

# Moisture absorption by epoxy resins: the reverse thermal effect

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Experiments are reported on the variations in moisture absorption properties of an epoxy resin produced by sudden changes in temperature. Where the temperature change occurred when only a little water had been absorbed, the change in moisture absorption was determined by the change in diffusivity. Where a temperature change occurred when near saturation, a reverse thermal effect was observed. An attempt has been made to understand the results in terms of thermodynamics. Results obtained for the swelling changes accompanying sudden changes in moisture content suggest that it is the more tightly bound water in the polymer which takes part in the reverse thermal effect.

## 1. Introduction

The good mechanical strength of epoxy resins has led to their wide use as adhesives and as the matrix in composite materials. However, it is well known that the mechanical properties of these resins are adversely affected by moisture absorption, especially at higher temperatures. The water acts as a plasticizing agent, reducing the glass transition temperature,  $T_g$ , of the resin [1].

The amount of water absorbed determines the severity of the changes in mechanical properties, and it is therefore important to determine the absorption characteristics of any resin to be used in a wet environment. The present work reports on some effects of temperature changes on the absorption characteristics of a TGDDM resin (Ciba Geigy MY720) crosslinked with DDS. This system is characterized by having a high  $T_g$ , above 200°C, and has many applications. The absorption characteristics of the resin at constant temperature have been known for some time [2].

The rate of absorption of water into epoxy resins, characterized by the diffusivity  $D$ , generally increases with increasing temperature. Hence if a sample of resin is transferred from a water bath at a high temperature to a bath at a lower temperature, it might be expected that the rate of absorption of water would decrease. However, it is known [3-5] that in some systems the opposite effect is observed, namely that additional absorption occurs at the lower temperature. This phenomenon has been termed the "reverse thermal effect", and forms the main interest of the study reported here.

## 2. The specimens

The material studied was the epoxy resin tetraglycidyl-4, 4'-diaminodiphenyl methane (TGDDM), cross-linked with an aromatic amine, 4, 4'-diaminodiphenyl sulphone (DDS). The TGDDM was Ciba Geigy's Araldite MY720.

Moulded panels of the resin, thickness 3 mm, were

cut into square specimens of approximately 25 × 25 mm<sup>2</sup> using a diamond wheel saw. The thickness of each specimen was reduced to 2.5 mm by grinding. The edges of the specimens were ground smooth to minimize their surface area.

The samples were degreased with acetone and then placed in a desiccator containing silica gel crystals to remove any moisture already present. The samples were then weighed periodically until there was no apparent further loss in weight, when their weights were recorded and their dimensions accurately determined.

## 3. Experimental procedures

Three water baths were used to provide conditioning temperatures of 10, 40 and 70°C. Initially, three sets of 28 specimens were immersed in water, one set at each of the conditioning temperatures. The aim of the programme was to determine the effect on absorption of a change of temperature when (i) little water had been absorbed by the samples, which was chosen to be at 6 days, (ii) a moderate amount of water had been absorbed, chosen to be at 59 days, and (iii) near saturation, chosen to be at 431 days.

At each of the chosen times, 8 specimens were removed from each bath, 4 were plunged into one of the other baths, and 4 added to the remaining other bath. For example, 8 specimens were withdrawn from the 40°C bath at 6 days, 4 of these specimens were added to the 70°C bath and the other 4 were added to the 10°C bath. Four samples of each set were maintained at their original temperature throughout to provide controls.

The changes in weight of all the samples were monitored as a function of time by weighing them on an Oertling microanalytical balance with a sensitivity of  $\pm 2 \times 10^{-4}$  g. Before weighing, the specimens were wiped and then dried for approximately 5 min to remove any excess surface moisture. The volume changes in the samples produced by swelling were also

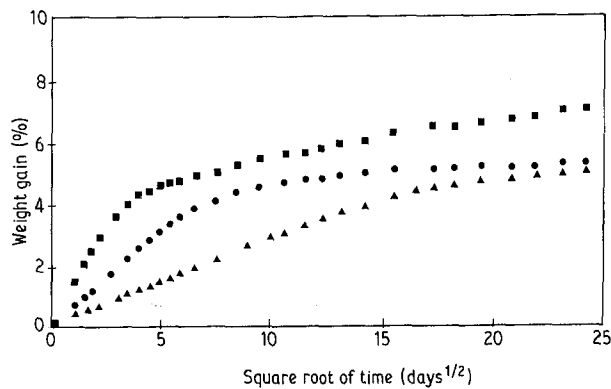


Figure 1 Isothermal absorption of water at  $\blacktriangle$ , 10°C;  $\bullet$ , 40°C and  $\blacksquare$ , 70°C.

continuously determined, using the Archimedian method.

On suffering a temperature change, it was found that after some time the weight of a sample became essentially constant, and at this point the sample was returned to the water bath at its original conditioning temperature. The series of temperature changes used are summarized in Table I.

#### 4. Results

Fig. 1 displays the isothermal absorption curves of specimens immersed in water at the three conditioning temperatures. It can be seen that at 10 and 70°C, saturation has not been reached after 576 days, which is similar to the behaviour found by other workers [2]. However, at 40°C it appears that saturation is being approached at 576 days. The diffusivities  $D$  of the samples, derived from the initial slopes of the curves, are displayed on an Arrhenius plot in Fig. 2. The results can be represented by the expression

$$D = 0.124 \exp(-4286/T) (TK) \text{mm}^2 \text{sec}^{-1} \quad (1)$$

over the temperature range studied.

Figs 3–8 show the effects of changing the tempera-

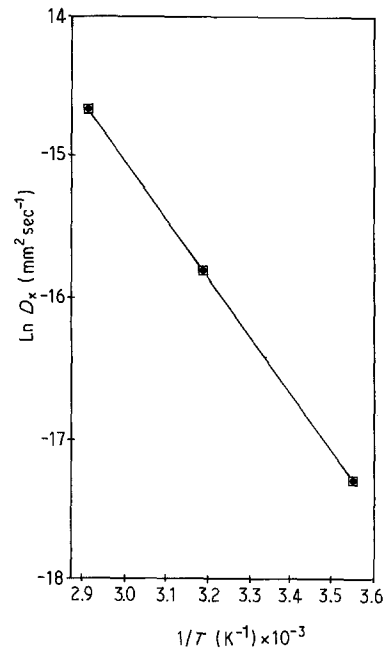


Figure 2 Arrhenius plot of diffusivity against inverse temperature.

tures of specimens while moisture is being absorbed. The characteristic features which emerge are best illustrated in the cases where the temperature changes are largest. Fig. 4 shows that when specimens initially at 10°C are transferred to a 70°C bath at an early stage in the absorption, absorption increases rapidly, as expected because of the higher diffusivity at the higher temperature. However, when these specimens are returned to the 10°C bath at later times, the absorption shows a sharp further rise, i.e. at this stage the specimens exhibit the “reverse thermal effect”.

Fig. 7 shows the absorption behaviour when a specimen initially at 70°C is placed in a 10°C bath and later returned to 70°C. In the case when the change to 10°C is made sufficiently early, the rate of absorption slows, which is consistent with a decrease in diffusivity. If the change to 10°C is made later, the reverse effect

TABLE I Details of the thermal histories of the samples

	No. of samples	Original temperature (°C)	Time (days)	New temperature (°C)	Time (days)	Final temperature (°C)
Set 1	4	10	6	40	149	10
	4	10	6	70	149	10
	4	10	59	40	268	10
	4	10	59	70	268	10
	4	10	431	40	585	10
	4	10	431	70	585	10
	4	10	—	—	—	10
Set 2	4	40	6	10	149	40
	4	40	6	70	149	40
	4	40	59	10	199	40
	4	40	59	70	431	40
	4	40	268	10	431	40
	4	40	268	70	431	40
	4	40	—	—	—	40
Set 3	4	70	6	10	149	70
	4	70	6	40	149	70
	4	70	59	10	199	70
	4	70	59	40	199	70
	4	70	431	10	585	70
	4	70	431	40	585	70
	4	70	—	—	—	70

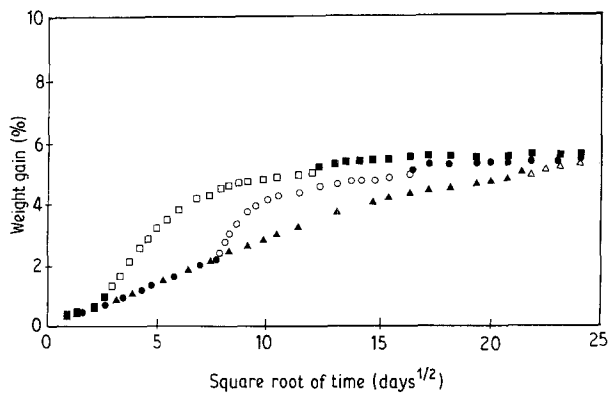


Figure 3 Samples initially at 10°C. The effects of changing the temperature to 40°C at various times, and of returning to 10°C at other times, are illustrated. ●, ■, ▲, 10°C; ○, □, △, 40°C.

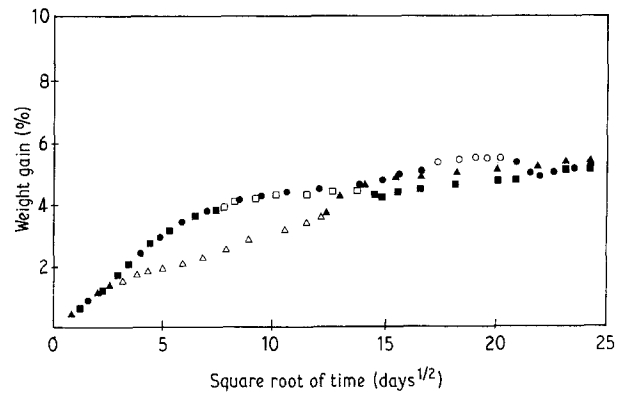


Figure 5 Samples initially at 40°C. The effects of changing the temperature to 10°C at various times, and of returning to 40°C at other times, are illustrated. ●, ■, ▲, 40°C; ○, □, △, 10°C.

occurs and the absorption increases. Moreover, in this situation a reverse thermal effect also occurs when the specimens are returned to the 70°C bath, because the absorption suddenly decreases, whereas a further rise might be expected.

The dimensional changes of the specimens under isothermal conditions are displayed in Fig. 9 as a function of the percentage volume of water absorbed. It can be seen that initially the swelling is much smaller than the volume of water absorbed. At approximately 2% volume of water, the swelling begins to increase more rapidly, and the rate of increase becomes larger with increasing temperature. Similar effects were observed by Adamson [4], who assumed that initially the water mainly entered free volume in the matrix, and hence the specimen volume hardly increased. Above a certain value, here approximately 2%, an expansion of the polymer matrix is required to accommodate the water. The results shown in Fig. 9 suggest that the free volume decreases with increasing temperature, which is the normal assumption [4].

Fig. 10 displays the swelling results corresponding to one of the absorption curves illustrated in Fig. 4, namely 10 (59 days) 70 (268 days) 10°C. The regions of rapid moisture absorption following the temperature changes are reflected by gaps in the swelling data.

A more interesting situation occurs when a sudden decrease in moisture absorption follows a temperature change, as illustrated in Fig. 7, namely the curve 70 (59 days) 10 (199 days) 70°C. Fig. 11 shows the corres-

ponding swelling behaviour throughout the experiment, and Fig. 12 presents in more detail the data near the point of desorption. It would appear that the decrease of moisture absorption is associated very much more with a decrease in specimen volume than with a decrease in free volume.

Following Adamson [4], the free volume as a function of temperature can be estimated as indicated in Fig. 9. The results, displayed in Fig. 13, show that the free volume decreases linearly with increasing temperature.

## 5. Reverse thermal effect

A number of possible mechanisms have been suggested to explain the reverse thermal effect. Adamson [4] has proposed a model in which the free volume of the matrix increases with decreasing temperature. When the temperature of a polymer is quickly reduced, water can enter the extra free volume, where it is only weakly bound, hence producing a reverse thermal effect. The more tightly bound water, which gives rise to swelling, is unable to respond as quickly.

It has been proposed by Apicella *et al.* [3] that the water absorbed produces damage in the polymer in the form of microcavities. The damage is irreversible and its extent is greater at higher temperatures. The additional absorption which occurs when a specimen is placed in a colder bath is explained by the water being able to enter the microcavities.

The results of the present experiments for isothermal

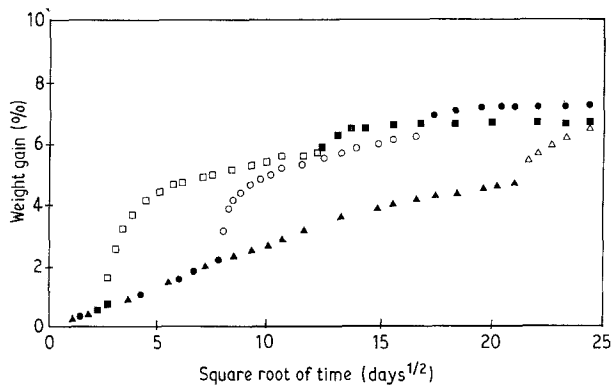


Figure 4 Samples initially at 10°C. The effects of changing the temperature to 70°C at various times, and of returning to 10°C at other times, are illustrated. ●, ■, ▲, 10°C; ○, □, △, 70°C.

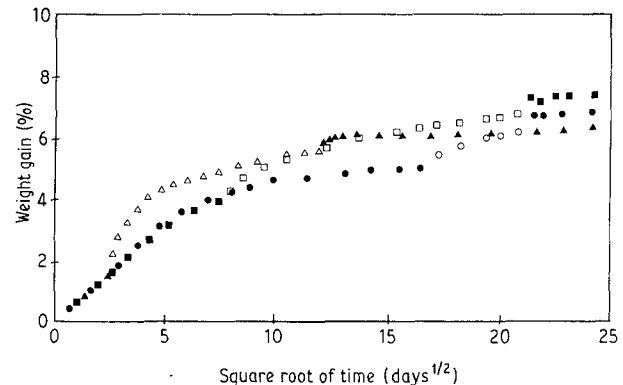


Figure 6 Samples initially at 40°C. The effects of changing the temperature to 70°C at various times, and of returning to 40°C at other times, are illustrated. ●, ■, ▲, 40°C; ○, □, △, 70°C.

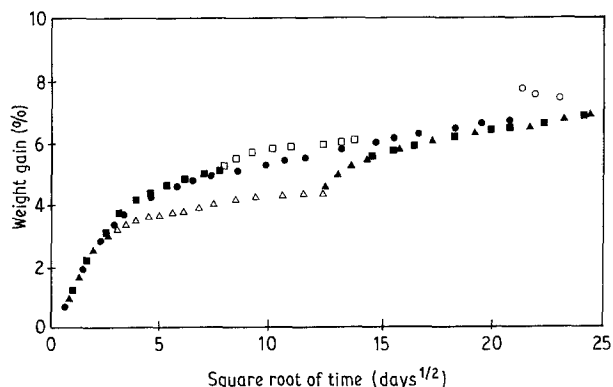


Figure 7 Samples initially at 70°C. The effects of changing the temperature to 10°C at various times, and of returning to 70°C at other times, are illustrated. ●, ■, ▲, 70°C; ○, □, △, 10°C.

conditions, illustrated in Fig. 9, show that the free volume increases with decreasing temperature as indicated in Fig. 13. The model of Adamson would therefore seem to be applicable. However, the swelling results do not support the proposal that it is predominantly the amount of weakly bound water in the free volume which changes when the temperature of the specimen changes. For example, from Fig. 4 it can be seen that the case 10 (59 days) 70 (268 days) 10°C exhibits a reverse thermal effect at the 70 to 10°C temperature change. It is clear from Fig. 10 that there is a corresponding sudden increase in specimen volume accompanying the rapid moisture absorption, suggesting that the water mainly enters in the more tightly bound state. Otherwise the volume of the specimen would change much less. Similarly, for the reverse thermal effects displayed in Fig. 7 for the 70 (59 days) 10 (199 days) 70°C case, particularly for the 10 to 70°C temperature change, it can be seen from Fig. 12 that the desorption of water is accompanied by a sudden reduction in specimen volume, again indicating that it is the more tightly bound water that is involved. Hence for the system under investigation the changes in free volume of the polymer cannot explain the observed reverse thermal effects: other possibilities must be considered.

A feature of the present experimental data is that no reverse thermal effect is observed when the temperature changes occur at times well before a specimen approaches saturation. This is illustrated in Fig. 4, in

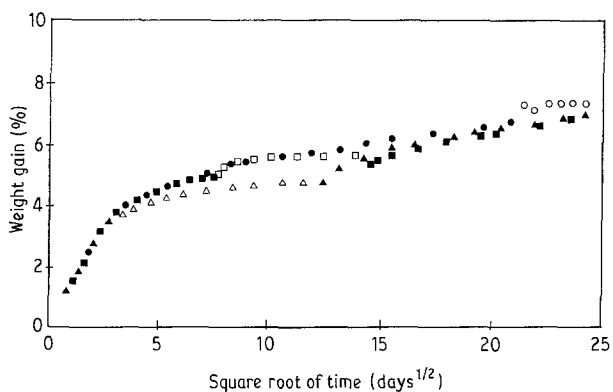


Figure 8 Samples initially at 70°C. The effects of changing the temperature to 40°C at various times, and of returning to 70°C at other times, are illustrated. ●, ■, ▲, 70°C; ○, □, △, 40°C.

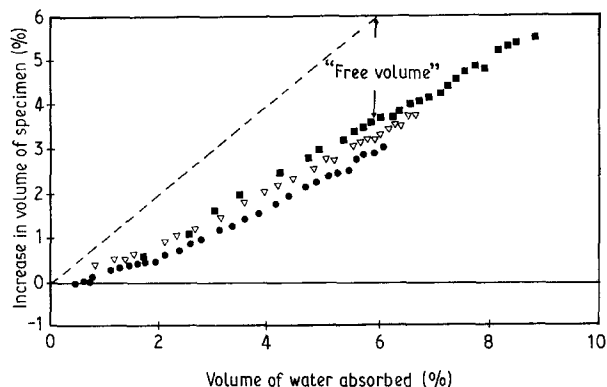


Figure 9 Swelling under isothermal conditions at ●, 10°C; ▽, 40°C and ■, 70°C. The free volume was estimated as shown.

all three cases when the temperature is increased from 10 to 70°C. It is therefore tempting to conclude that the reverse thermal effect can only occur when a specimen is (almost) saturated. Treating the system as a dilute solution of water in the polymer, in which an equilibrium concentration of water is reached at saturation, it is possible to understand how the equilibrium concentration could vary with sudden changes of temperature using Le Chatelier's principle [6]. Assuming that water absorption in the polymer is an exothermic process, if the temperature is reduced more water must be absorbed, in order to liberate heat and prevent the drop in temperature. Such an increase in concentration with a decrease in temperature is the essence of the reverse thermal effect. In the situation where the temperature of the polymer is suddenly raised, water must be desorbed, which requires heat to be supplied and hence tends to prevent the rise in temperature. The rate at which a specimen approaches thermal equilibrium will be determined by the rate at which the moisture concentration reaches a new quasi-equilibrium, because heat generation or absorption is associated with changes in the moisture content.

The above behaviour can be partially quantified using the theory of dilute solutions. Denoting by  $c_s$  the concentration of water in the polymer at saturation, and by  $L$  the heat of absorption when water enters the polymer, then thermodynamics [7] gives

$$\frac{dc_s}{c_s} = \frac{L}{RT^2} dT \quad (2)$$

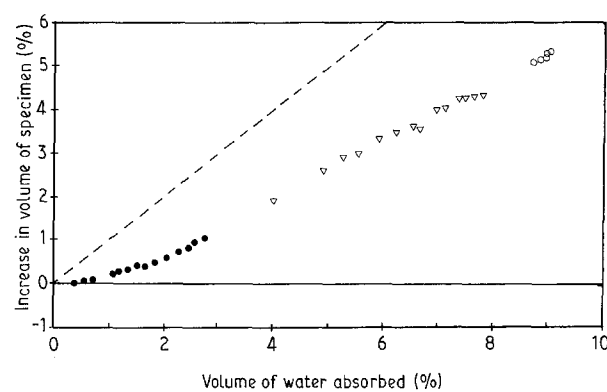


Figure 10 Swelling of a sample initially at 10°C showing volume changes accompanying a temperature change to 70°C and a return to 10°C. ●, ○, 10°C; ▽, 70°C.

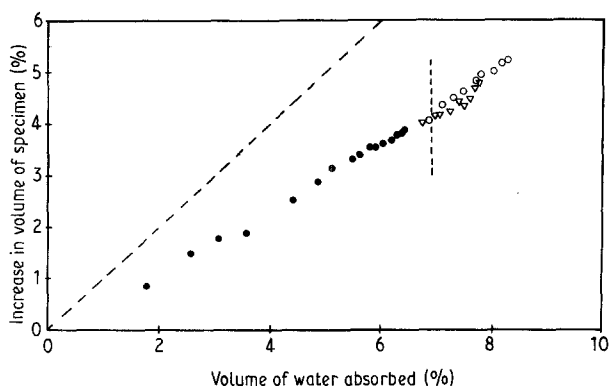


Figure 11 Swelling of a sample initially at 70°C showing volume changes accompanying a temperature change to 10°C and a return to 70°C. ●, ○, 70°C, ▽, 10°C.

where  $R$  is the gas constant. For an exothermic reaction  $L$  is negative, and hence  $dc_s$  is positive, i.e.  $c_s$  increases when the temperature decreases,  $dT$  negative. As a corollary, it can be seen from Equation 2 that no reverse thermal effect is predicted for an endothermic reaction, i.e. for  $L$  positive.

At times when the moisture concentration is not in equilibrium, i.e. it is well below the saturation level, the driving force for change in the moisture content is provided by the concentration gradient. It is therefore assumed that changes in concentration arising from sudden changes in temperature are principally determined by changes in the moisture diffusion process. The dominant effect of a change of temperature will therefore be to change the diffusivity  $D$ . Because  $D$  increases with increasing temperature, a sudden increase in the temperature of the polymer will lead to a sudden increase in diffusivity, and the water concentration will increase more rapidly. Conversely, if the temperature of the polymer is reduced, the rate at which water enters will decrease. This type of behaviour is clearly evident in Fig. 4 when the temperature increases from 10 to 70°C, and in Fig. 7 when the temperature decreases from 70 to 10°C before saturation is approached.

An important prediction of the dilute solution theory is that the saturation concentration of water in the polymer should increase with decreasing temperature. If  $L$  is taken to be a constant, Equation 2 is readily integrated to give

$$c_s(T) = c_{s0} \exp(-L/RT) \quad (3)$$

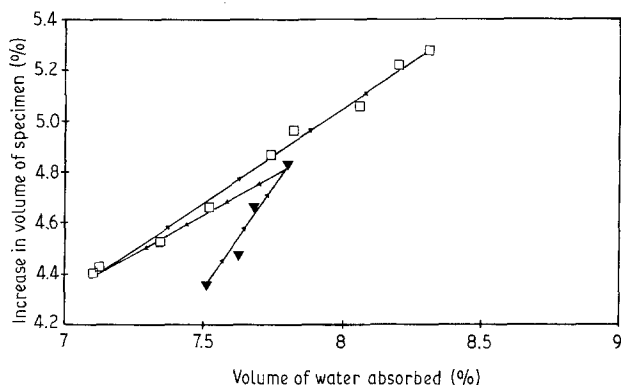


Figure 12 Swelling of a sample initially at 70°C, followed by a temperature change to 10°C, showing in greater detail the volume changes accompanying the return to 70°C. ▼, 10°C; □, 70°C.

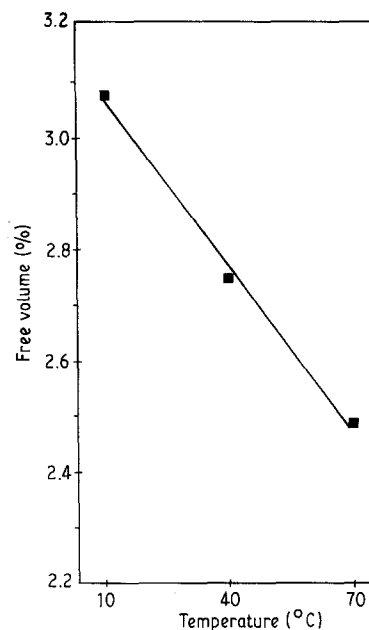


Figure 13 Estimated free volume variation with temperature.

It has been assumed that  $L$  is negative, in which case  $c_s$  increases as  $T$  decreases. In the present experiments the isothermal absorption data, presented in Fig. 1, appear to be anomalous for the 70°C case. The shape of the curve suggests that a second absorption mechanism becomes operative at a time when initial saturation is being approached. The shape of the 10°C isothermal curve indicates that saturation has not been reached after 576 days. It seems possible that the saturation concentration at 10°C may eventually exceed that at 40°C, but more data are required. On the evidence of the present data it is difficult to draw any conclusions on the temperature dependence of the saturation concentration.

## 6. Conclusions

The effects of temperature changes on moisture absorption by epoxy resins have been studied. In cases where the temperature changes were made when very little water had been absorbed by the resin, the change in moisture content was found to be determined by the temperature dependence of the diffusion coefficient. In cases where the temperature changes were made when near saturation, a reverse thermal effect was observed.

An attempt has been made to understand qualitatively the reverse thermal effect in terms of dilute solution theory. However, more data are required on the variation of saturation absorption levels with temperature.

Results have been obtained for the swelling produced when there is a change in moisture absorption accompanying a change in temperature. These suggest that it is the more tightly bound water, which is mainly responsible for swelling of the polymer, which takes part in the sudden changes in absorption or desorption, rather than the more weakly bound water in the free volume of the resin.

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