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Moisture absorption by cyanate ester modified epoxy resin matrices. Part II. The reverse thermal effect

Sunil K. Karad[a], Frank R. Jones[b,*], David Attwood[c]

[a]Maharashtra Institute of Technology, Paud Road, Pune 411038, India
[b]Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 3JD, UK
[c]BAE Systems, Department of Materials Sciences, Advanced Technology Centre, Sowerby Building FPC 267, P.O. Box 5, Filton, Bristol BS34 7QW, UK

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Abstract

The moisture absorption of cyanate ester modified epoxy resin matrices has been studied under constant hygrothermal conditions in an attempt to understand the so-called ‘reverse thermal effect’. It was found that the resin exhibits the reverse thermal effect whereby the concentration of water absorbed is enhanced when the coupons are transferred from a high conditioning temperature (50 or 70 °C) to a lower one (20 °C). Free volume calculations using the model of Adamson [1] at different conditioning temperatures showed that the free volume of the resin decreases with increase in conditioning temperature. From the ‘swelling’ study, it can be argued that in the initial stage of the absorption process the water diffuses into the regions of volume equal to or greater than volume of water molecules which does not result in swelling (unbound water). In the later stage, the water molecules penetrate the regions with a volume less than that of the volume of water molecules (bound water), with molecular reorganization of the resin network, resulting in swelling. © 2002 Published by Elsevier Science Ltd.

Keywords: Cyanate ester resins; Free volume; Reverse thermal effect

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1. Introduction

The rate of diffusion of water into polymeric resins, is an Arrhenius process so that the diffusivity D, increases with temperature. The maximum concentration of absorbed moisture should not, however, be affected when the mechanism is Fickian [2]. Hence, if a sample of resin is transferred from a water bath at a higher conditioning temperature to one with a lower temperature, it is expected that the rate of water absorption would decrease. However, it is known [1–6] that in some systems, the opposite effect is observed, where additional water is absorbed at the lower temperature. This phenomenon has been termed the ‘reverse thermal effect’.

A number of possible mechanisms have been proposed to explain the reverse thermal effect. Water molecules may either occupy the unoccupied volume (unbound water) without swelling or enter regions of smaller dimension than the water molecules, causing swelling (bound water). Adamson [1] proposed a model, which is based on the argument that below the glass transition temperature, the unoccupied or free volume of an epoxy resin increases with decrease in conditioning temperature. Accordingly, when the conditioning temperature is reduced, the bound water in a saturated resin can become mobile, and enter the extra free volume. Apicella et al. [3] suggested that the absorbed water produces damage in the resin 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 cold-water bath, can therefore be attributed to the water entering these microcavities. The reverse thermal effect has been predicted and thermodynamically justified by Rehage and Borchard [4]. El-Sa’ad et al. [5] support the statement that the unoccupied or free volume increases on decreasing the temperature which is in agreement with the model proposed by Adamson [1]. However, their results are not in agreement with the Adamson model [1], because the number of weakly bound water molecules in the free volume, changes with temperature. The cyanate ester/epoxy blend used in this study exhibits an enhanced moisture absorption when

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* Corresponding author. Tel.: +44-114-222-5477; fax: +44-114-222-5943.

E-mail address: f.r.jones@sheffield.ac.uk (F.R. Jones).

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conditioned at 50 °C and 96% RH with intermittent thermal spikes from 100 to 220 °C [7]. It was also shown that this resin behaved effectively in a reversible manner at the temperatures employed in this study. There was a small residual weight after desorption, which was constant after isothermal conditioning. We also concluded that the enhancement effect could be a function of the distribution of the unoccupied volume within the network. Therefore, to understand the mechanism involved in enhanced moisture absorption through thermal spiking, the reverse thermal effect has been investigated.

2. Experimental

2.1. Materials

The cyanate ester/epoxy blend used in this study, can be thermally cured without the use of a catalyst. The cyanate ester was Novolac tri-cyanate Primaset PT 30 resin which is based on cyanated phenol–formaldehyde (molecular weight 320–420 g mol^{-1}) with a cyanate equivalent weight of 103 (Allied Signal). The epoxy resin was DEN 431 (Dow Chemicals) which is a Phenolic Novolac resin with an epoxy equivalent of 172–179. Equal weight fractions of PT 30 and DEN 431 were mixed together and cured using the recommended schedule which involved 2 h at 180 °C followed by post-curing for 4 h at 250 °C.

2.2. Conditioning

For conditioning, the resin samples were cut to dimensions of $25 \times 25 \times 1$ mm^3 using a water-cooled diamond wheel. Before conditioning, all the samples were dried in a vacuum oven at 50 °C until a constant weight was attained. Three water baths were used to provide conditioning temperatures of 20, 50, and 70 °C. Initially, three sets of 28 specimens were immersed in water, one at each conditioning temperature (Table 1). The aim is to determine the effect of a change in temperature on moisture absorption: at early stages when the concentration of absorbed water is low as determined by immersion for 5 days (Stage I), at intermediate stages when the concentration is also intermediate, as at 27 days (Stage II), and near to saturation, as at 155 days (Stage III).

At each of the selected times, eight specimens were removed from each bath, and four plunged into the two baths at different temperatures. For example, eight specimens were withdrawn from the 50 °C bath after 5 days, four were added to the 70 °C bath and the other four to the 20 °C bath. Four samples of each set were kept at their original temperature throughout, as controls (Table 1).

The changes in weight of all the samples were monitored as a function of time by weighing them on an electrobalance: Metler AE 240 which can give digital reading accurate to 10^{-5} g. The volume change of the samples through swelling was continuously recorded using the Archimedean method. After the change in temperature when the weight of sample had become constant, it was returned to its original conditioning temperature. Table 1 gives details of the thermal histories of the samples.

2.3. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever bending mode using a Polymer Laboratories MK II analyser. The glass transition temperature was measured at a frequency of 1 Hz over a temperature of 50–300 °C. These samples were not returned to the conditioning environment so that a sufficient number of coupons were prepared for the experiment.

3. Results

3.1. Moisture absorption

Fig. 1 shows the isothermal absorption curves for the resin coupons immersed in water at different temperatures. The sorption process is Fickian at 20 °C. Some deviation from ideal behaviour is apparent at a conditioning temperature of 70 °C. This leads to a higher moisture concentration after 5500 h. Despite this, we have estimated the diffusion coefficients using the conventional analysis. At 20 °C, equilibrium is achieved but with the samples at 50 °C some continued absorption was observed after ≈5500 hours. The estimated diffusion coefficients in Table 2 increase with temperature, as expected. It is not appropriate to calculate Arrhenius activation energy. A complete discussion of the diffusion in humid environments is given elsewhere [13].

Figs. 2–5 show the effect of changing the conditioning temperature during absorption at various stages.

3.1.1. Effect of transferring the samples from one temperature to another during the early stages of water absorption

From Figs. 2 and 3 it can be seen that when the samples, initially at 20 °C, are transferred to a 50 or 70 °C bath during the early stages of the sorption process (after 5 days; point A), when the moisture concentration was approximately 1.5%, the rate increased rapidly because of the higher diffusivity at the higher temperatures. However, when these samples are returned to the 20 °C bath at a later time as saturation is approached (after 159 days; point B) the moisture content shows a further sharp rise, i.e. the samples exhibit a reverse thermal effect. From Figs. 4 and 5, it can be seen that when the samples, initially at an elevated temperature (50 or 70 °C) are transferred to the 20 °C bath at an early stage (after 5 days) of the absorption process, the rate slowed, which is consistent with a decrease in diffusivity. When these samples are returned to their

Table 1
Details of the temperature changes made at various times during reverse thermal experiments

	Number of samples	Original temperature (°C)	Time (days)	New temperature (°C)	Time (days)	Final temperature (°C)
Set I	4	20	5	50	159	20
	4	20	5	70	159	20
	4	20	27	50	159	20
	4	20	27	70	159	20
	4	20	159	50	229	20
	4	20	159	70	229	20
	4	20	–	–	–	20
Set II	4	50	5	20	159	50
	4	50	5	70	159	50
	4	50	27	20	159	50
	4	50	27	70	159	50
	4	50	159	20	229	50
	4	50	159	70	229	50
	4	50	–	–	–	50
Set III	4	70	5	20	159	70
	4	70	5	50	159	70
	4	70	27	20	159	70
	4	70	27	50	159	70
	4	70	159	20	229	70
	4	70	159	50	229	70
	4	70	–		–	70

original temperature (50 or 70 °C) at a later time (point B in Figs. 4 and 5), near saturation (after 159 days) a rapid decrease in the concentration of absorbed water was observed. Subsequently, the samples continued to absorb moisture to achieve a moisture concentration higher than that achieved before the transfer to the bath at the original temperature. The reverse thermal effect of increased water absorption at lower temperatures is clearly seen at X in Figs. 4 and 5 and B in Fig. 2 and B and Y in Fig. 3.

3.1.2. Effect of transferring the samples to baths of differing temperature at intermediate stages in water absorption

When samples initially at 20 °C, are transferred to the 70 °C water baths after an intermediate stage of moisture absorption (after 27 days; X in Fig. 3), no change in the absorption process was observed. A similar result was observed for transfer to 50 °C [7]. However, when these samples are returned to the 20 °C bath at a later time (after 159 days; Y in Fig. 3) the absorption increased indicating that the reverse thermal effect had occurred.

When the samples initially at 50 °C are transferred to the low temperature bath at 20 °C at an intermediate stage of the moisture absorption process (after 27 days), the reverse thermal effect occurs as indicated by a rise in the weight of the specimens (X in Fig. 4). However, when these are transferred back to their original temperatures (50 or 70 °C) after 159 days (B and Y in Fig. 4; B in Fig. 5) the concentration of absorbed water decreases.

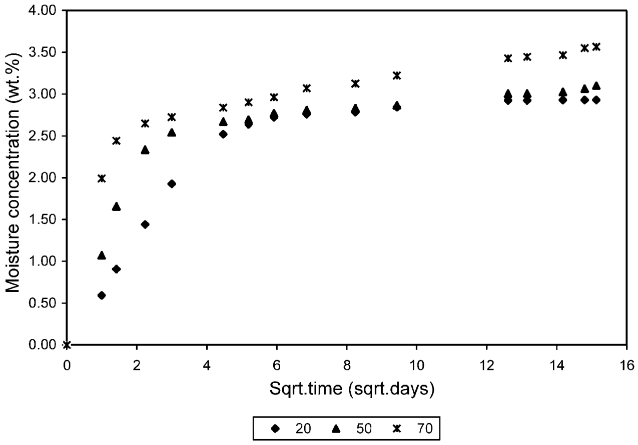

Fig. 1. Isothermal moisture absorption curves for PT 30/DEN 431 resin samples conditioned in water at 20, 50 and 70 °C for 5500 h.

3.1.3. The effect of changing the conditioning temperature during the latter stages of moisture absorption

When samples initially at 20 °C, are transferred to the 50 and 70 °C baths, near saturation (after 159 days) the concentration of absorbed water decreases (X in Fig. 2 and B in Fig. 5). However, when these samples are returned to 20 °C after 229 days, the rate of absorption shows a further sharp rise (Y in Fig. 2) indicating that the reverse thermal effect has occurred.

When the samples, initially at 70 °C, were transferred to

Table 2
Moisture content and diffusion coefficients for cyanate ester/epoxy resin samples conditioned in water at three different temperatures

Conditioning temperature (°C)	20	50	70
Moisture content (wt%)	2.92 ± 0.00	3.10 ± 0.03	3.56 ± 0.01
D_c (10^{-12} m^2 s^{-1})	0.21 ± 0.01	0.52 ± 0.11	0.62 ± 0.06

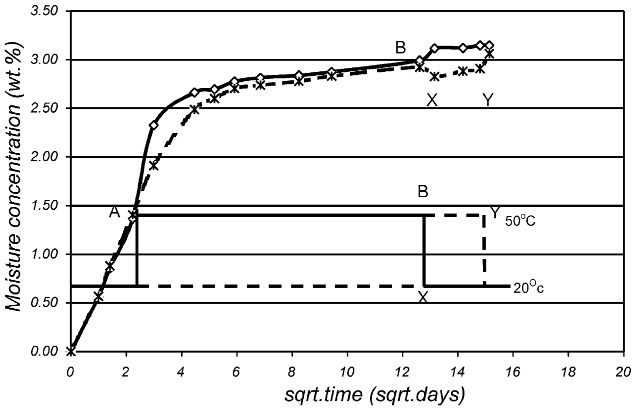

Fig. 2. Effect of changing the temperature of the conditioning bath (SET 1) from initially 20 to 50 °C after 5 days (point A) and returning them to 20 °C at point (B); transferring from 20 to 50 °C after 159 days (point X) and back to 20 °C; after 229 days (point Y). The continuous and dotted lines for the moisture curves and thermal profiles correspond.

the 20 °C bath near saturation (X in Fig. 5) after 159 days, the reverse thermal effect occurred as shown by an increase in weight. However, when they were returned to their original temperature of 70 °C after 229 days, the weight decreased (Y in Fig. 5). Similar observations were made at 50 °C [7], as shown in Fig. 4.

3.2. Swelling experiments

Fig. 6 shows the swelling of the resin samples under isothermal conditions.

Fig. 6 shows the percentage change in resin volume (compared with the volume of dry resin) as a function of the volume of absorbed water, calculated from the change in sample weight (normalized to the volume of the dry resin sample). The dashed line with a slope of 1, shown in Fig. 6 represents the swelling that would have been expected if the volumes of the dry resin and the absorbed water were additive. From Fig. 6, it can be seen that the swelling of the resin as a function of absorbed moisture can be divided into two regions: Region I, from 0 to 3% moisture, in which swelling of the resin is far less than the volume of water absorbed. As can be seen, for the samples conditioned at 70 °C after 3% moisture content, the sample volume has increased by only 1%. Region II, from 3% to the end of experiment where the rate of swelling of the resin is close to the volume of absorbed water for samples conditioned at 50 and 70 °C.

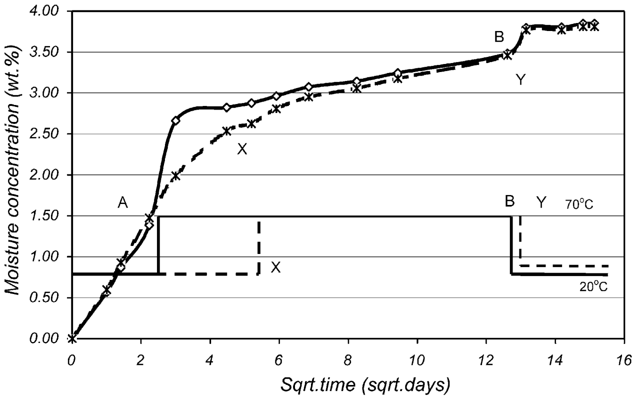

Fig. 3. The effect of changing the conditioning temperature of set I; from 20 to 70 °C after 5 days (point A) and returning to 20 °C after 159 days (point B). Transferring from 20 to 70 °C (point Y). The continuous and dotted absorption and temperature profiles correspond.

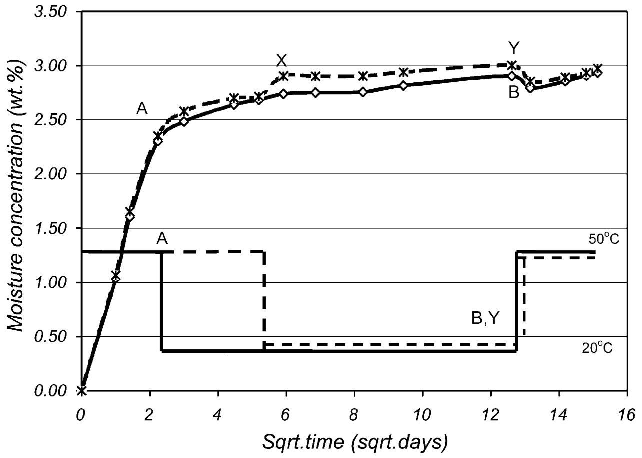

Fig. 4. The effect of transferring the samples (set II) initially at 50 to 20 °C after 5 days (point A) and 27 days (point X), and of returning to 50 °C after 159 days (points B and Y) on water absorption. The dotted and continuous temperatures profiles and moisture curves correspond.

3.2.1. Free volume

The last data points for each of the three curves in Fig. 6, obtained at three conditioning temperatures, show that the increase in volume of the resin coupons in water as a function of water concentration and temperature are very similar. Thus, the water is being absorbed additively. Clearly at 70 °C, equilibrium has been achieved. The difference between the actual volume and that for additive

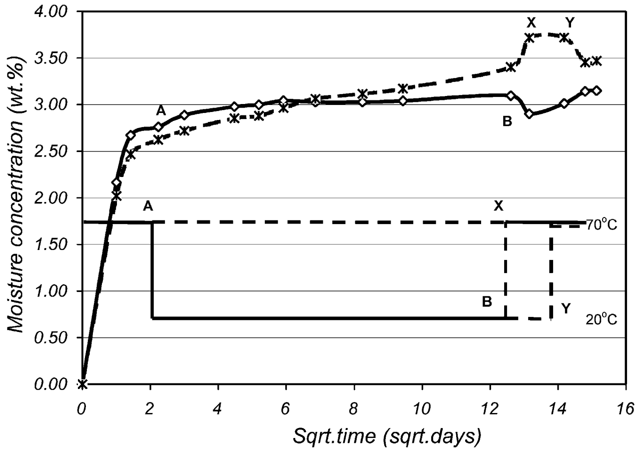

Fig. 5. The effect of changes in water bath temperatures on the moisture absorption process. Samples from set III initially at 70 °C, were transferred after 5 days (point A) to a lower temperature of 20 °C and returning to 70 °C at 159 days (point B). Samples were also transferred to 20 °C after 159 days (point X) and returned to 70 °C after 229 days (point Y).

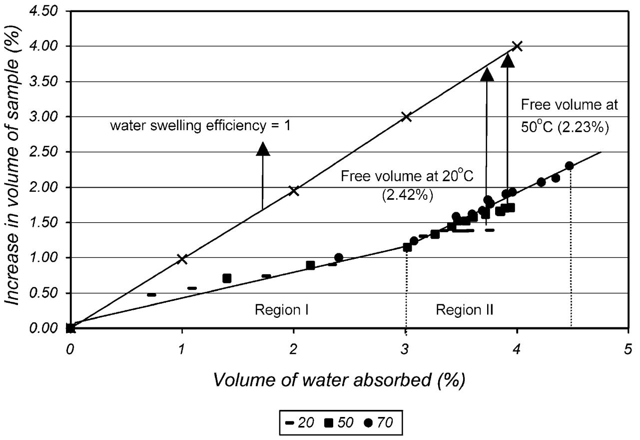

Fig. 6. Swelling of resin samples under isothermal conditions at 20, 50, and 70 °C. Free volume (Adamson model [1]) are calculated from the final moisture concentration achieved at each temperature and line which corresponds to water swelling efficiency of 1. The free volume calculation for data at 70 °C is not shown in the figure.

volumes (the dashed line with slope of 1) represents the difference between the original dry volume and the volume of absorbed water. According to Adamson [1] the water enters the free or unoccupied volume without swelling. Therefore, the free volume can be calculated from the difference between the curves at each conditioning temperature, as shown in Fig. 6. This gives free volumes of 2.42, 2.23, and 2.10% at the conditioning temperatures of 20, 50, and 70 °C, respectively. These values imply that the free volume of the resins may vary with temperature.

For example, from Fig. 5 it can be seen that when the samples initially at 70 °C are transferred to 20 °C close to saturation (after 159 days), the reverse thermal effect occurs and absorption increases. However, when these samples are transferred to 70 °C at a later stage (after 229 days) the rate of absorption slows. The swelling behaviour shown by resin samples for this cycle is shown in Fig. 7.

From Fig. 7, it can be seen that there is a corresponding sharp increase in specimen volume from 1.72 to 2.12% accompanying the sharp increase in absorption from 3.94 to 4.73% (when samples are transferred from 20 to 70 °C bath near saturation). Similarly when moisture absorption slows at the time the samples are transferred to 70 °C bath (after 229 days), the volume of the sample suddenly drops from 2.12 to 1.83%. The concentrations of moisture absorbed are those for a self-standing experiment. This accounts for the slight difference between the values in Figs. 5 and 7.

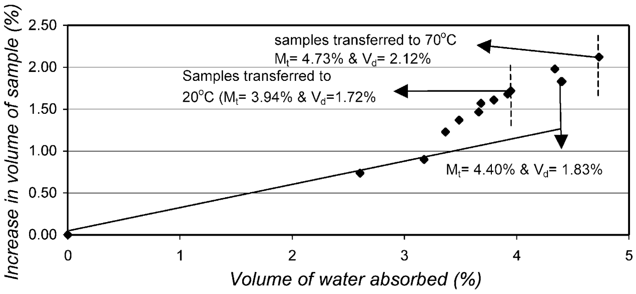

Fig. 7. The swelling of samples, initially at 70 °C, showing volume changes accompanying a temperature change to 20 °C (after 159 days; X in Fig. 4) near saturation and a return to 70 °C after 229 days (Y in Fig. 4). M_t and V_d correspond to the moisture concentration at the above times and percentage change in the volume of sample, respectively.

4. Discussion

In an extensive examination of the effects of thermal spiking [13] it was shown that this resin was thermo-mechanically reversible after intermittent thermal excursions during the moisture absorption at 50–180 °C. The moisture content having reached >3.8% on drying, T_g recovered to within 5 °C of the original value of 272 °C. (T_g when wet was 238 °C and recovered to 267 °C after drying).

Tables 3 and 4 show that during the reverse thermal effect experiments, the T_g of the wet resin remained above a value which would indicate some irreversible degradation. We can, therefore, conclude that during the experiments described here the resin remains effectively thermomechanically stable [13].

These cyanate ester modified epoxy resins are shown to exhibit the so-called reverse thermal effect whereby, moisture absorption is enhanced on transferring the samples from a higher temperature water bath to one with a lower

Table 3
Moisture content and corresponding T_g for resin samples initially at 20 °C transferred to 70 °C and returned to 20 °C at later stage

Conditioning time and temperature	5 days/20 °C	9 days/70 °C	159 days/70 °C	170 days/20 °C	240 days/20 °C
Moisture content (wt%)	1.36	2.32	2.99	3.11	3.14
T_g (°C)	260	250	248	243	243

Table 4
Moisture content and corresponding T_g for resin samples initially at 70 °C transferred to 20 °C, near saturation and returned to 70 °C at a later stage

Conditioning time and temperature	159 days/70 °C	170 days/20 °C	229 days/20 °C	235 days/70 °C	240 days/70 °C
Moisture content (wt%)	3.40	3.71	3.72	3.46	3.45
T_g (°C)	242	238	238	240	240

temperature. This phenomenon occurs at or near the 'saturation' value. Furthermore, the effect also occurs in the 'inverse' experiments whereby samples are transferred to baths of higher temperature with a reduction in weight. A related phenomenon (of opposite direction) is the enhanced moisture absorption in humid environments occurring as a result of thermal spiking in non-humid atmospheres.

A number of possible mechanisms [1–6] have been proposed to explain the reverse thermal effect. These all involve the role of unoccupied volume in the sorption process. The moisture swelling of a polymeric resin below the glass transition temperature is influenced by the 'occupied' and 'unoccupied' volumes. The occupied volume is defined as that which is occupied by the mass of the molecules plus the additional volume associated with thermally dependent harmonic vibrations. The occupied volume depends on the temperature because of a thermally induced motion which causes each molecule (or molecular segment in the case of a cross-linked polymer) to oscillate about its equilibrium position, thereby occupying more space than that determined by its mass [8]. If the molecules were packed so that the domains were in perfect contact, the occupied volume of the polymer at any temperature would exactly equal the sum of the volume associated with the actual mass of the molecules and their vibrational volume. The domains are not in perfect contact, however, and the unoccupied volume is defined here as the difference between the measured volume of a polymer and the occupied volume. This is the result of 'holes' or 'voids' caused by packing irregularities [9,10].

The unoccupied volume in a polymer is a combination of free volume of molecular dimensions and of microvoids of larger dimension. The free volume, which can be readily plasticized by moisture, arises from the presence of interchain attractive forces such as hydrogen bonding, between adjacent segments of the polymer network containing polar groups in juxtaposition. Microvoids are present in highly cross-linked polymers because of the restrictions to conformational changes of the network chains [11,12].

Attempts to estimate the unoccupied volume from swelling experiments under isothermal conditions are shown in Fig. 6. Here, the free volume appears to increase with a decrease in conditioning temperature. This is consistent with the model proposed by Adamson [1]. However, these differences in free volume, which were obtained using the method of Adamson [1], were not significant, considering the experimental errors involved. The free volume was estimated to be 2.25 ± 0.15%.

In Fig. 6 it can be seen that at a constant temperature, the resin samples swell initially by an amount significantly less than the total volume of the absorbed water. On approaching saturation, the rate of swelling is increased becoming equal to the rate of absorption of water. Water molecules may either occupy free volume (unbound water) without swelling or enter into smaller sized regions than the water molecule causing swelling (bound water). Initial moisture absorption by a resin occurs very rapidly, as the moisture fills the readily available unoccupied volume and partially swells the resin structure. As a result, the specific volume of the resin increases at a much lower rate than the volume of the moisture absorbed. Once the readily accessible unoccupied volume is filled with water molecules, the moisture absorption slows significantly and approaches saturation. In this stage of absorption, the resin will swell at a similar rate to that for moisture absorption.

At the start of sorption process, the water molecules diffuse into regions of volume equal to or greater than volume of the water molecules which does not result in swelling. In the later stages, the water molecules enter regions of lower volume with molecular reorganization of the network. This results in swelling of the resin.

The swelling of resin samples which show a reverse thermal effect, do not support the Adamson [1] model because the quantity of weakly bound (unbound) water in the free volume appears to change with temperature. From Fig. 7 it can be seen that the rapid moisture absorption or desorption is accompanied by a sudden increase or decrease in specimen volume. This suggests that water mainly enters the regions of free volume smaller in volume than the water molecules, with molecular reorganization. This is consistent with the model given in Part I of this series [13], for thermal spiking effects.

5. Conclusions

The effects of temperature excursions on the moisture absorption by cyanate ester modified epoxy resin matrices have been studied. In cases, when the conditioning temperature was increased or decreased during the early stages of the absorption process (after 5 days), rate of absorption of water was consistent with the change in diffusion coefficient. However, near to saturation the reverse thermal effect was observed, whereby the water content decreased. This is caused by a molecular reorganization of the network. This is confirmed by the swelling results which showed that in the later stages, the water diffuses into regions of free volume of molecular dimensions, resulting in the sudden changes in swelling and absorption or desorption. For this to occur, the molecular network needs to be reorganized in a manner discussed previously [13].

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