The Effect of Network Structure on Moisture Absorption of Epoxy Resins

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Synopsis

An investigation of the effect of modifying the network structure on moisture absorption of epoxies was performed. The network was modified by crosslinking the epoxides with various mono/diamine proportions, resulting in decreasing density and increasing free volume. It was discovered, however, that concomitant effects, i.e., the formation of a two-phase structure, and changes in resin polarity and in resin–water affinity predominated. Thus, compositions with higher chain molecular weights between crosslink points yet exhibited lower diffusion coefficients. Also, when drastic swelling conditions (such as a water-boil treatment) were employed, moisture absorption was facilitated by penetration via newly formed microcracks.

INTRODUCTION

The diffusion of penetrant molecules into polymers depends on two factors,[1] namely, the availability of appropriate molecular size holes in the polymer network and the attraction forces between the penetrant molecules and the polymer. The presence of holes is determined by the polymer structure and morphology reflected in its degree of crystallinity, in its crosslink density, and in the molecular chain stiffness and ability to closely pack in the amorphous state. The formation of an appropriate hole also depends on the cohesive energy density of the polymer and on the size of the penetrating molecules. Water molecules, for example, are hydrogen-bonded and form clusters within the polymer.[2] Thus the first factor affecting diffusion processes is essentially a geometrical one: How much free volume is available within the polymer for occupation by penetrant molecules.

The second factor concerns the chemical nature of the penetrant versus that of the polymer. This factor determines the penetrant-polymer affinity. For example, the relatively high water absorption capacity of epoxy resins derives from the presence in the epoxy chains of —OH groups attracting the polar water molecules.

The present study investigates the effect of varying one of the polymer structural factors on water diffusion into epoxy resins. The polymer network structure was altered while influencing its chemical nature as little as possible. This was carried out by replacing stoichiometric amounts of the original diamine hardener (metaphenylene diamine) by a monoamine compound (aniline) intended to react with the excessive epoxides. As shown in Figure 1, a crosslink point may form when three or four amino hydrogens of the diamine react with

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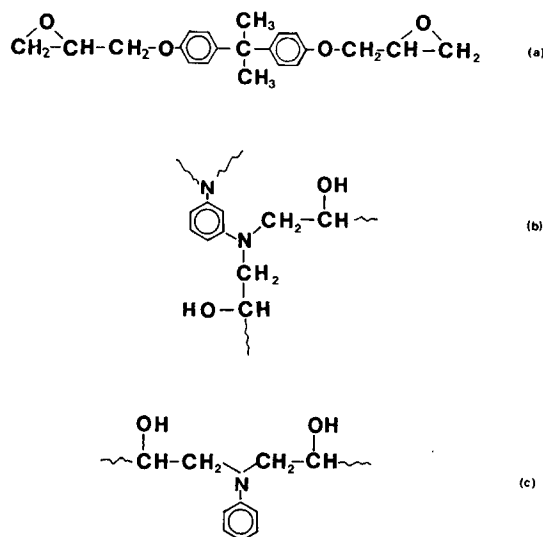* Permanent address: Casali Institute of Applied Chemistry, The Hebrew University, Jerusalem, Israel.

Fig. 1. Diglycidyl ether of bisphenol A (a) forming crosslink (b) and junction (c) points, when *m*-phenylenediamine and aniline react with four and two epoxides, respectively.

three or four epoxides, while only a junction point is formed when just two amino hydrogens react with two epoxides.

Hence, such formulations resulted in decreasing the crosslink density and in increasing the chain molecular weight between adjacent crosslinks, M_c. Since the original diamine of *m*-phenylenediamine was substituted by aniline, it was thought that the effect of the substitution on the polarity of the polymer functional group would be negligible compared with the effect on the polymer network structure. It is pointed out that an alternative way to increase M_c is by using diamine in excess of the stoichiometric amount. However, this results in the presence of unreacted primary amines, which alter the polarity of the resin.

THE MATERIAL SYSTEM

The epoxy resins investigated were prepared from Epon 828, a diglycidyl ether of bisphenol A, cured with a stoichiometric amount of *m*-phenylenediamine/ aniline mixtures. The compositions and the resulting densities and glass transition temperatures of the resins are given in Table I. This table also gives the calculated values of M_c, the average molecular weight between crosslink points. M_c for the composition containing diamine only (E-1) was calculated considering

TABLE I
Epoxy Resin Compositions and Properties

Composition	Components, %			Density, g/cm^3	T_g °C	M_c
	Epon 828	*m*-PD	Aniline			
E-1	86.0	14.0	—	1.210	150[a]	448[b]
E-2	83.6	8.8	7.6	1.204	127[a]	605[b]
E-3	83.3	6.5	10.2	1.201	113[a]	874[b]

[a] Measured using a DSC instrument manufactured by Omnitherm Corp.
[b] Calculated values.

the probabilities of the diamine molecules to react by two, three, or four of its amine hydrogens.[3] In the compositions where aniline was used as a partial replacement of m-phenylenediamine (E-2, E-3), M_c was evaluated from the probability of having an aniline molecule in the chain, based on the assumption that the reaction rates with epoxy of aniline and of m-phenylenediamine are close.[3] The glass transition temperature was determined by differential scanning calorimetry (DSC) using a DSC instrument manufactured by the Omnitherm Corporation.

SPECIMEN PREPARATION

The epoxy and the amines were mixed for 15 min at 65–70° C; thereafter the mixture was poured into a hot open mold to form a 0.07-cm-thick casting. The curing cycle consisted of 20–24 h of room temperature gelling, 1 h of 80° C curing, and 1 h of 175° C postcuring. Specimens of 2.5 × 7.0 cm and 0.07 cm thick were cut from the castings.

DIFFUSION STUDIES

The diffusion of moisture into the epoxy was determined using an environmental chamber (Blue-M), which controlled the temperature and the relative humidity. After drying in a vacuum oven (at 65° C for 48 h) and weighing the dried samples, they were placed in the environmental chamber and subjected to 98% RH at 25, 40, 55, and 70° C. The moisture absorption, as a function of time, was measured by weighing the specimens periodically until equilibrium was reached. Then the specimens were dried again and weighed. No difference in weight was found when compared to the original dry weight. In separate experiments, the moisture absorptions of specimens immersed in water at 25 and 95° C were also determined. The results obtained are averages of six to ten specimens.

The moisture absorption M_t was determined from the weight gain of the specimens, as a function of time according to

$$M_t = \frac{W_t - W_0}{W_0} \times 100$$

where W_0 and W_t are the weights of the dry and wet specimen at a time t, respectively. The moisture absorptions obtained for the different materials investigated are plotted in Figures 2–4 as functions of the square root of time. Also, the time-dependent parameter G, defined as the ratio between the moisture weight gain at time t and the moisture weight gain at equilibrium (with zero initial moisture content) is plotted in Figure 5 for the E-1 composition.

For a Fickian diffusion process

$$\frac{M_t}{M_\infty} = \frac{4}{b} \left(\frac{D}{\pi}\right)^{1/2} t^{1/2}$$

where M_t and M_∞ are the percent of moisture absorbed in the specimen at time t and equilibrium, respectively, and b is the thickness of the specimen; the diffusion constant D can be calculated from the slope of the curve. By rearrangement of the above equation and expressing t (in s),

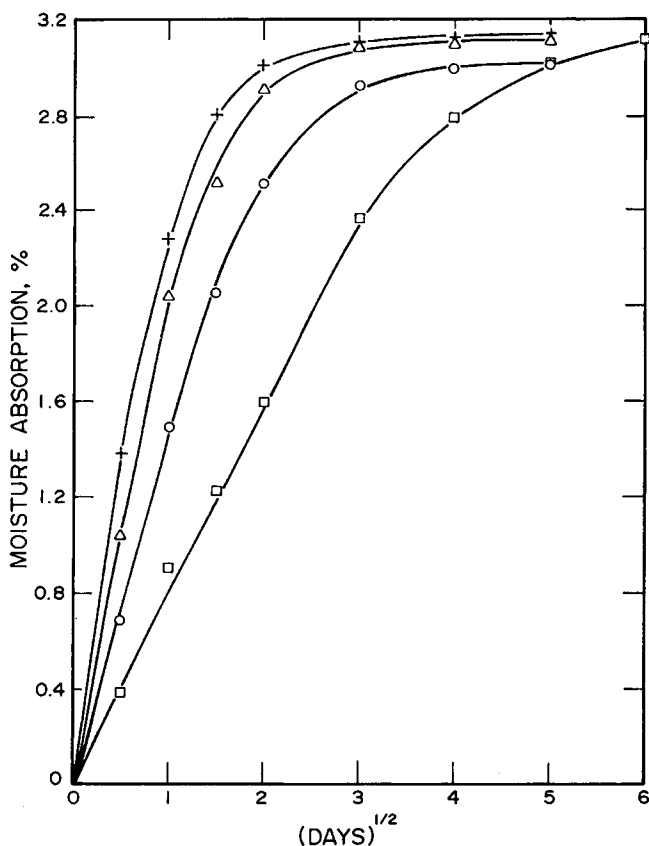$$D = \frac{\pi}{86,400} \left(\frac{bk}{4M_\infty}\right)^2 \quad (\text{cm}^2/\text{s})$$

Fig. 2. Moisture absorption behavior of E-1 composition. (□) 25° C; (○) 40° C; (△) 55° C; (+) 70° C.

where k is the initial slope (%/day$^{1/2}$) of the plot of M_t vs. $t^{1/2}$. The calculated slope, using a least-squares technique, and the diffusion constants obtained are given in Table II.

The temperature dependence of the coefficient of diffusion can be expressed by an Arrhenius-type relationship[4]

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

where the pre-exponential term D_0 is the permeability index, E_a is the activation energy of the diffusion process, and R is the gas constant. Figure 6 presents plots of $\ln D$ vs. $1/T$, where the slopes of the resulting straight lines produce the values of E_a, and the intercepts of the lines with the ordinate yield the D_0 terms. The calculated values are listed in Table II.

In addition to the above experiments, water absorption measurements were also made by immersing the epoxy specimens in water at various temperatures. The samples and conditioning procedures were identical to those previously described for the measurements at constant relative humidity. The samples were immersed in water maintained at constant temperature using a constant temperature immersion circulator. The results of these experiments are presented in Table III.
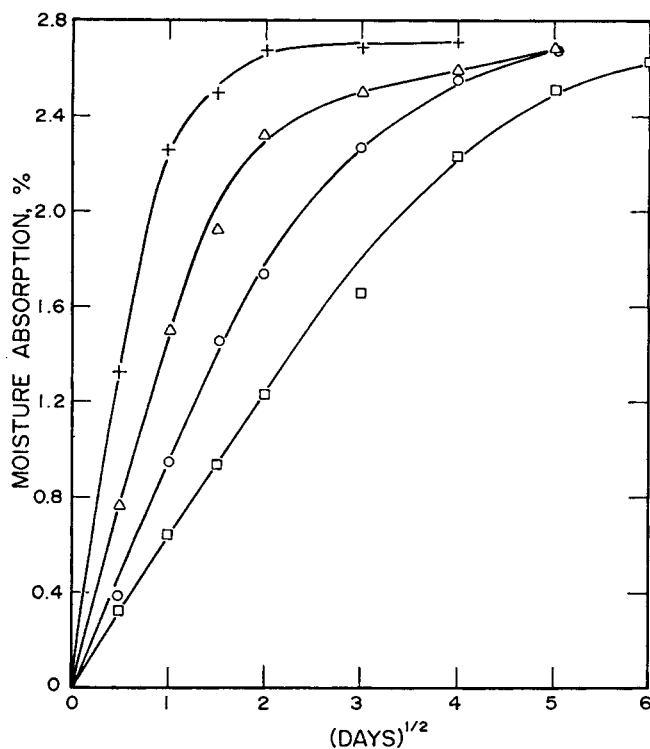
Fig. 3. Moisture absorption behavior of E-2 composition. (□) 25° C; (○) 40° C; (△) 55° C; (+) 70° C.

TABLE II
Moisture Absorption Data of Environmental Chamber Exposure Experiments

Variable	Composition											
	E-1				E-2				E-3			
T, °C	25	40	55	70	25	40	55	70	25	40	55	70
k, %/day$^{1/2}$	0.79	1.28	2.04	2.77	0.61	0.91	1.50	2.26	0.54	0.86	1.37	2.00
D, 10^{-9} cm^2/s	0.83	2.18	5.53	10.17	0.66	1.46	3.99	8.95	0.60	1.50	3.85	8.18
M_∞, %	3.1				2.7				2.5			
E_a, kcal/mol	11.60				11.85				11.77			
D_0, cm^2/s	0.24				0.36				0.30			

DISCUSSION

Referring to the two factors affecting moisture penetration into polymers (namely, the presence of holes in the polymer network and the attraction forces between the penetrant molecules and the polymer), it is noted that water molecules can exist in a polymeric medium in two states: unbound as well as bound to the polymer molecules. The unbound molecules are contained in the free volume, are relatively free to travel through the holes and do not cause swelling. The bound water molecules are immobilized and are responsible for the dimensional increase of the polymer.[5] Whereas the availability of a larger free volume within the polymer results in increasing the amount of water molecules in the first state, a higher resin polarity accounts for more water molecules in the second state.
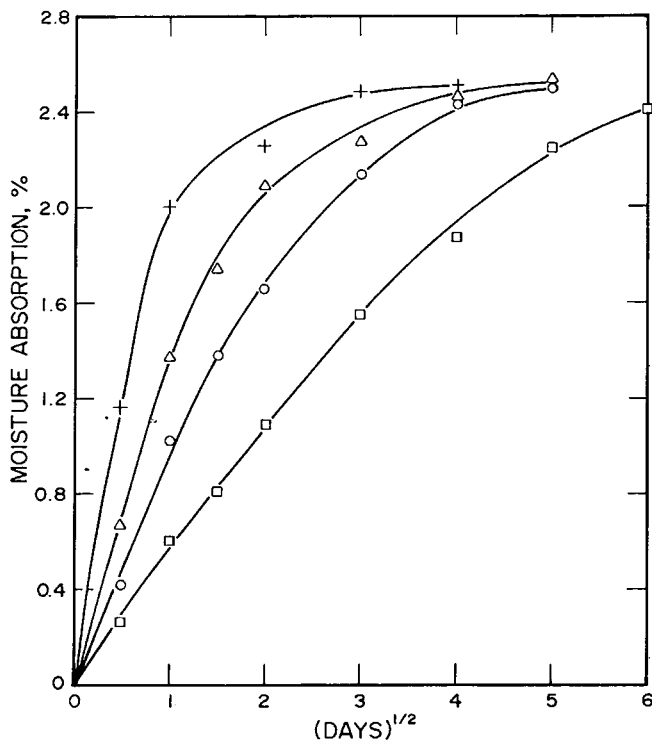
Fig. 4. Moisture absorption behavior of E-3 composition. (□) 25° C; (○) 40° C; (△) 55° C; (+) 70° C.

TABLE III
Diffusion Coefficients in Immersion Experiments

Variable	Composition					
	E-1		E-2		E-3	
T, ° C	25	95	25	95	25	95
D, 10^{-9} cm²/s	1.08	62.9	0.79	77.0	0.81	82.6
M_∞		3.29		3.02		2.88

The results in Tables II and III show that by increasing the molecular weight between crosslink points, the resin density decreases, indicating the presence of more free volume. Thus, the main issue of the discussion is the systematical decrease with increasing M_c of the diffusion parameters (with the exception of the 95° C immersion results), in contradiction to the anticipated increase as a result of the larger free volume available for moisture penetration. The epoxy resin crosslinked only by m-phenylenediamine exhibits the highest diffusion parameters (i.e., rate of moisture takeup, equilibrium weight gain, and coefficient of diffusion), which become smaller as parts of the m-phenylenediamine are replaced by aniline. This indicates that other effects which compete with that of M_c might have been overlooked, while in fact they dominate the moisture absorption process.

One such possible effect could result from changes in the morphology and the microstructure of the cured resin deriving from the replacement of m-phenyl-
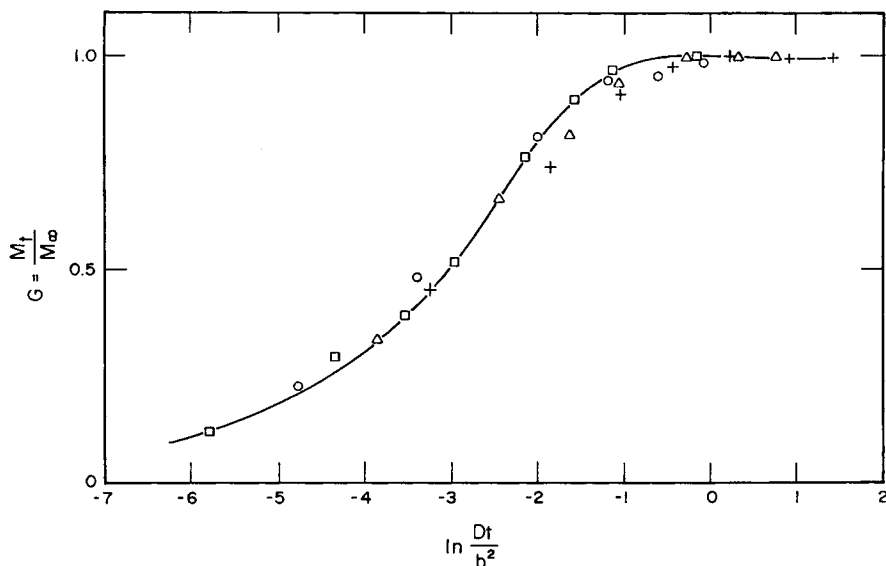
Fig. 5. Comparison of theoretical and measured G values of the E-1 composition. ($\square$) 25° C; ($\bigcirc$) 40° C; ($\triangle$) 55° C; (+) 70° C.

enediamine with aniline. Microstructural changes were observed by Manson et al.,[6] who altered M_c by using a series of epoxy prepolymers with increasing epoxy equivalents crosslinked by stoichiometric amounts of methylene dianyline. Etching experiments revealed the formation of a two-phase morphology, where highly crosslinked shells encapsulated less crosslinked material. The discontinuous phase size was found to increase with increasing molecular weight of the prepolymer. The domain sizes of the large discontinuous phase were in the range 10–70 μm. Other evidence for the existence of a two-phase structure as a result of the chemical composition is provided in Refs. 7 and 8.

Following this evidence, similar etching experiments were carried out in the present study. Mild etching conditions were sufficient to reveal discontinuous
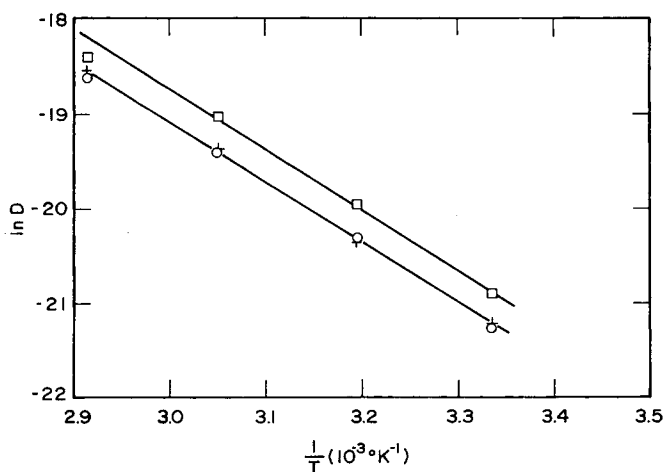

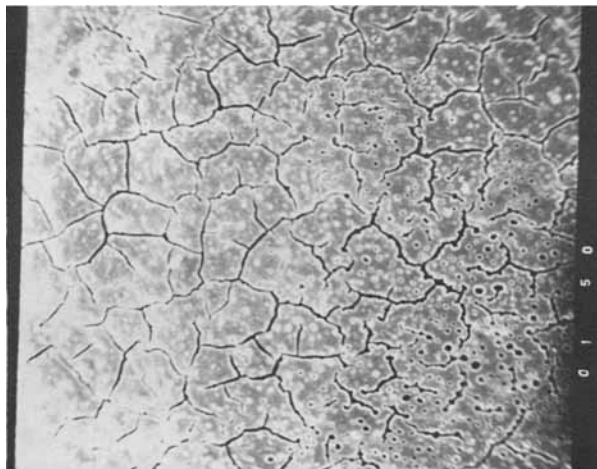Fig. 6. Arrhenius plot for the diffusion coefficient. ($\square$) E-1; (+) E-2; ($\bigcirc$) E-3.

Fig. 7. Cr_2O_3-etched surface of an E-3 epoxy, $\times$ 30.

domains in the E-3 composition, indicative of the leaching out of less crosslinked resin (Figs. 7 and 8); stronger conditions revealed a similar situation in the E-2 composition (Figs. 9 and 10); the E-1 composition, however, did not exhibit a two-phase structure even under stronger etching conditions. The difference in the domain size range compared with Ref. 6 may result from variations in resin composition and etching conditions.

It is possible that the highly crosslinked phase slows down markedly or even prevents moisture penetration into the encapsulated less crosslinked epoxy. This is expected to reduce the rate of moisture absorption significantly. The maximum water takeup level is also expected to reduce, since less water can accumulate within the highly crosslinked resin, while the less crosslinked resin is inaccessible. The rate k is probably more sensitive than M_∞, and, therefore, the diffusion coefficient also decreases with increasing M_c, being related to k/M_∞.

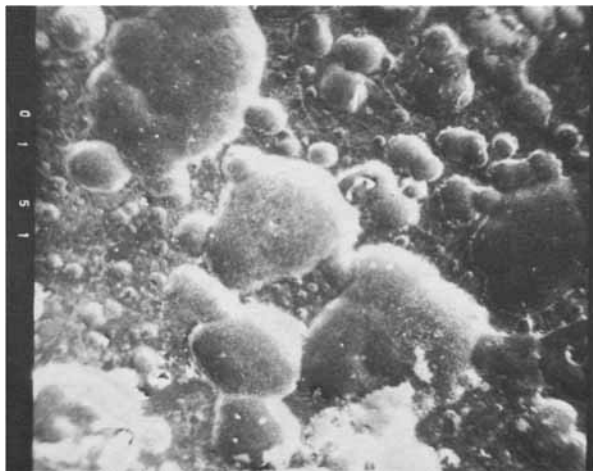Much along the same lines, it was proposed recently that sorption and trans-

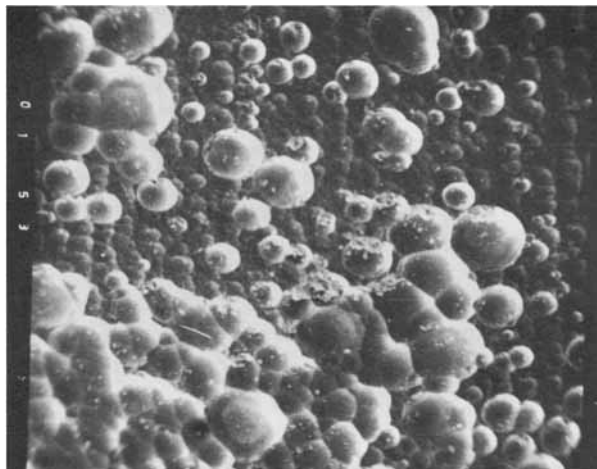Fig. 8. Cr_2O_3-etched surface of an E-3 epoxy, $\times 300$.

Fig. 9. Cr_2O_3/H_2SO_4-etched surface of an E-2 epoxy, ×30.

port of water in the glassy state of the epoxy is controlled predominantly by morphological features, that is, by the crosslink density rather than by the increase in the number of possible sorption sites.[9] It was suggested that steric conditions imposed by the crosslinked network—viz., heterogeneous systems with regions of higher density dispersed in a matrix of lower density—may be responsible for the inaccessibility of all sorption sites. Experimental results with another epoxy showed that actual moisture absorption equilibrium might not be achieved for perhaps years in that resin. These observations were interpreted as showing that the final absorption process was difficult due to the difficulty with which water enters the highly crosslinked microgel particles within the resin.[5]

Another effect which might possibly compete with the expected effect of increasing M_c is that of the resin polarity. Although it was possible to increase M_c either by the addition of excessive amounts of diamine or by replacing parts of the diamine with aniline, the latter option was chosen. Thus, aniline was
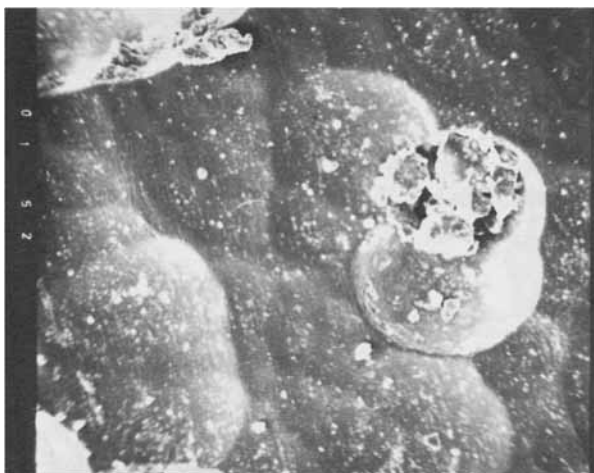

Fig. 10. Cr_2O_3/H_2SO_4-etched surface of an E-2 epoxy, ×300.

added in order to retain a stoichiometric ratio between the epoxides and the reactive amine hydrogens, so that M_c is increased while avoiding a presence of unreacted primary amine groups which induce changes in resin polarity. This replacement, however, neglects the inherent difference between the aniline and the m-phenylenediamine, whereby the first is less polar than the latter. The m-phenylenediamine molecule has more resonative states which allocate a higher negative charge on the benzene ring. This difference between the two amines is also reflected by the fact that whereas m-phenylenediamine is highly soluble in water, aniline is almost ininsoluble. Thus, m-phenylenediamine in the polymer network might be expected to attract moisture more than aniline.

When the resins are immersed in hot water (95° C) microcracks or crazes form almost immediately, facilitating diffusion by creating new channels for water penetration. Indications of such damage and of its acceleration of moisture diffusion was recently given for epoxy resins[10] and for composites.[11,12] Under these conditions the rate of water penetration depends less on factors such as the polymer morphology, the network structure, and the polymer-moisture affinity and more on the microdamage.[13–15] Accordingly, the trend of the diffusion coefficient values with increasing M_c is inverted in the 95° C immersion experiments, since the lower T_g of the E-2 resin and more so of the E-3 resin, make it more susceptible to a damaging mechanism.

In view of the variety of possible effects on moisture absorption by epoxy resins, it becomes very difficult to predict their moisture absorption behavior or to isolate the contribution of each effect. In fact, as indicated by a recent study comparing water/epoxy interactions in three epoxy resins,[13] the complexity of the absorption mechanism might lead in some resins to a deviation from Fickian behavior.

It is clear, however, that when swelling conditions are such as to inflict damage to the material, or in cases where the material has had some hygrothermal history, an additional internal state variable is strongly active.[10,14,15] Although so far no definite experimental proof has been given, it has been proposed that this additional variable is the volume percent of microcavities that form in the material under the combined action of temperature and humidity.[10] In a more general concept this variable has been considered as a change in resin structure.[13]

It should be pointed out that a similar observation to the one reported above on the variation of the crosslink density effect on moisture absorption was reported for crosslinked PMMA.[16] It was shown that when the materials differed in their degree of crosslinking, the most highly crosslinked polymers exhibited the largest equilibrium water absorption. It was also suggested that the morphology of the materials be studied should an explanation of the phenomenon by sought.

CONCLUDING REMARKS

The coefficient of moisture diffusion into epoxy resin depends on four main factors as follows: (i) the polymer network structure; (ii) the polymer polarity, determining polymer-moisture affinity; (iii) the physical morphology of the polymer (e.g., a two-phase structure); and (iv) the development of microdamage under severe humidity conditions. It is difficult to predict which of these factors

or a combination thereof dominates the moisture diffusion process into a given epoxy resin.

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