows the variation of  $M_m$  with  $V_f$  for jute–epoxy composite specimens. The data clearly show that the composite’s diffusivity increases with increased  $V_f$  values.

Table I shows the moisture absorption characteristics ( $M_m, t_m'$  and the initial slope of the moisture absorption curve, which is a measure of the composite diffusivity) of both the composites (jute–polyester and jute–epoxy) and of their constituent phases. The increase of the slopes is a clear indication that the composite diffusivity increases with its superficial fiber volume fraction  $V_f$ . The same holds true even when  $V_f'$ , the actual fiber volume fraction, is evaluated and considered. This is in line with the trend predicted as per eq. (12) for a constant fiber orientation angle  $\alpha$ .

The data of Figure 8 are further represented as a ternary diagram shown in Figure 9. Under equilibrium conditions, moisture may be regarded as a stable phase in the composite along with the resin and the fiber. This is quite reasonable since the equilibrium reached under immersion conditions is stable as compared to a dynamic equilibrium reached in specimens exposed to fluctuating or cyclic conditions of humidity and temperature.

The equilibrium moisture content ( $M_m$ ) of the jute–epoxy specimens is plotted as a function of the fiber volume percent in Figure 10.  $M_m$  is seen to increase with  $V_f$ . This is expected since the composite’s permeability should increase with the increased permeable fiber content.

Figure 11 shows that  $t_m'$  varies inversely as the  $V_f$  value, which is true since as  $V_f$  increases, equilibrium conditions are reached faster due to increased diffusivity as noted earlier. This observation is in accordance with the theoretically developed eq. (15). Extrapolation of the plot to the right side in Figure 11 indicates that  $t_m$  value will be about 1400 h for pure epoxy resin specimens, whereas it is 225 h for pure polyester resin specimens, as seen from Figure 6. This difference is obviously due to a higher moisture resistance of epoxy resins as compared to polyesters, which are noted for their poor moisture resistance due to their susceptibility for hydrolytic degradation.

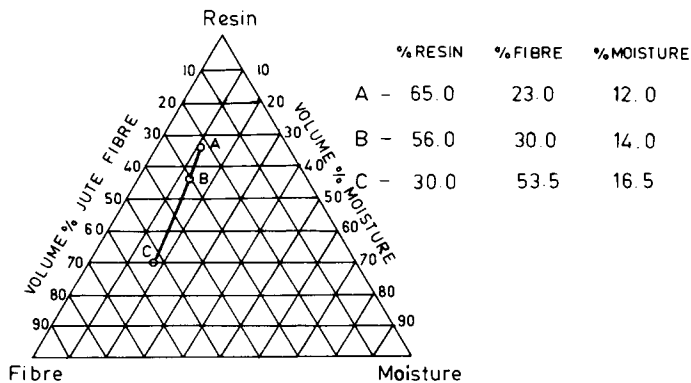


Fig. 9. Ternary diagram showing composition of resin, fiber, and equilibrium moisture content at different fiber vol. %.

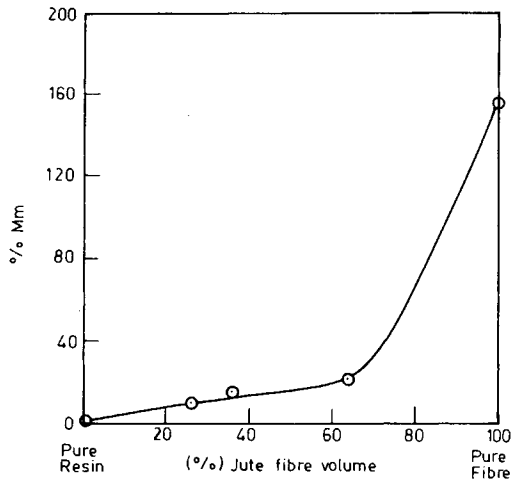


Fig. 10. Variation of equilibrium moisture content ( $M_m$ ) with fiber vol. % for jute-epoxy composite.

### CONCLUSIONS

The diffusivities of resins (polyester, epoxy) are far less than those of highly permeable natural fibers (jute), and as a result the diffusivities as well as the moisture absorption levels of untreated pure jute fiber are brought down drastically, due to their impregnation in resin systems. The effects of increased superficial fiber volume fractions of permeable fibers is to increase the maximum moisture absorption levels and to decrease the time needed to attain such levels, due to increased composite diffusivity under such conditions.

In permeable fiber composites, the mechanism of moisture diffusion is controlled by the impregnated fiber phase.

Studies on the complete applicability of the existing theoretical expressions developed for the impermeable fiber (glass, graphite) composites to permeable

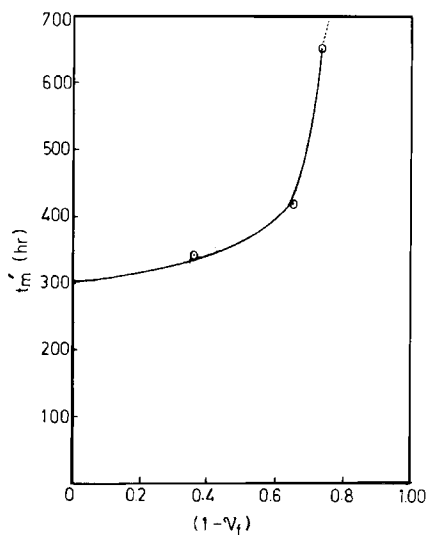


Fig. 11. Variation of time ( $t_m'$ ) to approach  $M_m$  value with  $(1 - V_j)$  for jute-epoxy composite.

fiber (jute) composites need more precise considerations connected with the use of a correct fiber volume fraction term, the volume fraction of a resin-saturated fiber (i.e.,  $V_f'$ ), rather than the superficial fiber volume fraction (i.e.,  $V_f$ ) as is applicable for impermeable fiber composites.

Evaluation of the influences of fiber proximity on the moisture absorption across the permeable fiber is necessary through an analysis of a structure factor as applicable to these composites.

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