

The effect of water absorption on the electrical properties of glass-fibre reinforced epoxy composites

M. COTINAUD, P. BONNIAU, A. R. BUNSELL

Ecole Nationale Supérieure des Mines de Paris, Centre des Matériaux, B.P. 87, 91003 Evry Cédex, France

The effects of water absorption on the dielectric properties of glass-fibre reinforced epoxy resin have been examined as a function of three types of hardeners used to promote cross-linking of the resin. The tests have been conducted under humid atmospheric conditions 0% relative humidity (r.h.) to 100% r.h. and in immersion in the temperature range 25° C to 90° C. The interpretation of the observed water uptake has been made using diffusion laws and this has revealed three distinct mechanisms of water absorption of which one is only observed in immersion. Under humid conditions there exists a water concentration threshold reached at a specimen weight gain of 0.6 to 0.7% beyond which irreversible changes are observed in the mechanical properties together with ionic conduction. Despite this observation the dielectric properties are reversible in all cases and are function only of the quantity of water absorbed in the body of the material.

1. Introduction

Several previous studies have demonstrated the important effects that absorbed water can have on the properties of organic matrix composites [1]. Most of these studies have concerned carbon-fibre reinforced epoxy resin and have indicated that water absorption can be described by a model involving only diffusion in the resin [2-4]. It is known however that beyond certain limits of temperature and humidity other mechanisms can become important and cause swelling, plastification of the resin and water penetration by capillary action along the interfaces [5, 6]. Unfortunately the description of these mechanisms remains qualitative and depends on the type of resin used and the curing conditions employed.

In the light of the results already available in the literature it was decided to examine the limitations of the laws of diffusion with the aid of dielectric measurements on three types of glass-fibre reinforced epoxy; different hardeners having been used for their curing. All three types of composites were excellent insulators and it was considered very

likely that their dielectric properties would be greatly influenced by the introduction of water molecules in the structure and the manner by which the properties were modified would help reveal the nature of the different mechanisms involved.

2. Theory of diffusion

Two diffusion models have been considered in this study, and both are based on diffusion into a continuum which is described by Fick's Law and which considers that the concentration gradient is the force behind the diffusion. The first theory considered was the classical model for absorption of a single free-phase into a continuum. The second was of the Langmuir type which introduces two phases, one which is free to diffuse and the other which implies strong attachment of water molecules at sites in the materials and which prevents diffusion. For these two models it is possible to make the following assumptions in order to simplify the equations:

(a) the diffusivity, D , is independent of the concentration, C ,

(b) diffusion occurs in one direction, x ; this assumption implies a certain specimen shape.

If these two conditions are met then the diffusion equation can be written as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \quad (1)$$

In this study, plates of thickness, h , have been examined; they were initially dried and then placed under conditions of constant humidity and temperature. In addition it was supposed that the water concentration at the surface of the plate was a maximum and remained constant throughout the absorption. It is a consequence of both models that the composite comes into equilibrium with its surrounding environment so that the weight gain, M (%), can be expressed as a function of the weight gain at saturation, Mm (%).

3. First model, single free-phase diffusion

It has been shown [2-7] that under conditions such that $Dt/h^2 < 0.05$, where t is the time in seconds, the weight gain given by single free-phase diffusion is given by

$$M = Mm \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{h^2} \right)^{1/2}. \quad (2)$$

For $Dt/h^2 > 0.05$,

$$M = Mm \left[1 - \frac{8}{\pi^2} \exp \left(-\frac{Dt}{h^2} \pi^2 \right) \right]. \quad (3)$$

4. Second model, two-phase diffusion

The two-phase diffusion model requires the introduction of two additional parameters, α and β , so that the probability of a water molecule passing from the combined state to the free phase is given by α and the probability of the reverse phenomenon occurring is given by β . In this case we can write [7-9]:

for $Dt/h^2 < 0.05$,

$$M = Mm \frac{\alpha}{\alpha + \beta} \frac{4}{\sqrt{\pi}} \left(\frac{Dt}{h^2} \right)^{1/2}; \quad (4)$$

and for $Dt/h^2 > 0.05$,

$$M = Mm \left[1 - \frac{\beta}{\alpha + \beta} \exp(-\alpha t) - \frac{\alpha}{\alpha + \beta} \frac{8}{\pi^2} \exp \left(-\frac{Dt}{h^2} \pi^2 \right) \right], \quad (5)$$

where α and $\beta \ll \frac{D\pi^2}{h^2}$.

5. Dielectric measurements and electrical theory

Debye considered that the dielectric properties of polymers were due to the existence of polar groups in the structure which constituted permanent dipoles which could be orientated by an applied electric field. Brownian motion, which is superimposed on the rotation of the dipoles, has the effect of counteracting the induced dipole polarization. Thus, when an alternating electric field is applied, the amplitude and the response of the dipole orientation depends on the frequency of the imposed field and on the temperature [10]. It will be recalled that in the case of a perfect dielectric the quotient of the capacitance of the dielectric and the capacitance of a vacuum is defined as the relative permittivity, ϵ^* . In the case of a dielectric in an alternating field it is necessary to define a complex relative permittivity,

$$\epsilon^* = \epsilon' - i\epsilon'', \quad (6)$$

in which ϵ' is the dielectric constant, ϵ'' is the loss factor and $i = \sqrt{-1}$. It is known from studies of different polymers at various frequencies and temperatures that three principal loss mechanisms exist in polymers [10, 11]. The first mechanism is Debye dipole relaxation and the second, which is revealed at high temperatures, involved electrical conduction. The third mechanism, seen in heterogeneous polymers, is interfacial polarization. The loss factor can be therefore due to several mechanisms and in the case of three mentioned above we can write:

$$\begin{aligned} \epsilon'' &= \epsilon'' (\text{Debye}) + \epsilon'' (\text{conduction}) \\ &+ \epsilon'' (\text{interfacial}). \end{aligned} \quad (7)$$

In this study all measurements were made at one frequency, 50 Hz, and as a consequence no precise conclusions can be drawn concerning the nature of the interaction between the water molecules and the polymer. However from a qualitative stand point all transitions observed in the measurements of the dielectric constant, the loss factor or electrical resistivity can be interpreted as the appearance of an additional loss mechanism. It was considered highly likely from the beginning of these tests that large variations of these parameters would be seen, simply because of the presence of the water molecules which have a high relative permittivity ($\epsilon' = 80$) compared to that of the resin ($\epsilon' = 3$) and that of the glass fibre ($\epsilon' = 6$) [12, 13].

TABLE I Characteristics of the three studied materials

		Material 1	Material 2	Material 3
	Hardener used with Bisphenol A resin	Diamine	Dicyandiamide	Anhydride
Glass fibre cloth	Filament type	E.C.9.68	E.C.9.68	E.C.9.68
	No. of threads in warp (cm ⁻¹)	17	17	17
	No. of threads in weft (cm ⁻¹)	13	13	13
Composite	No. of cloth layers (mm ⁻¹)	7	6	6
	Fibre content (vol %)	56%	48%	48%
	Density (g cm ⁻³)	1,90	1,80	1,80
	Usual upper service temperature (°C)	155	140	140

6. Experimental details

The three materials which have been examined were provided by the UDD. FIM company in the form of plates. All three consisted of a 0.90° woven E-type glass fibre cloth in a Bisphenol-A epoxy resin. The three materials differed in that different hardeners were used for each material; they were diamine (Material 1), dicyandiamide (Material 2) and anhydride (Material 3). Details of these materials are shown in Table I. In order to conduct the tests the large plates provided by the manufacturer were cut into two types of specimen. Those used for measurements of the dielectric constant were 78 ± 0.5 mm by 150 ± 0.5 mm and the

specimens used for direct current measurement were 100 ± 0.5 mm by 105 ± 0.5 mm. All specimens had a thickness of 1 ± 0.16 mm. Two types of environmental chamber were used to condition the plates. Ten chambers of one type allowed conditions of 0 to 100% relative humidity (r.h.) in a range of temperature 25 to 90° C to be achieved. The r.h. was controlled by using different salt solutions. A schematic view of a chamber is shown in Fig. 1.

Temperature measurement was made with the aid of a numerical thermometer, type PN 2 S*, which had a precision of 0.1° C. The lithium chloride hygrometer, type DMS-100, was made by Richard-Pekly, and had an operating range of 20 to 100% r.h. between 0 to 70° C with a precision

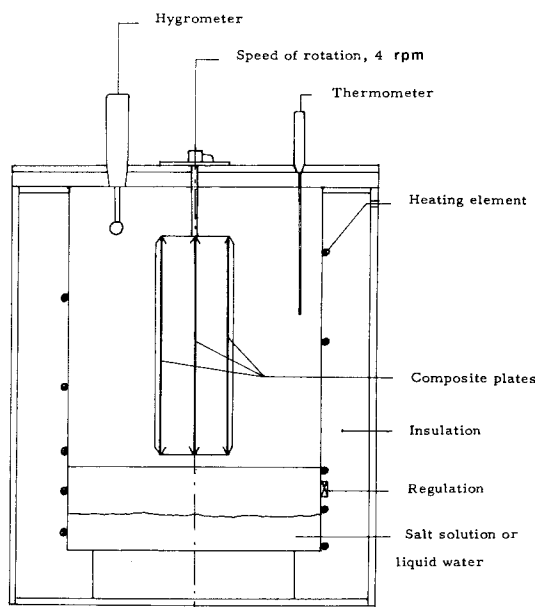


Figure 1 Schematic view of an environmental chamber, approximately 520 × 620 mm.

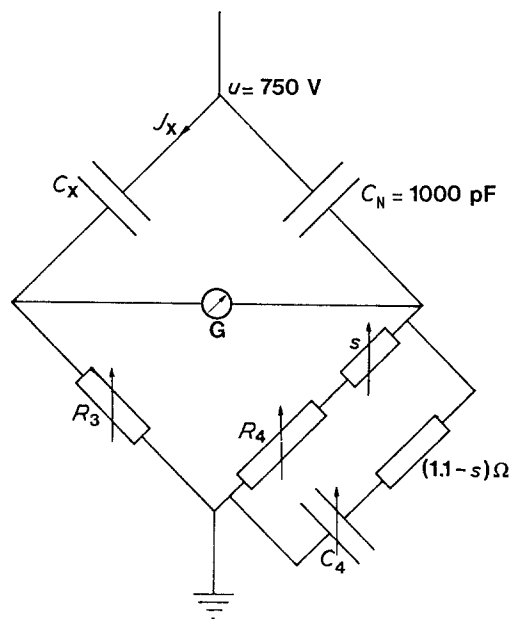


Figure 2 Circuit diagram of the Schering bridge.

*Manufactured by A.O.I.P.

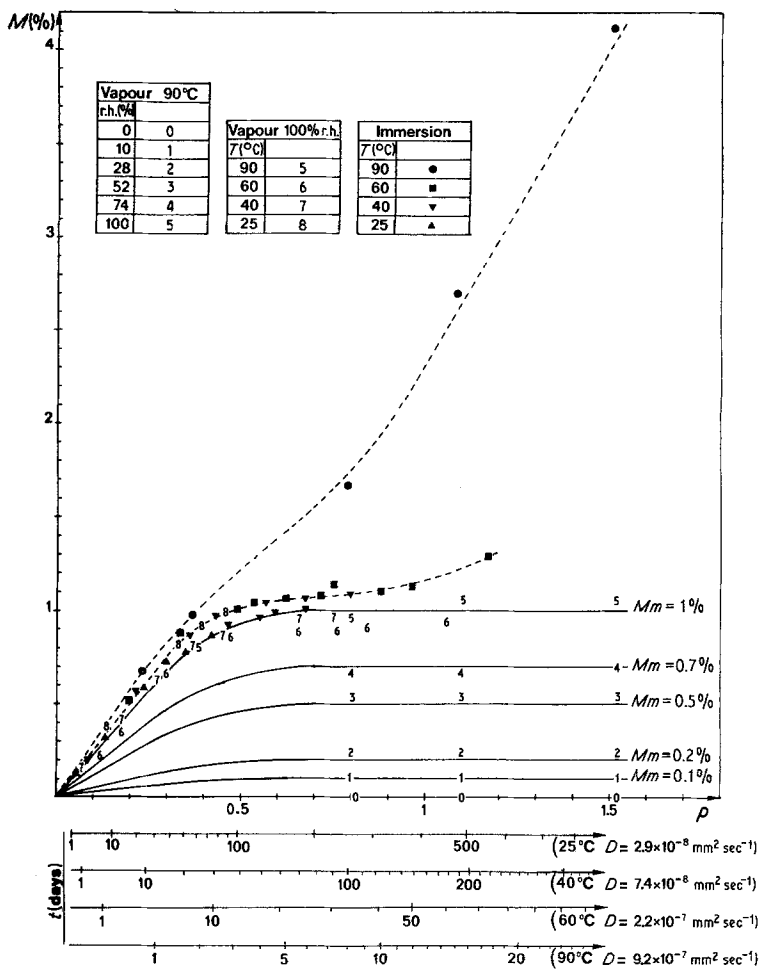


Figure 3 Absorption curves for the first material. The solid curves are theoretical and obtained by consideration of single free-phase diffusion. The experimental points (symbols and numbers) on the curves correspond to the conditions used for the electrical tests.

of 2% r.h. at 25°C. The second type of chamber was only used for immersion experiments and consisted of a thermally insulated glass chamber in a water jacket which could be heated. The temperature of the distilled water in which the specimens were immersed was controlled by an iron-constantan thermocouple. The weight gain of the plates was measured using a Sartorius type 2474 balance which has a precision of 0.01 mg in the range 0.5 mg to 100 g. The measurement of the capacitance of the specimen was made with the aid of a Shering bridge, as shown in Fig. 2. When the bridge is balanced the loss tangent, $\tan \delta$, and capacitance, C_x , is given by

$$\tan \delta = (R_4 + 1)\omega C_4 \quad (8)$$

and

$$C_x = C_N \left(\frac{R_4 + S}{R_3} \right), \quad (9)$$

where ω , the frequency of the applied electric field, was 50 Hz.

In this case, it can be shown that

$$\epsilon' = \frac{C_x}{17.7}, \quad (10)$$

and

$$\epsilon'' = \epsilon' \tan \delta. \quad (11)$$

The equipment used for these electrical measurements was made by Tettex and included a condenser and incorporated a ring guard to eliminate the possibility of stray current losses.

The precisions of the measurements were as follows. Capacitance, C_x , in the range 0.1 pF to 0.11 μ F, 0.04%, and $\tan \delta$ in the range 5×10^{-8} to 0.38, 0.5%.

The arrangement for detecting a direct current was not sophisticated but was sufficient for detecting resistivities less than $4 \times 10^{14} \Omega \text{ cm}$. A direct voltage of 1000 V was applied to the specimen using the same type of electrodes as were provided with the Tettex equipment and the current flow was measured by a nano-ammeter.

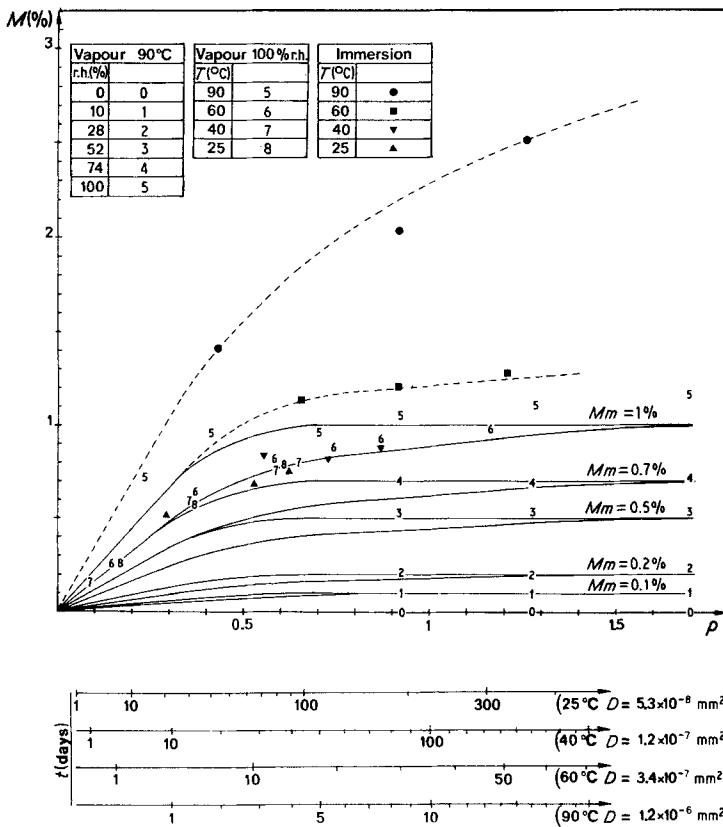
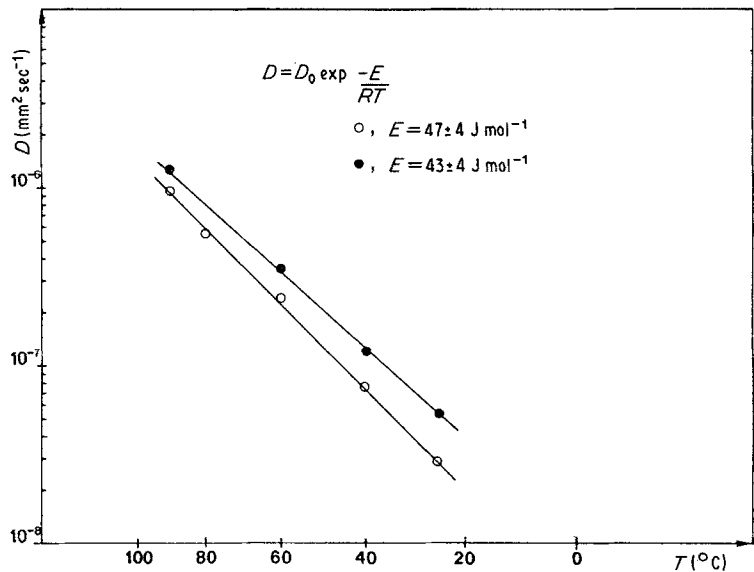


Figure 4 Absorption curves for the second material. The solid curves are theoretical and obtained by consideration of two-phase model. The experimental points (symbols and numbers) on the curves correspond to the conditions used for the electrical tests. Those curves described by the two-phase model were calculated using $\alpha/(\alpha + \beta) = 0.7$.

Figure 5 Diffusivity against temperature for the first two materials in water vapour showing an Arrhenius relationship. (○) represents Material 1, (●) represents Material 2.



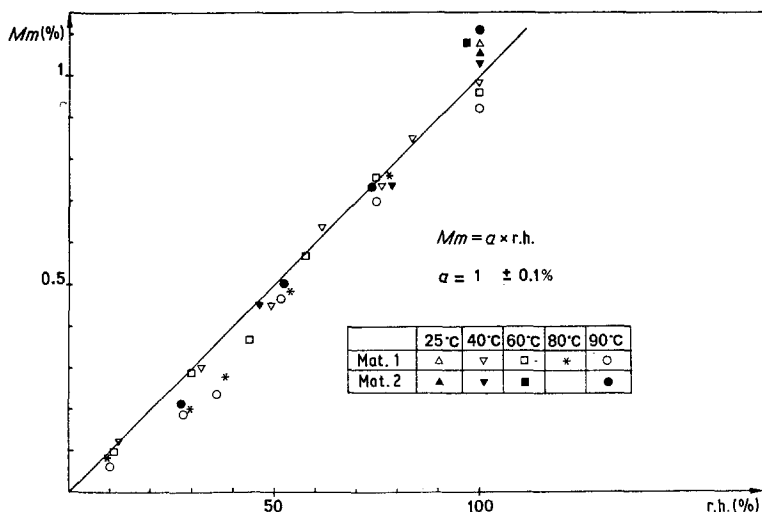


Figure 6 Saturation limit against relative humidity for the first two materials in water vapour.

Tensile tests were conducted using an Instron tensile testing machine and some of these results will be mentioned here, although fuller details will be reported elsewhere [14].

7. Experimental results and discussion

It has previously been shown that the first two materials tested in humid air showed absorption which was exactly described by Fick's law [14] and this is confirmed in Figs 3 and 4. Material 1, for which a diamine hardener had been employed, showed single free-phase diffusion which was described by Equations 2 and 3. Material 2, for which a dicyandiamide hardener was used, exhibited absorption which corresponded to two-phase diffusion and which was described by Equations 4 and 5. Under these conditions it proved possible to determine the two diffusion parameters, D and Mm , and confirm the observations of Springer [2] that the diffusivity was only a function of the temperature and the saturation level only a function of the relative humidity, see Figs 5 and 6. Knowing these parameters it was possible to use the reduced parameter for diffusion, $p = \sqrt{Dt}/h$ for normalizing the absorption curves in Figs 3 and 4. For Material 3, for which an anhydride hardener was used, the same reduced parameter was employed as for the second material, as under less severe conditions they showed similar behaviour. However, as can be seen from Fig. 7, Material 3 showed weight losses due to leaching which masked the diffusion mechanisms above 40°C.

Figs 8 and 13 show the variations of the dielec-

tric constant and the loss factor for the three materials as a function of the percentage of water absorbed under the different conditions examined. All of the curves show two zones. The first corresponds to weight gains up to 0.6 to 0.7% and shows a slight and quasi-linear variation in the dielectric properties. This slight variation is in agreement with the hypothesis of a simple diffusion of the water into the body of the resin producing, at saturation, a uniform distribution of water molecules and hence dipoles which were orientated in the electric field. The second zone occurs at weight gains above 0.6 to 0.7% and is revealed by a sudden increase in the dielectric constant and loss factor. Fig. 14 shows that at this stage it is possible to detect a continuous electric current which is not the case at lower values of water uptake.

The above results imply the existence of a water concentration limit beyond which a redistribution and regrouping of the water molecules occurs leading to ionic conduction which adds to the dielectric losses due to dipole reorientation.

The hypothesis of a water concentration limit agrees with the results obtained by immersion which are shown in Figs 8, 9 and 14. In this case the conduction which was detected was greater as all three materials proved to be more susceptible to the liquid environment and more water was absorbed than was the case under humid conditions, see Figs 3, 4, 7. Immersion revealed the possibility of capillary action and, by this means, infiltration along micro cracks into the matrix possibly accumulating at the fibre-matrix inter-

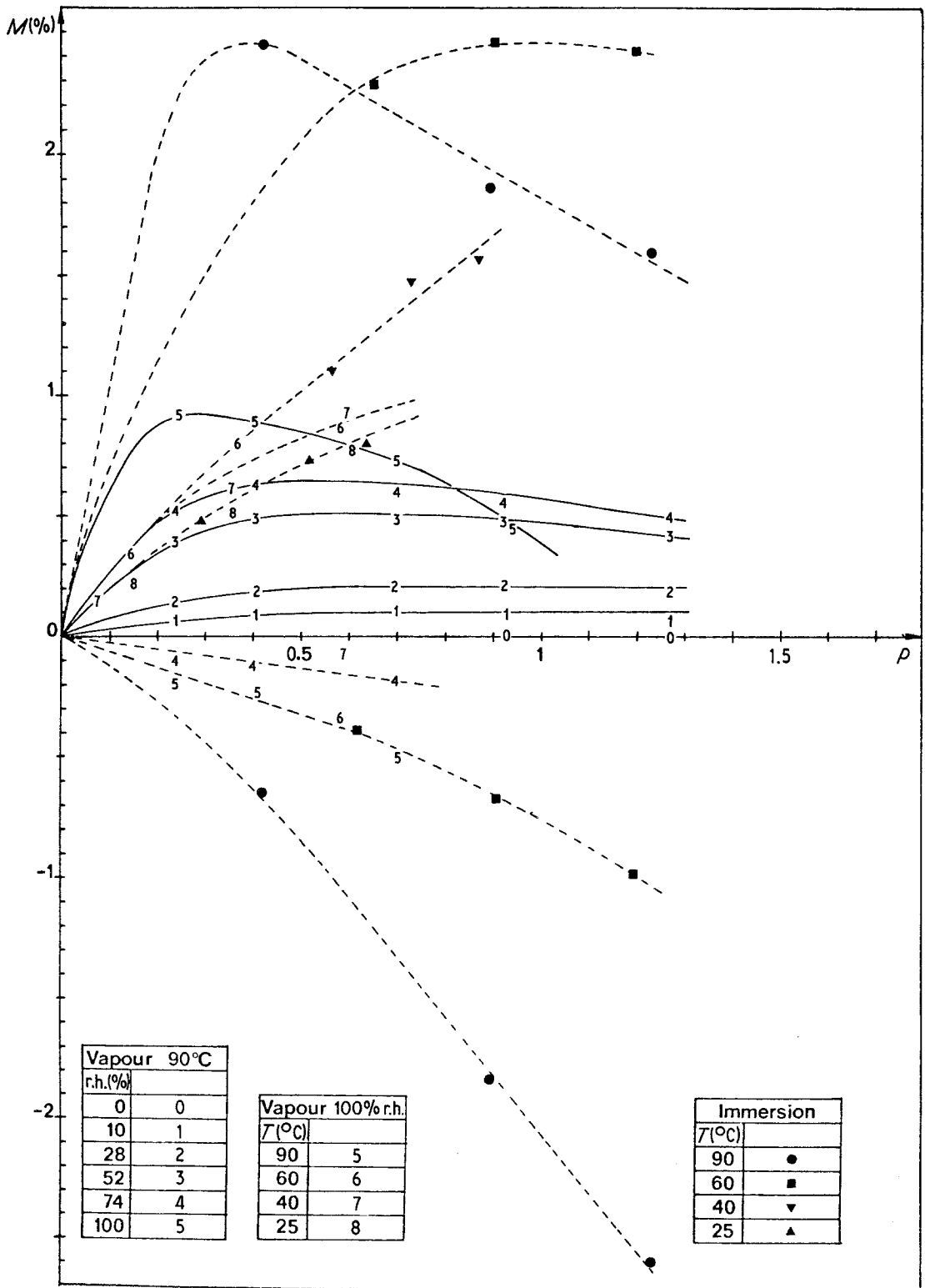


Figure 7 Absorption curves for the third material. The experimental points on the curve correspond to the conditions used for the electrical tests. The negative points show the weight loss due to leaching and were revealed by redrying.

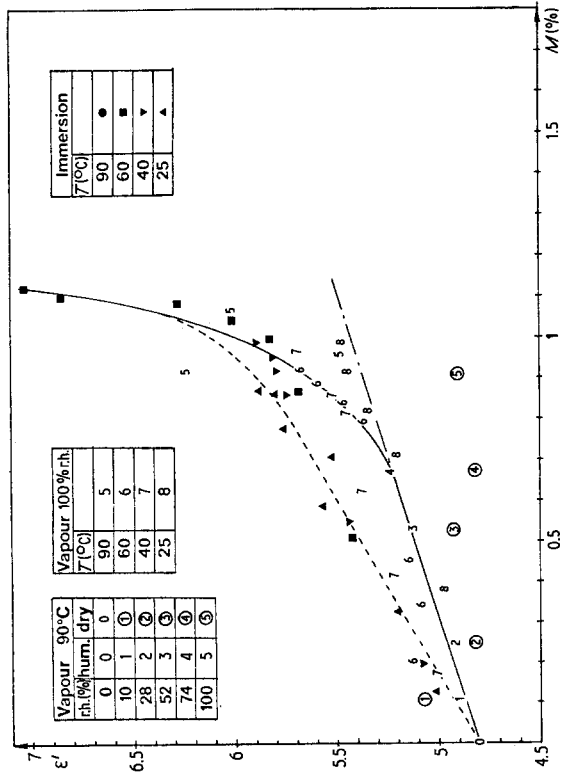


Figure 8 Relative permittivity against absorbed water percentage under different conditions for the first material.

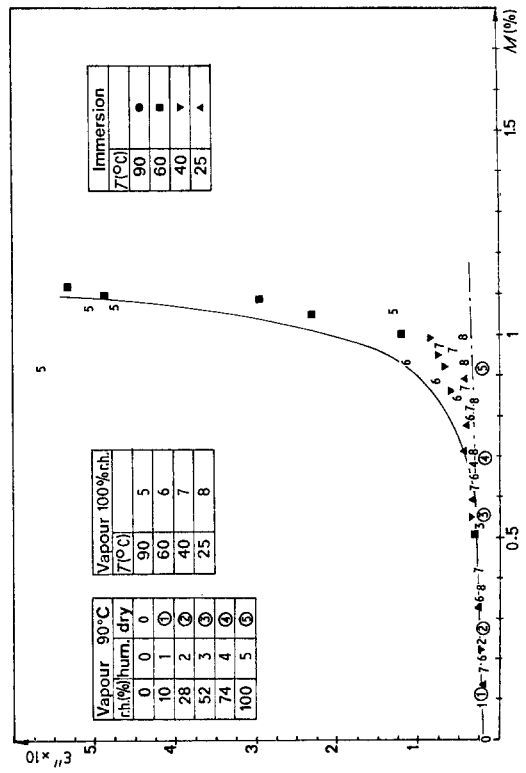


Figure 9 Loss factor against absorbed water percentage under different conditions for the first material.

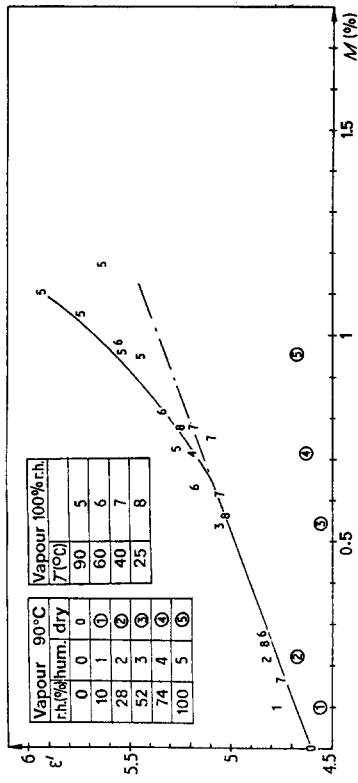


Figure 10 Relative permittivity against absorbed water percentage under different conditions for the second material.

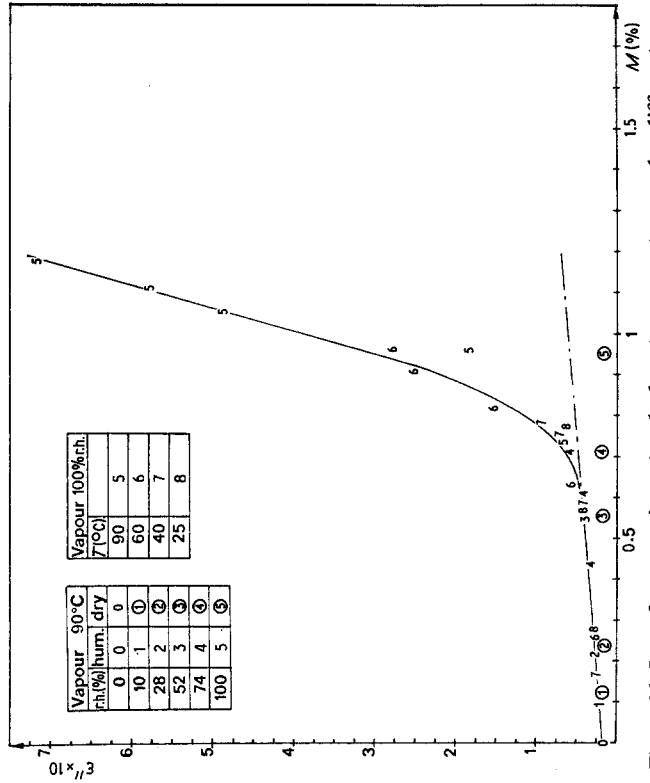


Figure 11 Loss factor against absorbed water percentage under different conditions for the second material.

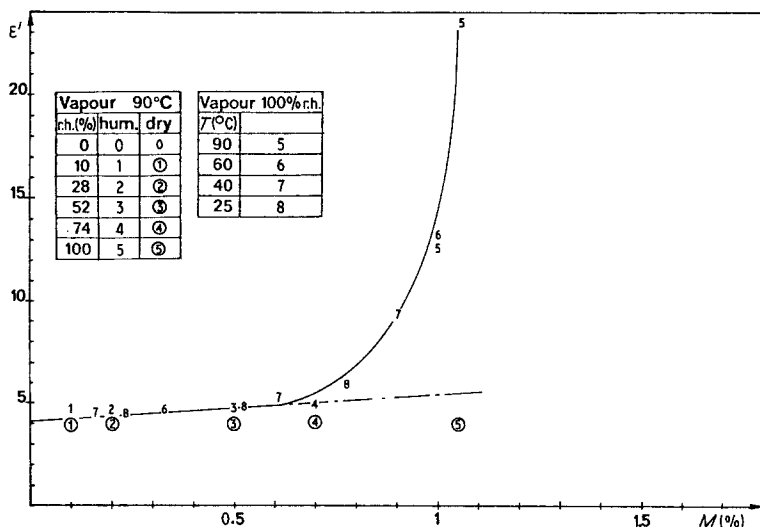


Figure 12 Relative permittivity against estimated absorbed water percentage under different conditions for the third material.

faces. Kadotani [13] has already underlined the importance of the interface in water absorption.

The previous study conducted on these materials under humid conditions has already revealed the existence of the concentration limit beyond which was found a sharp and irreversible fall in tensile strength. On the other hand the electrical measurements undertaken in this present study show reversibility of all the measured parameters on drying, i.e., dielectric constant, loss factor and electrical resistivity for all three materials and in all situations. It seems reasonable to conclude from this observation that the large variations in dielectric properties are due solely to the presence and distribution of the water molecules in the material and

not to any significant modification of the molecular structure of the resin.

The reduction of mechanical properties is most probably due to a localized softening of the resin produced by an increase in molecular mobility and resulting in a swelling which is at least partially irreversible. This is confirmed by the observation that the loss in mechanical properties is not only due to the quantity of water absorbed but also due to the exposure time and the temperature of the environment.

8. Conclusions

In the cases of all three materials studied, for which diamine, dicyandiamide or anhydride

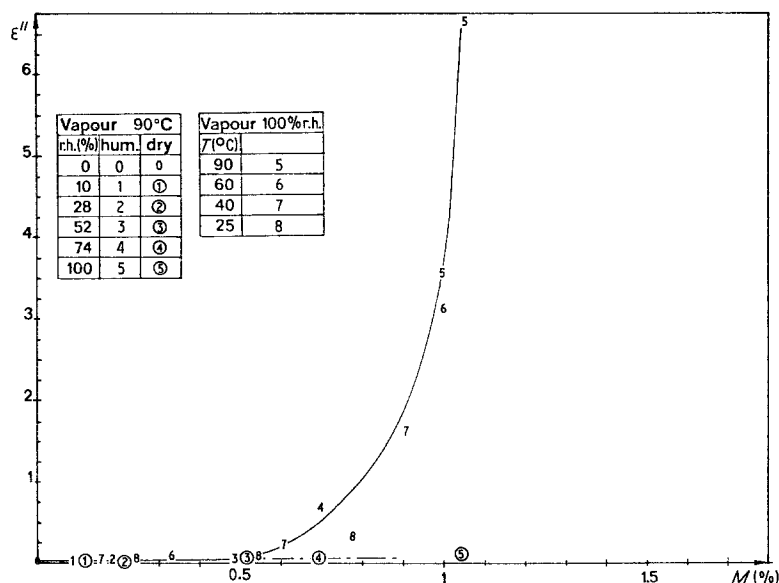


Figure 13 Loss factor against estimated absorbed water percentage under different conditions for the third material.

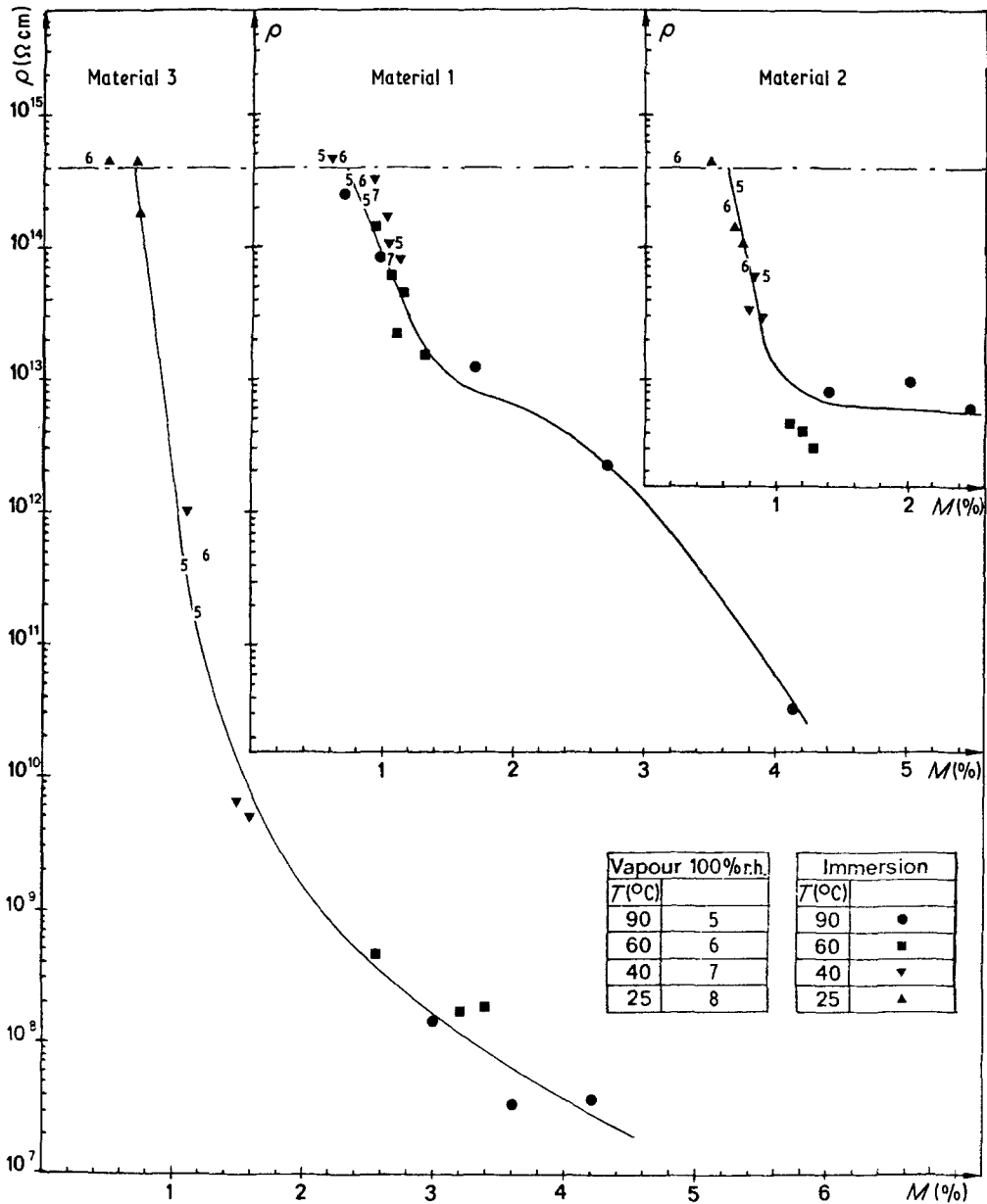


Figure 14 Electrical resistivity against absorbed water percentage under different conditions for the three studied materials.

hardeners were used, three mechanisms of absorption have been observed.

The first corresponded to simple diffusion of the water molecules into the body of the composite and this is not accompanied by an irreversible change of properties although leaching of the third composite was observed.

The second mechanism was observed under humid conditions at levels of relative humidity greater than 0.6 to 0.7%. A large increase in dielec-

tric losses was observed together with electrical conduction.

The third mechanism, seen only in immersion, was the transport of water by capillary action along microcracks in the matrix. This phenomenon seemed to occur because a limit of water concentration had been exceeded and it was accompanied by a fall of electrical resistivity.

The changes in dielectric properties were found to be directly related to the quantity of water in

the composite whereas it has been found that changes produced in mechanical properties were always irreversible.

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*Received 8 June
and accepted 16 August 1981*