A THERMAL STUDY ON MOISTURE ABSORPTION BY EPOXY COMPOSITES

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The water sorption kinetics of an epoxy matrix-carbon fiber composite with different degrees of polymerization was studied. It was observed that the diffusion coefficients, determined perpendicularly to the fiber direction, are increased by increasing the cure degree. Only a small portion of the bonded water is released when the specimen are heated to 200 °C.

The effects of moisture on some properties of the composite were also investigated. The T_g values determined on fully polymerized samples, show lowerings of 70 degrees; moreover, the plasticization power of the bonded water increases on decrease of the temperature of conditioning of the specimens.

Finally, the water present in the matrix considerably reduces the thermal stability of the composite.

Owing to their very high mechanical strength and lightness, composites are becoming very popular materials in the aerospace, aeronautical, electronic and automotive industries.

The mechanical properties and thermal stabilities of the epoxy-based composites are negatively affected by their high sensitivity to humidity. The water absorbed is in part linked by hydrogen-bonds to the epoxy matrix, and in part may be incorporated along the cracks present and in the fiber-matrix interface [1]. Therefore, in order to predict the long-term behaviour of such composites, it is necessary to study quantitatively their interactions with moist environments.

In this paper, some aspects of the absorption of moisture by high-performance graphite fiber-epoxy composites have been investigated. In particular, the following goals were pursued:

a) determination of the maximum moisture content absorbed at different temperatures and partial pressures of water;

b) the water absorption kinetics and evaluation of the water diffusion coefficient for the diffusion-controlled stage;

c) the influence of the moisture absorption processes on the mechanical properties and thermal stabilities of these materials.

To this end, samples with different cure degrees and annealed at different temperatures and relative humidities were studied by means of thermogravimetric, differential scanning calorimetric and thermomechanical measurements.

Experimental

The epoxy matrix employed (composed essentially of tetraglycidylmethylenedianiline, a novolac resin and 4,4'-diaminodiphenylsulfone), reinforced with unidirectional graphite fiber, was cured according to the following cycle: heating (in an autoclave) from room temperature to 175° at a rate of 1 deg/min, holding at this temperature for periods ranging between 20 and 90 min, and finally cooling at 1 deg/min to room temperature. All tests were performed on four different "phases": (A) material cured for 20 minutes, (B) material cured for 90 min, (C) cured for two cycles of 90 minutes, and (D) "prepreg" non-polymerized.

During tests, the dry specimens were placed in a hydrothermal chamber (which could be programmed to relative humidities (R.H.) of 12 to 98% in the temperature range 5–85°) and the mass increase was then measured periodically by weighing.

Table 1 reports some characteristics of the sample and the conditions employed in the runs.

In order to understand the kinetics and the chemical and morphological changes induced in the system by the cure history and water aging, a Perkin–Elmer 4 System

Table 1 Sample characteristics and conditions of moisture absorption experiments

Sample	Specimen size, mm	Curing time, min	Conditioning		
			T, °C	R.H. %	t, day
	$50 \times 50 \times 1.55$	20	45	84	143
A	$50 \times 50 \times 1.47$	20	45	84	185
	$50 \times 50 \times 1.49$	20	70	84	128
	$50 \times 50 \times 1.49$	90	45	84	142
B	$50 \times 50 \times 1.50$	90	70	84	107
	$50 \times 50 \times 1.49$	90	70	84	150
	$50 \times 50 \times 1.44$		45	84	185
C	$50 \times 50 \times 1.50$	2 cycles of 90	70	84	107
	$50 \times 50 \times 1.47$		70	84	150
			22	60	100
			30	90	58
D	$50 \times 50 \times 0.16$	0	45	84	60
Prepreg			50	100	21
			70	84	30

(with DSC–4 and TMS–2 units) and a DuPont 950 Thermogravimetric Analyser were used.

Results and discussion

Sorption kinetics

Figure 1 reports for samples A, B and C the percentage water content, $M\%$, as a function of $t^{1/2}$, obtained for the isotherms at 45° and 70° with R.H. = 84%. It may be noted that all isotherms initially follow Fick's equation, and it is therefore possible to determine the water diffusion coefficients. Moreover, the experiments were performed for long enough to allow estimation of $M_\infty\%$, i.e. the maximum percentage which can be attained under given environmental conditions.
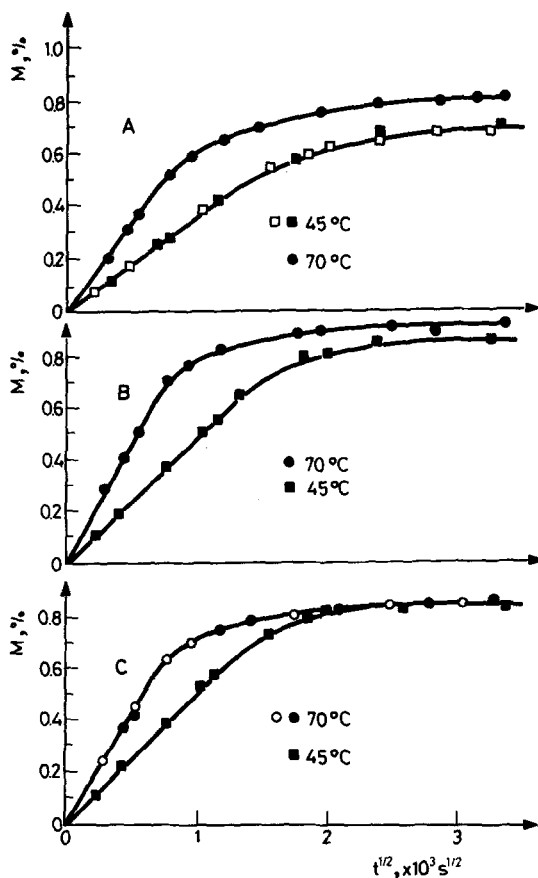

Fig. 1 Absorption curves for samples A, B and C

Data relevant to distinct runs are reported in Fig. 1 for two isotherms; the very good correspondence demonstrates the high reproducibility of the measurements. There are very few differences between the data particularly for samples B and C; this is due to the very close polymerization grades of the specimens which were cured for 90 min and for two cycles of 90 min: as determined by DSC, the residual heats of polymerization (ΔH_r are equal to -50.2 J/g, -8.4 J/g and -6.3 J/g respectively for A, B, C samples. To study thoroughly the influence of the degree of polymerization on the water transport in this composite, we also made some determination on sample D (prepreg): here we consider only the isotherms at 45° and 70°. In Fig. 2, the differences (M%$-$Mi%) are reported vs. $t^{1/2}$: the Mi% values were determined by extrapolating the curve M% vs. $t^{1/2}$ to $t^{1/2} = 0$.

To obtain the water diffusion coefficients in a material as heterogeneous as a composite, we have to consider the presence of at least three different phases: the epoxy matrix, the fibers and the epoxy matrix–fiber interface.
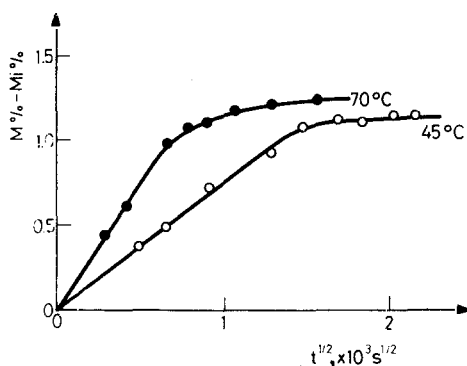

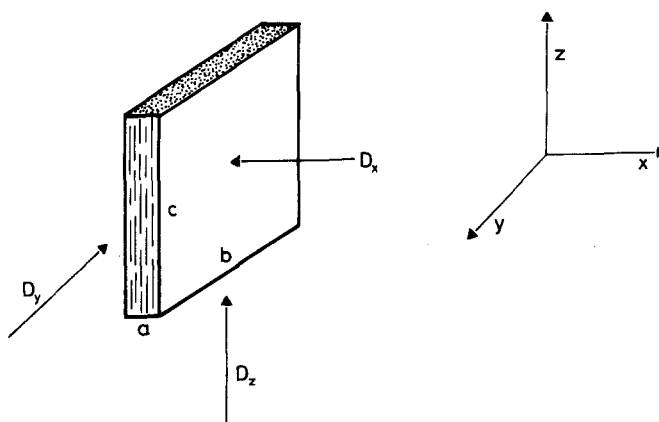Fig. 2 Sorption curves for sample D

Fig. 3 Geometry of the specimens

It is well known that carbon fibers do not absorb humidity appreciably [2]; furthermore, Blikstad [3] recently in his review of the diffusion data on graphite-epoxy type composites [4], found that the diffusivities (at 50° and R.H. between 70 and 98%) along the fiber direction were about ten times larger than the diffusivities normal to the fiber directions: he suggested that these differences were in part due to diffusion, via high diffusivity paths, in the fiber-matrix interface.

With regard to these results and since composites are usually employed as thin laminate panels, in this work we used (see Fig. 3) specimens cut in such a way that, at least to a first approximation, the diffusion might be considered to be one-dimensional.

If it is assumed that the moisture absorption is diffusion-controlled with a constant coefficient, and that the laminate is not swollen by the water during the acquisition process, the Fick's second law solution may be writte as follows [5]:

$$\frac{M\%}{M_\infty\%} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-D(2n+1)^2\pi^2\frac{t}{a^2} \right] \qquad (1)$$

where a is the thickness of the specimen.

In Eq. (1), the value of t/a^2 when $M\%/M_\infty\% = 1/2$, i.e. $(t/a^2)_{1/2}$, is given by (5)

$$\left(\frac{t}{a^2}\right)_{\frac{1}{2}} = - \frac{1}{\pi^2 D} \ln\left[\frac{\pi^2}{16} - \frac{1}{9}\left(\frac{\pi^2}{16}\right)^9 \right]$$

and therefore

$$D = \frac{0.049}{\left(\dfrac{t}{a^2}\right)_{\frac{1}{2}}} \qquad (2)$$

It is then possible to obtain the diffusion coefficient D from the $t_{1/2}$ value of the moisture intake process; this diffusivity could be considered to be D_x, if we neglected the moisture getting into the specimens through the areas ab and ac.

However, since $D_z \simeq 10D_x$ and $D_x \simeq D_y$ in our case, we cannot disregard this; thus, from the global diffusion coefficient D, the diffusion coefficient in the direction normal to the fibers, D_x, can be calculated via the equation [6]

$$D = D_x\left[1 + \frac{a}{b} + \frac{a}{b}\sqrt{\frac{D_z}{D_x}} \right]^2 \qquad (3)$$

The D and D_x values determined from Eqs (2) and (3) are reported in Table 2.

It can be seen that, either at 45° or at 70°, the D and, obviously, D_x values increase progressively with increase of the degree of polymerization; this result accords with the fact that, on increase of the curing time the intramolecular interactions

Table 2 Diffusion coefficients D and Dx, cm²/s, for   samples A, B, C and D, conditioned at 45 °C and 70 °C with R.H. = 84%

Sample	45 °C	70 °C
A	$D = 1.2 \cdot 10^{-9}$	$D = 3.4 \cdot 10^{-9}$
	$Dx = 0.95 \cdot 10^{-9}$	$Dx = 2.7 \cdot 10^{-9}$
B	$D = 1.45 \cdot 10^{-9}$	$D = 4.6 \cdot 10^{-9}$
	$Dx = 1.15 \cdot 10^{-9}$	$Dx = 3.6 \cdot 10^{-9}$
C	$D = 1.75 \cdot 10^{-9}$	$D = 4.8 \cdot 10^{-9}$
	$Dx = 1.4 \cdot 10^{-9}$	$Dx = 3.8 \cdot 10^{-9}$
D	$D \simeq Dx = 2.0 \cdot 10^{-11}$	$D \simeq Dx = 6.2 \cdot 10^{-11}$

(crosslinks) increase, and consequently the hydroxyl and other polar groups which can hinder the water in its transport by interacting with it are decreased.

Furthermore, the $M_\infty\%$ value of sample D ($1.25 \pm 0.05\%$) is larger than those (very near) of samples A, B and C ($0.85 \pm 0.1\%$) determined under the same conditions; this behaviour is also justified by the change in concentration of the hydrophilic groups present: the non-polymerized sample D does not present crosslinks and all groups are able to interact with water, increasing the maximum moisture content $M_\infty\%$. The diffusion coefficients of samples A, B, C and D depend on the temperature in the same way: from the Arrhenius equation, we estimate an activation energy for diffusion $E = 38.5$ kJ/mol.

Some significant result relevant to the other isotherms for sample D are given in Table 3.

For the isotherm at 22° and 60% R.H., no weight gain was observed over a period of 40 days; then suddenly, there was an increase of 0.2%, which slowly rose to 0.3% in a further 20 days. This trend can only be explained by assuming a swelling of the specimen: such an occurrence has been observed and discussed by other authors [7, 8]. As far as the 30° and 50° isotherms are concerned, the D values are in agreement with those at 45° and 70°, however quantitative comparison is not possible owing to the different R.H. values employed.

Table 3 Some results obtained with specimens of sample D annealed under different conditions

Conditioning			$M_i\%$	$M_\infty\%$*	D, cm²/s
T, °C	R.H., %	t, day			
22	60	100	0.0	0.3	—
30	90	58	0.10	1.35	$4.1 \cdot 10^{-12}$
50	100	21	0.6	1.65	$4.0 \cdot 10^{-11}$

* Calculated via the equation $M_\infty\% = a(\text{R.H.})^p$ [6] by considering $M_\infty\%$ to be independent of T in the range of temperature used here.

Effects of moisture on composite properties

Table 4 reports the results of a thermogravimetric study on specimens of samples A, B, C and D annealed at 45°, at a R.H. of 84% and containing the maximum water percentage M_∞%. For the sake of comparison, the initial decomposition temperature T_i observed for samples C and D that were not conditioned and dried are also reported.

Table 4 Weight loss (M_{TG}%) with relevant T range observed in TG on samples conditioned at 45 °C and R.H. 84%. The temperatures of decomposition (T_i) are also reported for two samples not conditioned

Sample	M_{TG}%	T range, °C	T_i, °C	M_i%
A	0.15	70–200	220	0
B	0.20	70–205	220	0
C	0.20	70–200	220	0
C (not cond.)	—	—	270	—
D	0.70	30–150	220	0.4
D (not cond.)	—	—	300	—

Independently of the curing time, samples A, B and C exhibit a weight loss M_{TG}% (caused by the loss of water) of 0.15–0.20% in the temperature range 70–200° whereas specimen D presents a greater weight loss (0.7%) in the range 30–150°. If these values are compared with the M_i% values, the following remarks can be made.

For samples A, B and C, the observed weight loss must be associated with the breaking of weak bonds between the molecules of water and a particular hydrophilic group present in the matrix.

For specimen D, the weight loss (0.7%), which begins at room temperature, also provides evidence of "surface" water in the microactivities between the matrix and the fibers.

The greater part of the water involved in hydrogen-bonding with the —OH, —NH_2 and —NH groups of the polymeric matrix is then retained in the sample up to 220°; it is not possible to measure the relevant weight loss because all specimens begin to decompose at around 200°, a weight loss of 15–20% being reached at 350°.

If we compare this temperature with those observed for the dry samples (270–300° for samples C and D), respectively we can deduce that the presence of moisture has a devastating action on the structure of this composite material.

In the case of the surface water, we performed some TG measurements on sample D conditioned at 45° an 84% R.H. after different annealing times (from 1 to 5

hours), and observed a constant loss of 0.4%: this percentage (equal to the $M_i\%$ values) is therefore quickly assumed by the prepreg.

The specimens studied by TG were also studied by DSC: owing to decomposition of the composite, it was possible to observe only the dehydration step relevant to the surface water, presented by sample D; as an example, the TG and DSC curves of a specimen conditioned for one hour at 45° and 84% R.H. are reported in Fig. 4: from the broad peak area, a dehydration heat $\Delta H = 8.4$ kJ/mol H_2O may be estimated.
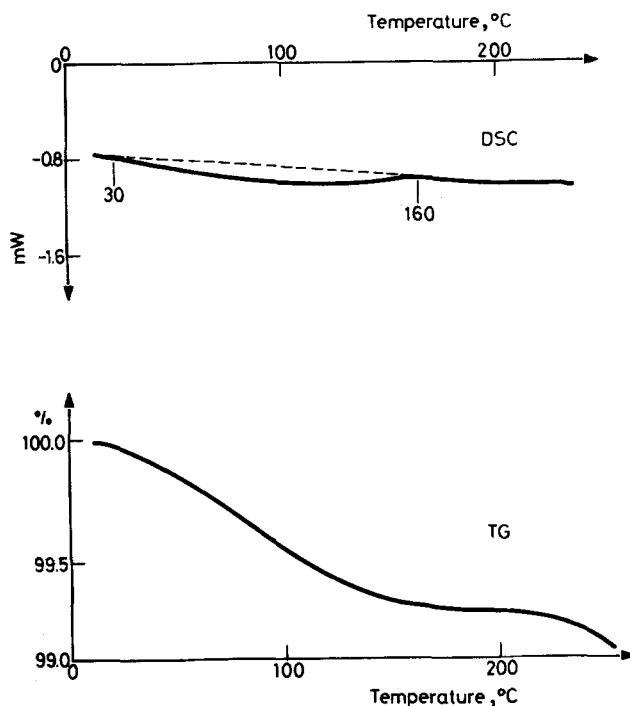

Fig. 4 DSC and TG curves of a prepreg sample (D) conditioned for one hour at 45 °C and R.H. = 84%

Finally, we studied the influence of water on the glass transition temperature (T_g) by TMA. The results obtained are listed in Table 5.

The samples cured for 90 min (B), or for two cycles of 90 min (C), present nearly equal T_g values and very close cure degrees, as already confirmed by the DSC measurements. The presence of water in the matrix lowers T_g by more than 70°.

All our results suggest the following picture for the interaction of this composite with humidity.

While the prepreg alone undergoes a very fast intake of surface water, all the

Table 5 Values of T_g obtained by means of TMA on samples A, B and C annealed at 45 °C with R.H. 84%

Sample	T of conditioning, °C	T_g, °C
	45	104
A	70	119
	not cond.	143
	45	121
B	70	123
	not cond	195
	45	121
C	70	125
	not cond.	200

types of samples exhibit diffusion-controlled water sorption, with diffusion coefficients increasing with increase in the degree of polymerization; this trend is coupled with a lowering of the M_∞% values. The M_i% values are larger than the M_{TG}% values in all cases; this means that part of the bonded water leaves the composite when it is heated to 200°.

As far as the effect of water on the composite properties is concerned, the lowering of T_g due to the bonded water, particularly for the completely polymerized samples confirms the high plasticization effect of the humidity on the laminates [9]: in particular the water decreases the crosslinks and the segment rigidity [10], thereby worsening the mechanical properties. Moreover, for every sample, the observed T_g values are increased on increasing the annealing temperature: therefore, the water has a greater effect when incorporated at lower temperatures; in other words, at least in the temperature range and for the composite considered here, the plasticization power of water is decreased when the temperature is increased. An analogous result has been found on an epoxy resin by other authors [11] through elastic modulus determinations.

Finally, we also confirmed a great reduction in thermal stability: for A, B and C samples, the T_i values fall from 270° to 220° on passing from anhydrous to hydrated samples.

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Zusammenfassung — Es wurde die Wassersorptionskinetik eines Graphitfaserverbundstoffes auf Epoxymatrixbasis mit verschiedenen Polymerisationsgraden untersucht. Es zeigte sich, daß die senkrecht zur Faserrichtung bestimmten Diffusionskonstanten mit anwachsendem Vernetzungsgrad zunehmen. Beim Erhitzen des Materials auf 200 °C wird nur ein geringer Teil des gebundenen Wassers abgegeben. Der Einfluß des Feuchtgehaltes auf einige Eigenschaften des Verbundstoffes wurde ebenfalls untersucht. Die an vollkommen polymerisierten Proben bestimmten Tg Werte zeigen eine Abnahme von 70 Grad; die Plastifizierungswirkung des gebundenen Wassers ist um so höher, je niedriger die Konditionierungstemperatur der Probe war. Das in der Matrix gegenwärtige Wasser senkt beträchtlich die Wärmebeständigkeit des Verbundstoffes.

Резюме — Изучена кинетика сорбции воды композитом графитное волокно-эпоксидная матрица с различной степенью полимеризации. Установлено, что коэффициенты диффузии, определенные в направлении перпендикулярно волокнам, увеличиваются с увеличением степени отверждения. Только небольшая часть связанной воды выделяется при нагревании этого композита до 200 °C. Изучено также влияние влаги на некоторые свойства композитного материала. Значения Tg, определенные на полностью полимеризованных образцах, показали понижение температуры на 70 °C. Однако степень пластикации связанной воду увеличивается с уменьшением температуры обработки образцов. Вода, находящаяся в эпоксидной матрице, значительно понижает термоустойчивость композитного материала.