

Hygrothermal Aging Studies of Short Carbon Fiber Reinforced Nylon 6.6

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SYNOPSIS

A study of hygrothermal aging, in terms of the kinetics of moisture absorption by nylon 6.6 and its carbon fiber-reinforced composites, has been undertaken. The diffusion of water into the various materials was investigated at 100% relative humidity, by immersion of specimens in water at temperatures of between 25 and 100°C. A mathematical treatment used in analyzing the data was that of a single free phase model of diffusion, which assumed Fickian diffusion and utilized Fick's second law of diffusion. Good agreement was observed between the experimental and theoretical values. The equilibrium moisture content and the apparent diffusion coefficient of the various composites were evaluated. Hygrothermal aging has reduced the tensile properties of both unreinforced and reinforced nylon 6.6, albeit a better recoverability of the properties was achieved by the former after drying. This behavior is explained in terms of the combined action of moisture-induced plasticization and interfacial degradation. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In service, fiber-reinforced plastics are exposed to an environment in which the temperature and moisture contents vary in a prescribed manner. This combined change of temperature and moisture, which is known as the hygrothermal effect can be more damaging to the mechanical properties of the fiber-reinforced plastics than to either of the components separately. Moisture penetration into composite materials is conducted by one major mechanism, namely diffusion. The other common mechanisms of moisture penetration into composite materials are capillarity and transport by microcracks.¹ Each of these mechanisms becomes active only after the occurrence of specific damage to the composites. Frequently, that damage, which enhances moisture penetration by activating those additional mechanisms, is in itself a direct consequence of the exposure of the composite to a hot and moist environment. The rate of moisture absorption by a

composite depends on several factors. For instance, the type of matrix and fiber, the fiber orientation distribution with respect to the direction of diffusion, the conditioning temperature, the difference in water concentration between the composite and the environment, and whether or not the absorbed water reacts chemically with the matrix.

Naturally, hygrothermal aging has two sources, one that is chemical and the other that is physical. The former results from chemical interactions between the penetrating water and one of the constituent materials of the composite. Chemical interaction is mainly hydrolysis of polymer bonds and dissolution and leaching of water-soluble species. Polyesters are hydrolysis-prone resins, due to the ester groups that are highly susceptible to saponification.² The hydrolysis of polybutylene terephthalate and its glass fiber composites has been investigated by Ishak and Lim.^{3,4} Examination of fracture surfaces, using scanning electron microscopy (SEM), revealed the formation of microvoids, the absence of a plastic deformation process, and the degradation at the fiber-matrix interface. The physical source of hygrothermal aging of composite materials is reflected in the plasticization of the ma-

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trix, resulting in a reduction in its glass transition temperature. An example of this manifestation is the absorption of water by polyamides.⁵

Several hygrothermal aging studies have been carried out on fiber-reinforced plastics.^{6,7} However, the studies have mainly been concerned with thermoset matrix-based composites. This article presents the results of a study on the hygrothermal aging of short carbon fiber-reinforced nylon 6.6. Investigation of hygrothermal aging of the composites has been carried out through the study of the kinetics of moisture absorption. The effect of conditioning temperatures and volume fraction of fibers on the diffusion coefficient and equilibrium moisture content is discussed. While many of the mechanical properties of nylon 6.6 composites have been studied,^{8,9} its durability has not been investigated in depth, particularly with regard to hygrothermal aging. Thus, the effect of such an aging process upon the mechanical properties of nylon 6.6 and its composites is reported.

Kinetics of Moisture Absorption

When designing with hygroscopic polymers, such as polyamides, it is essential to know the effect of the absorption of water on this class of polymer, but knowledge of the principles governing the absorption processes is required for a fuller understanding of the behavior of components in service.

In many cases, moisture absorption processes often follow the predictions of Fick's Law,⁶ that is, the mass of water absorbed increases linearly with the square root of time, and then gradually slows until an equilibrium plateau, that is, saturation, is reached. However, there are also cases when deviations from Fickian behavior are observed frequently, that is, when saturation is not achieved or two plateaux in the absorption curve are observed.⁷ This happens when there is damage of the interface or resin degradation.

It has been shown by Crank¹⁰ that for an infinitely large plate of thickness h with single phase diffusion, the mass of water absorbed in time t , M_t , as a percentage of the mass of water absorbed at saturation or equilibrium, M_m , is given by:

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \times \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2(2n+1)^2\right] \quad (1)$$

The whole curve can be resolved into two parts, described by two simple equations.¹¹

For $\frac{Dt}{h^2} > 0.05$, the above relationship reduces to

$$\frac{M_t}{M_m} = 1 - \frac{8}{\pi^2} \exp\left[-\left(\frac{Dt}{h^2}\right)\pi^2\right] \quad (2)$$

The second part, for $\frac{Dt}{h^2} \ll 0.05$, eq. (1) can be reduced to:

$$\frac{M_t}{M_m} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{h^2}\right)^{1/2} \quad (3)$$

From eq. (3), the diffusivity or diffusion coefficient, D , can be calculated from the initial linear portion of the absorption curve.

When the diffusion is (a) Fickian, and (b) is a function of temperature only, the diffusivity is related to temperature by the Arrhenius relationship, given by:

$$D = D_0 \exp(-E_a/RT) \quad (4)$$

where D_0 is the preexponential coefficient, or permeability index, R , E_a , and T are the gas constant, activation energy, and absolute temperature, respectively.

EXPERIMENTAL

Materials

The matrix material used was commercially available "Maranyl" A100 Nylon 6.6, manufactured by Imperial Chemical Industries, and the material was in granular form.

The fiber used was Courtaulds "Grafil" XA-S high-strength chopped carbon fibers.

Processing

The nylon 6.6 granules and various loadings (10, 20, 30, and 40% by wt) of 6 mm chopped carbon fibers were compounded in a Schwabenthan single screw extruder. The extruded strands were chopped in a granulator to obtain reinforced granules. The reinforced granules were injection-molded into the test specimen on a Negri Bossi NB60 microprocessor-controlled reciprocating screw-type injection mold-

ing machine. An automatic shut-off nozzle was used to prevent nylon leakage between injections. The molding temperatures and other processing conditions were set up as closely as possible to those recommended by Courtaulds for the molding of carbon-fiber reinforced nylon 6.6.¹² The nylon 6.6 and reinforced granules were dried overnight at 100°C under vacuum prior to extrusion and injection molding.

Sample Characterization

The volume fraction of fibers was measured by chemical digestion of matrix. From a knowledge of the fiber and matrix densities, the volume fraction of fibers, V_f , was calculated using the equation below:

$$V_f = \left[\frac{\rho_f}{\rho_m \times M_f} (M_s - M_f) + 1 \right]^{-1} \quad (5)$$

where ρ is the density, M is the weight, and subscripts f , m , and s refer to fiber, matrix, and sample, respectively.

The measurement of fiber length was carried out on a Reichert-Jung MOP-1, a digital image analyzer, interfaced to a microcomputer. At least five hundred fibers were measured from each batch.

The determination of the degree of crystallinity of the nylon 6.6 and its composites was carried out on a differential scanning calorimeter, Perkin-Elmer DSC-2. Samples weighing approximately 20 mg were used. The heating rate used was 20°C/min and Indium was adopted as a standard substance for calibration. A value of 45.0 cal/g was taken as the heat of fusion for the perfectly crystalline nylon 6.6 sample.¹³

Kinetics of Moisture Absorption

The specimens were dried at 100°C over silica gel in a vacuum oven at 100°C until a constant weight was attained prior to immersion in water in thermostated vessels at 25, 40, 60, 80, and 100°C. The 100°C vessel was a 5-liter glass reactor, fitted with a water condenser; the other temperatures were achieved in a stainless steel water bath. Weight gains, after exposure, were recorded by removal of the specimen from the environment and by weighing them periodically on a Stanton balance with a precision of 1 mg.

The percentage gain at any time t , as a result of moisture absorption, was determined by:

$$M_t(\%) = \frac{(W - W_d)}{W_d} \times 100 \quad (6)$$

where W_d and W denote, respectively, weight of dry material (i.e., the initial weight of the material prior to exposure to the environment) and weight of moist material. The percentage equilibrium moisture absorption, M_m , was calculated as an average value of several consecutive measurements that showed no appreciable additional absorption.

Tensile Test

The study of the effect of hygrothermal aging on the tensile properties was carried out on both unreinforced and reinforced nylon 6.6 ($V_f = 0.27$). The specimens were conditioned to 100% RH at different immersion temperatures, that is, 25, 60, 80, and 100°C prior to testing. The tensile test was conducted on an Instron Universal Testing Machine model 1122 at 20°C, with a strain rate of $1.2 \times 10^{-3} \text{ s}^{-1}$, using ASTM procedure D-1708.

Scanning Electron Microscope

Examination of the fracture surface was carried out using an ISI Scanning Electron Microscope. The objective was to get some idea of the mode of fracture and the condition of the matrix and fiber surfaces. The fracture ends of the tensile specimens were mounted on aluminium stubs and were sputter coated with a thin layer of gold to avoid electrical charging during examination.

RESULTS AND DISCUSSION

Samples Characterization

The average fiber volume fractions of the nylon 6.6 composite samples were found to be 0.06, 0.13, 0.19, and 0.27. Figure 1 shows the cumulative fiber length distribution for the various composite samples. It can be seen that the fiber lengths have been seriously degraded from their initial length of 6 mm. The number average lengths, l_n , are in the range of 0.2 to 0.25 mm. The likely causes of fiber damage are fiber-fiber interaction, fiber contact with processor surface, and fiber interaction with the viscous polymer melt during processing.¹⁴

The DSC melting endotherms of nylon 6.6 and its composites ($V_f = 0.27$) are shown in Figures 2 and 3, respectively. The actual values of melting

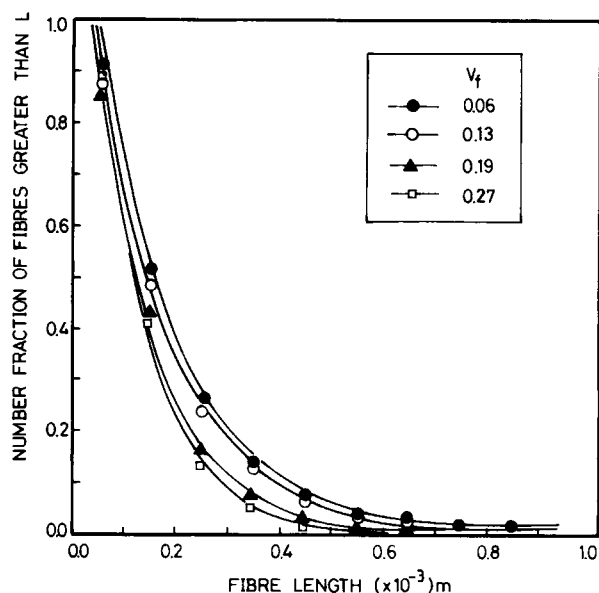


Figure 1 Cumulative fiber length distribution.

point and degree of crystallinity are listed in Table I. In all cases, the melting points, T_m , are in the range of 265° to 268°C. The percentage degree of crystallinity is found to be approximately 34% for the unfilled nylon 6.6. This value is in agreement with the range of values, that is, 31–34%, reported by other workers.¹⁵ The reinforced nylon 6.6 samples are observed to have slightly higher degrees of crys-

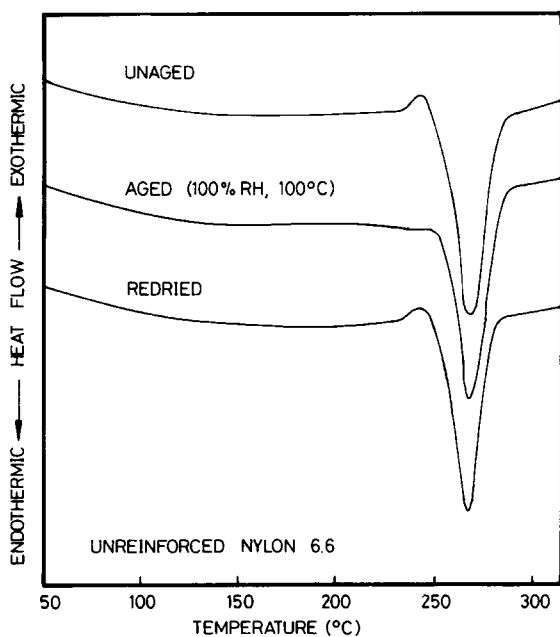


Figure 2 DSC thermograms of unaged, aged, and redried nylon 6.6.

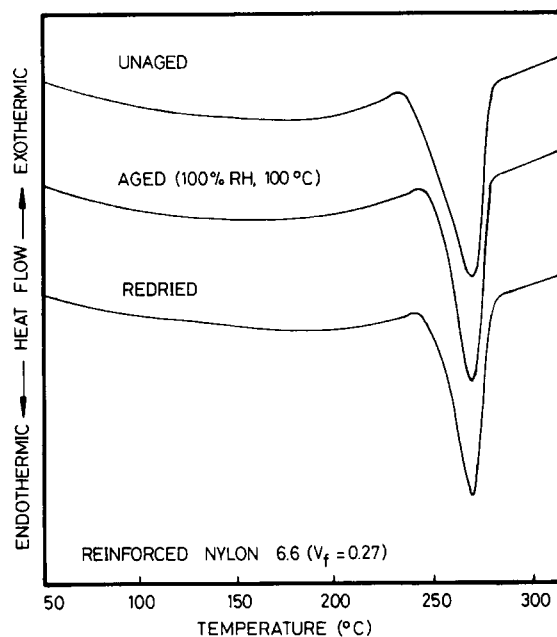


Figure 3 DSC thermograms of unaged, aged, and redried, reinforced nylon 6.6 ($V_f = 0.27$).

tallinity. This indicates that some modification in the morphology of the nylon 6.6 matrix has taken place as a result of the incorporation of carbon fibers. Other studies have shown¹⁶ that carbon fibers, used to reinforce nylon 6.6, can modify the microstructure of the surrounding matrix by providing nucleation sites for spherulitic growth along fiber surfaces.

From the DSC thermograms of aged nylon 6.6 and its composites, it can be seen that there is no apparent influence of moisture absorption on the shapes and positions of the melting peaks. The slight reduction in the degree of crystallinity of the aged samples may be attributed to small-scale reorganization of the molecules, which results in a small disruption of the ordered structure as a consequence of moisture absorption. In another study, involving nylon 6, Russell and Beaumont¹⁷ have observed that

Table I DSC Results for Unaged, Aged, and Redried Nylon 6.6 and its Composites ($V_f = 0.27$)

Condition	V_f	T_m (°C)	Crystallinity (%)
Unaged	0.00	266.92	33.94
	0.27	267.64	37.75
Aged	0.00	265.07	29.33
	0.27	266.32	33.51
Redried	0.00	265.68	31.44
	0.27	267.13	35.17

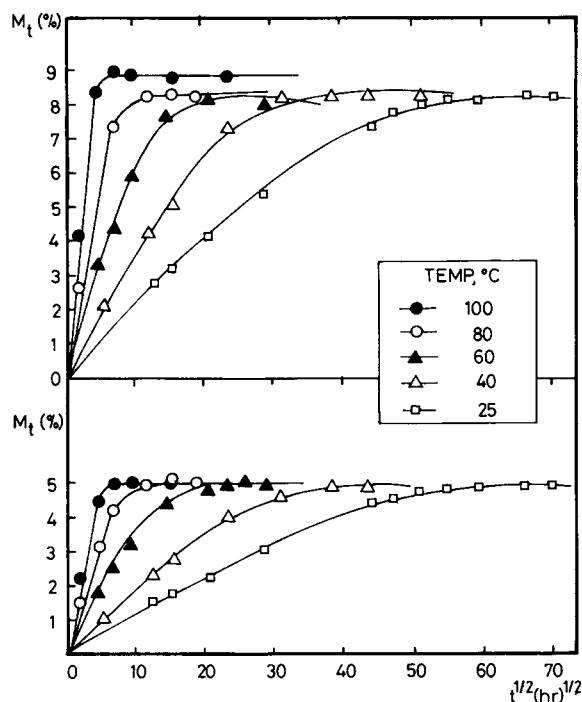


Figure 4 The effect of conditioning temperature on the moisture absorption process of (a) unreinforced nylon 6.6 ($V_f = 0.00$), and (b) reinforced nylon 6.6 ($V_f = 0.27$).

exposure to boiling water has no significant effect on the structure and morphology of the spherulites of the moldings. In the present work, upon redrying, the melting point and the degree of crystallinity of aged nylon 6.6 and its composites shifted back to slightly higher values. This may be attributed to the improvement in the crystal perfection of nylon 6.6. For the case of unaged and redried nylon 6.6 samples, a prominent crystallization exotherm peak is observed to take place during the heating process, that is, just before the melting peak is reached. This may

be due to a rearrangement of segments frozen in by rapid cooling at the mold wall during the injection molding process. A similar observation has been encountered by Karger-Kocsis and Friedrich,¹⁸ who also discovered that the intensity of the exotherm peak diminishes when the DSC samples were taken from the core region of the molded nylon 6.6.

Kinetics of Moisture Absorption

Figures 4 (a) and (b) show the percentage moisture absorption of both unreinforced and reinforced nylon 6.6 ($V_f = 0.27$), at various conditioning temperatures, as a function of $t^{1/2}$. The initial linear relationship between M_t and $t^{1/2}$ is clearly observed in each case, followed by saturation. In all cases, good agreement is obtained between the theoretical prediction of eq. (2) (shown by the solid lines) and the experimental points, which clearly indicates that Fickian behavior is observed. While the equilibrium or maximum moisture content is almost independent of temperature, the diffusion rate is greatly influenced by temperature. Increasing the conditioning temperature has significantly reduced the time required to reach equilibrium moisture content.

The values of apparent diffusion coefficients and equilibrium moisture content, obtained at various conditioning temperatures, are summarized in Table II. No correction for edge effects has been made in the present study, due to the complexity of fiber length and the fiber orientation distribution in the composite system. It is accepted that short fiber reinforced thermoplastics, SF RTP, are among the most complex of composite materials. In their final, molded form, they consist of misaligned arrays of variable length fibers, dispersed in a viscoelastic matrix. The subject of SF RTP has been extensively reviewed by Folkes.¹⁹ The values of diffusion coef-

Table II The Effect of Conditioning Temperature on the Apparent Diffusivity, D , and Equilibrium Moisture Content, M_m , of Unreinforced ($V_f = 0.0$) and Reinforced ($V_f = 0.27$) Nylon 6.6

V_f T (°C)	0.00		0.27	
	$D \times 10^{-12}$ ($m^2 \text{ sec}^{-1}$)	M_m (%)	$D \times 10^{-12}$ ($m^2 \text{ sec}^{-1}$)	M_m (%)
25	0.48	8.1	0.42	4.83
40	1.29	8.25	1.05	4.85
60	4.76	8.13	3.81	4.87
60	14.69	8.23	14.19	4.90
100	44.49	8.80	40.50	4.90

ficients, obtained in the present study, are in agreement with the range of values reported by Loos and Springer.²⁰ According to these workers, the values of diffusion coefficients for most polymers and their composites fall in the range of 10^{-11} to 10^{-12} $\text{m}^2 \text{s}^{-1}$.

A plot of $\ln D$ vs. the reciprocal of absolute temperature, $1/T$, is shown in Figure 5. The apparent diffusivities show a linear Arrhenius plot over the entire temperature range studied. There is no T_g -related discontinuity observed. The corresponding values of the activation energy, E_a , of 56.74 and 60.47 kJ mol^{-1} are obtained for the unreinforced and reinforced nylon 6.6, respectively. Apicella et al.²¹ have obtained a value of 55.6 kJ mol^{-1} for the activation energy of epoxy resin.

Figure 6 shows the effect of volume fraction of fibers, V_f , on the moisture uptake at a conditioning temperature of 60°C . As before, in all cases, good agreement is observed between the theoretical predicted values and the experimental values. It can be seen that equilibrium moisture content decreases with increasing fiber volume fraction and this can be attributed to the decrease volume fraction of the matrix, V_m , with increasing V_f . The values of apparent diffusivity and equilibrium moisture content for the various composites are tabulated in Table III. The theoretical amount of equilibrium moisture content for the composite, $(M_m)_c$, can be deduced from the corresponding equilibrium moisture con-

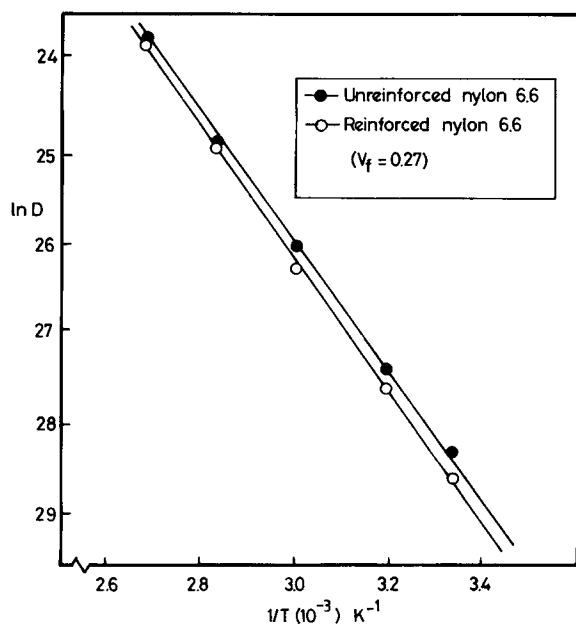


Figure 5 Arrhenius plot to determine the apparent activation energy for nylon 6.6 and reinforced nylon 6.6 ($V_f = 0.27$).

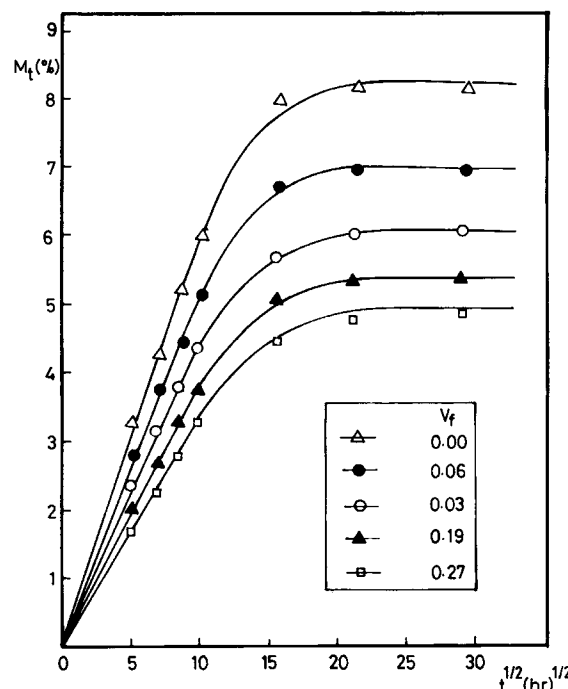


Figure 6 Plots of M_t vs. $t^{1/2}$, showing the effect of volume fraction of fibers, V_f , on the moisture uptake of nylon 6.6 at 60°C .

tent of the unfilled resin, $(M_m)_r$. By assuming that the fibers do not absorb any moisture, $(M_m)_c$ and $(M_m)_r$ are related by the expression²⁰:

$$(M_m)_c = (M_m)_r \times W_r \quad (7)$$

where W_r is the weight fraction of the resin in the composites. It is suggested that, in addition to diffusion, the presence of fibers may give rise to other mechanisms of moisture absorption, such as capillarity and transport by microcracks. The activation of the latter two mechanisms is expected to result in an increase in the equilibrium moisture content. However, such an observation is not apparent, as can be seen in Table III. In all cases, the experimental values are always lower than the theoretical values. This discrepancy may be due to changes in the morphology of the nylon 6.6 matrix. From the previous discussion, the degree of crystallinity of nylon 6.6 has been found to increase with the incorporation of short carbon fibers. It is known that increasing the degree of crystallinity results in a considerable reduction of water uptake of polyamides.²² In the case of nylon 6.6, Starkweather et al.²³ observed that the equilibrium water absorption at 100% RH is reduced from 11 to 8% as its crystallinity is increased from 30 to nearly 50%. Table III also

Table III The Effect of Fiber Volume Fractions on the Apparent Diffusivity, D , and Equilibrium Moisture Content, M_m , at 60°C

V_f	$D \times 10^{12}$ ($\text{m}^2 \text{sec}^{-1}$)	M_m (%) Experiment	$(M_m)_c$ (%) Theory
0.00	4.76	8.13	—
0.06	4.80	6.88	7.40
0.13	4.54	5.99	6.62
0.19	4.36	5.33	5.84
0.27	3.81	4.87	4.94

indicates that incorporation of carbon fiber into the nylon 6.6 matrix has led to a slight reduction in the apparent diffusivity. Since carbon fibers are insensitive to moisture²⁴ the reduction observed may have been due to the hinderance of the direct moisture diffusion into the matrix, as a result of complex fiber orientation distribution within the composites. This complex fiber orientation, coupled with a wide fiber length distribution, can give rise to discontinuity of the diffusion path in the resin.

Tensile Test

Figures 7 and 8 show the stress-strain curves for both unreinforced and reinforced nylon 6.6 ($V_f = 0.27$), conditioned at different temperatures, along with the dry samples for comparison. In Figures 7 and 8, only specimens conditioned at 25 and 100°C are shown. The rest of the specimens have been

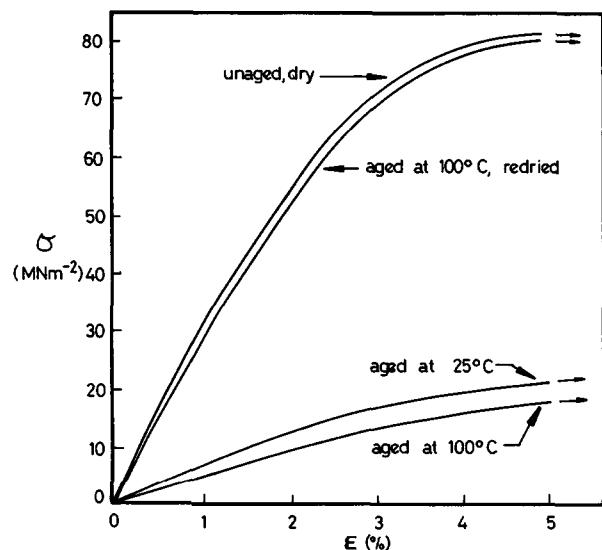


Figure 7 Stress-strain curves for unaged, aged, and re-dried nylon 6.6, tested at 20°C.

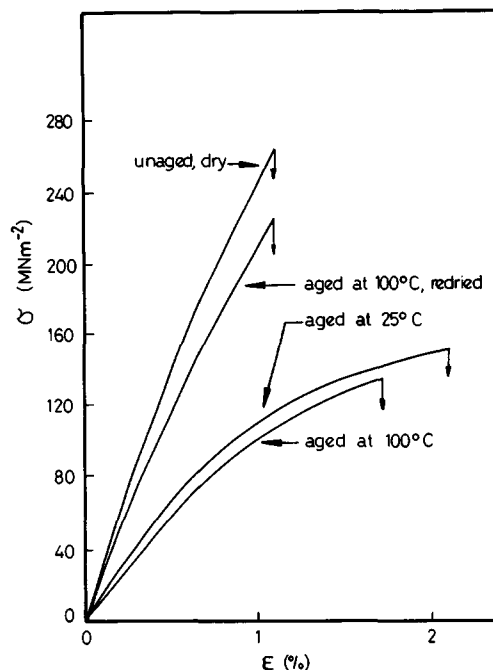


Figure 8 Stress-strain curves for unaged, aged, and re-dried, reinforced nylon 6.6 ($V_f = 0.27$), tested at 20°C.

omitted for reasons of clarity, but their respective stress-strain curves lie between these two extremes. From Figure 7, it can be seen that the presence of water has decreased the stress level at a given strain, as compared to the dry nylon 6.6. This decrease occurs because of the plasticization effect of absorbed moisture. The extent of this plasticization process seems to increase with increasing conditioning temperature, as reflected from the further lowering of stress-level at any given strain, as the conditioning temperature increases to 100°C. In Figure 8, similar trends are also observed in the case of reinforced nylon 6.6. Hygrothermal aging has caused a dramatic reduction in both strength and stiffness of the composite. From the stress-strain curves, it appears that the absorbed moisture has significantly changed the mode of fracture of the composite from being brittle, that is, low fracture strain to a ductile fracture with relatively higher fracture strain.

The extent of deterioration in the derived stress-strain parameters, caused by hygrothermal aging, is shown in Table IV. Table IV illustrates the effect of conditioning temperatures on the tensile modulus of both unreinforced and reinforced nylon 6.6 and also illustrates composite tensile strength. It is evident that there are slight reductions in the derived tensile parameters as the conditioning temperatures increases. In the case of reinforced nylon 6.6, the decreases in both tensile modulus and tensile

Table IV The Effect of Conditioning Temperature, T on Tensile Modulus of Unreinforced Nylon 6.6, E_m , Tensile Modulus of Nylon 6.6 Composites, E_c , and Tensile Strength of Nylon 6.6 Composites, σ_c^* ($V_f = 0.27$)

T (°C)	E_m (GPa)	E_c (GPa)	σ_c^* (MPa)
25	0.89	15.93	151.67
40	0.76	14.65	149.04
60	0.70	14.32	146.98
80	0.70	13.65	141.35
100	0.63	12.71	137.23

strength probably arise as a result of the combined effect of plasticization of the matrix, as well as the degradation of the polymer-fiber interface. As the water conditioning temperature increases, the moisture attack on the interface becomes more significant, so that at higher temperatures the efficiency

Table V Tensile Properties of Unaged, Aged (100% RH at 100°C), and Redried, Unreinforced, and Reinforced Nylon 6.6

V_f	Tensile Parameters	Unaged	Aged	Redried
0.00	E_m (GPa)	3.42	0.63 (18.42) ^a	3.37 (98.57) ^b
0.27	E_c (GPa)	28.94	12.71 (43.92) ^a	24.58 (84.95) ^b
	σ_c^* (MPa)	260.52	137.23 (52.67) ^a	224.33 (86.11) ^b

^a Percentage retention of the tensile properties after aging.

^b Percentage recovery of the tensile properties after redrying.

of stress transfer decreases and an overall reduction in derived parameters is observed. In an earlier study on short glass fiber-reinforced nylon 6.6, Berry and Stanford²⁵ observed that absorbed moisture has resulted in a large reduction in the tensile modulus

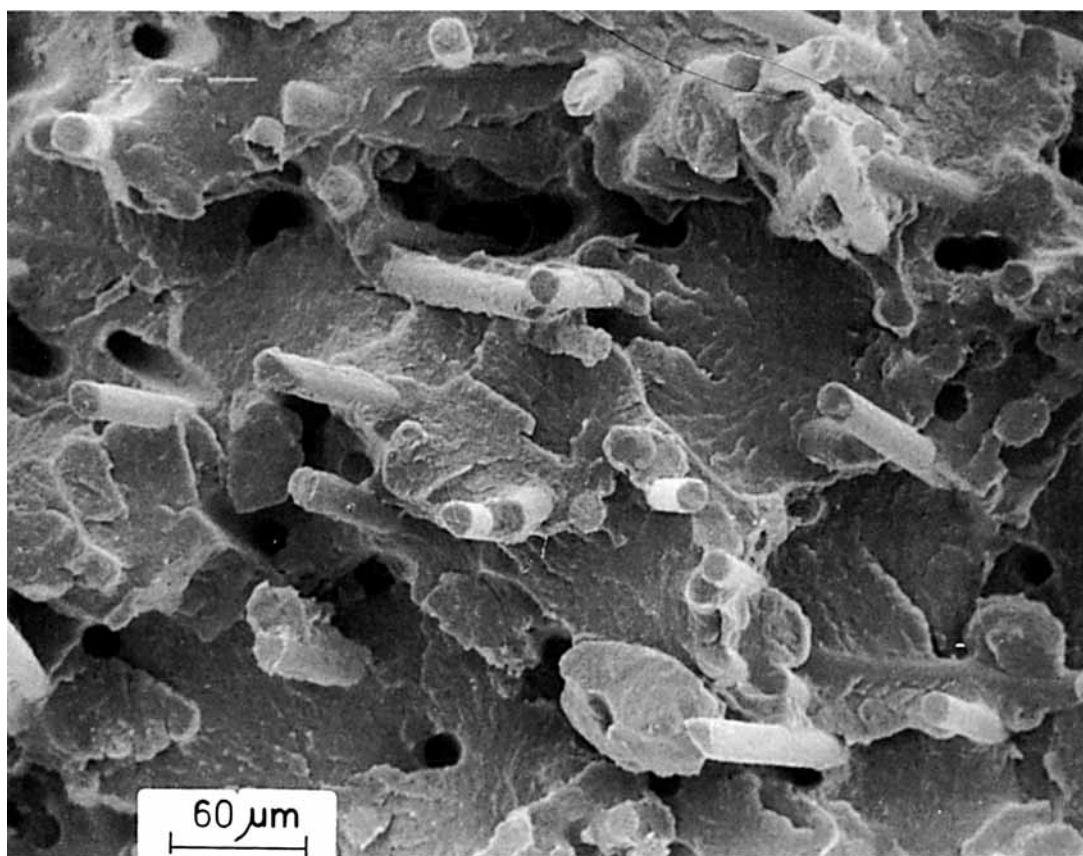


Figure 9 SEM micrograph of the fracture surface of unaged nylon 6.6 composites ($V_f = 0.27$).

and tensile strength of the materials. The interfacial shear strength, calculated using a modified Kelly-Tyson model, varied from 7.5 MPa for the aged composites to 58 MPa for the dry, unaged composite materials.

Further investigations on the extent of deterioration of the stress-strain properties of nylon 6.6 and its composites have been performed by drying both materials, which have been conditioned under the most extreme immersion temperature, that is, at 100°C. After these specimens have reached a constant weight (then assumed to be fully dried), they were subjected to a tensile test. The stress-strain curves obtained are shown in Figures 7 and 8. As expected, the residual stress-strain properties of the unreinforced nylon 6.6 are almost fully recovered. After drying, the stress at any given strain level increases dramatically, although it appears to be slightly less than the unaged specimen. This excellent recovery indicates that hygrothermal aging in unreinforced nylon 6.6 is purely physical in nature. The effect of water is merely that of a plasticiser

and, on its removal, the stress-strain properties are almost fully restored. On the contrary, as is shown in Figure 8, the stress-strain properties of the reinforced nylon 6.6 are not fully recovered, as in the case of unreinforced nylon 6.6 (see Fig. 7). The percentage recovery of the derived stress-strain parameters for both of these materials are compared in Table V.

The differences in the percentage recovery between nylon 6.6 and its composites lie in the fact that, in the latter, the action of water may have resulted in the partial disruption of the bonds between the fiber and matrix (such as debonding) and the formation of additional microcavities, which would be filled with water. Upon drying, these cavities will act as stress concentrators, which can then initiate matrix cracking, leading to reductions in both stiffness and strength of the composite. While plasticization is a reversible phenomenon, microcavitation damage is permanent one. It is the latter that seems to play a major role in determining the residual properties of the composites.

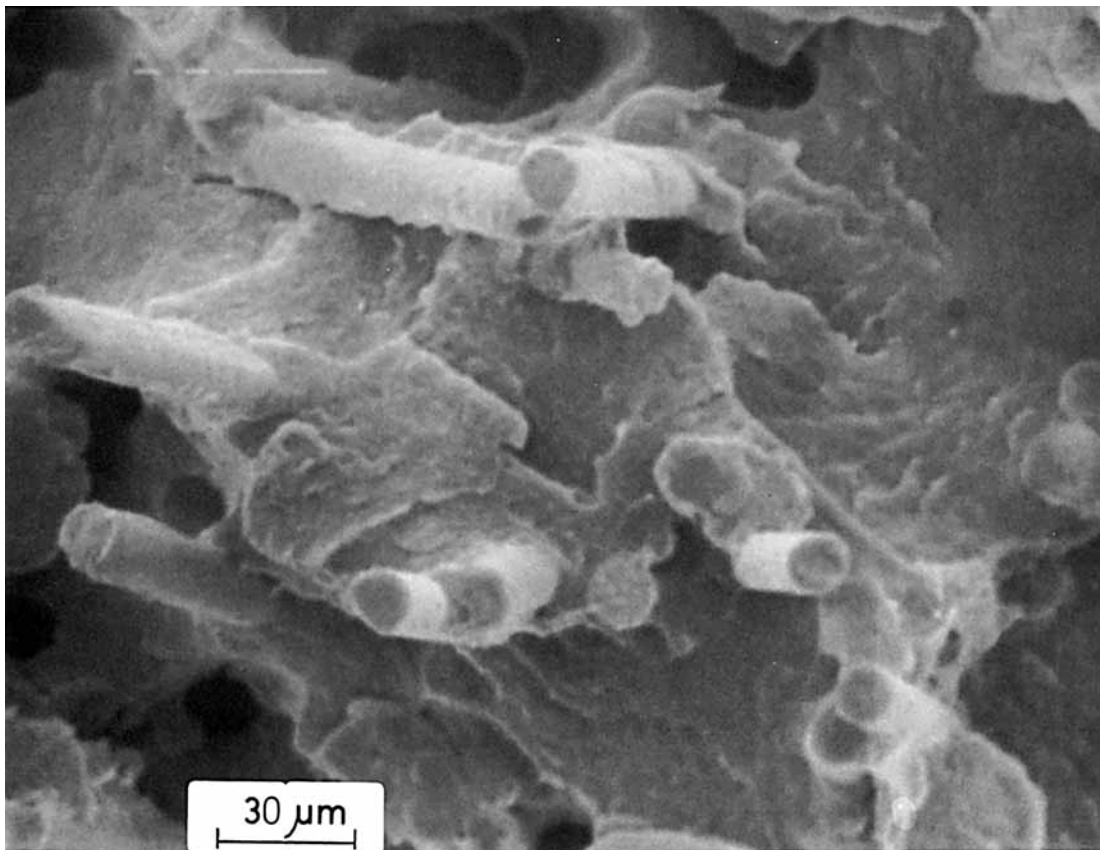


Figure 10 SEM micrograph of the fracture surface of unaged nylon 6.6 composites ($V_f = 0.27$), indicating some matrix retention on the fiber surfaces.

Fractographic Studies

Figure 9 shows the fracture surface of unaged reinforced nylon 6.6 ($V_f = 0.27$) tested at room temperature. The nylon 6.6 matrix indicates a predominantly brittle behavior with extensive fiber pull-out and little fiber fracture is evident in the crack plane. The condition of the pull-out fiber surfaces is generally considered as an indication of the strength of the fiber matrix interfacial bond where clean fibers indicate poor bonding and the reverse indicate good bonding. Initial examination of the fibers shows apparently clean fibers, but closer observation at high magnification, as shown in Figure 10, reveals some degree of matrix retention on the fiber surface.

Figure 11 shows the fracture surface of an aged composite ($V_f = 0.27$), conditioned at 100% RH and 100°C. It can be seen that the presence of moisture has the effect of increasing matrix ductility and reducing the effectiveness of the interfacial bond. This is indicated by the overall increase of fiber pull-out length and by the absence of matrix on the surface of the fibers.

CONCLUSION

Under all conditions studied, the absorption process was found to follow the predictions of Fick's Law, where the amount of moisture absorbed increases linearly with the square root of time and then gradually slowed down until an equilibrium moisture content is reached. The classical, single free-phase model of absorption has been applied successfully to the kinetic data and thereafter the values of apparent diffusion coefficient have been evaluated. Unlike the equilibrium moisture content, the apparent diffusion coefficient was found to be greatly affected by the conditioning temperatures, where it increases with increasing conditioning temperature. The effect of increasing volume fraction of fibers, into the nylon 6.6 matrix, has been found to reduce the values of both the apparent diffusion coefficient and the equilibrium moisture content. The reduction in the values of the latter parameter indicate that the major amount of moisture is absorbed by the hygroscopic nylon 6.6 matrix. Hygrothermal aging has reduced the tensile properties of both nylon 6.6

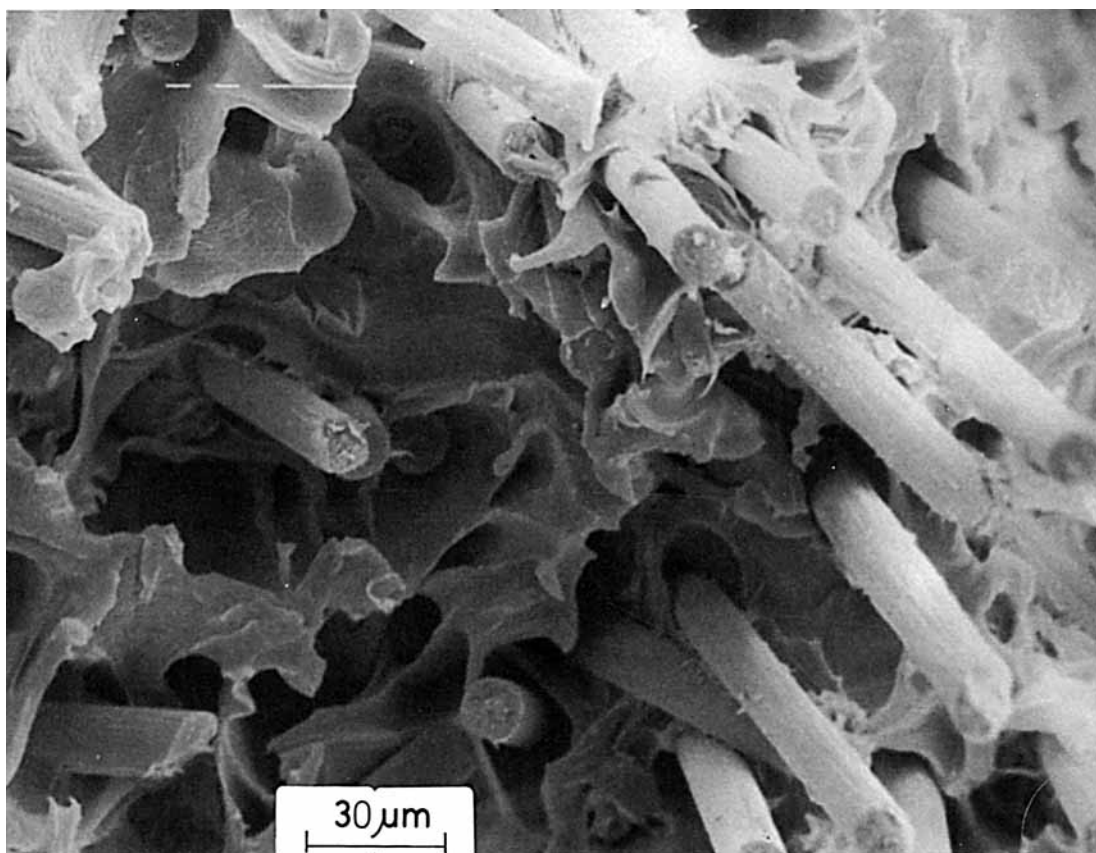


Figure 11 SEM micrograph of the fracture surfaces of aged nylon 6.6 composites ($V_f = 0.27$), indicating extensive fiber pull-out.

and its composites. This has been attributed to plasticization of the matrix and interfacial degradation.

NOMENCLATURE

D	Diffusion coefficient or diffusivity
D_o	Permeability index
E_a	Activation energy
l	Fiber length
l_n	Number average fiber length
M_t	Percentage of water or moisture absorbed at time t
M_m	Percentage of moisture absorbed at saturation, equilibrium, or maximum moisture content
$(M_m)_c$	M_m for composite
$(M_m)_r$	M_m for matrix
R	Gas constant
t	Time
T	Temperature
T_g	Glass transition temperature
T_m	Melting temperature
V_f	Volume fraction of fiber
V_m	Volume fraction matrix
W	Weight of sample

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