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Moisture absorption by cyanate ester modified epoxy resin matrices. Part I. Effect of spiking parameters

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Abstract

The moisture absorption of cyanate ester modified epoxy resin matrices has been studied under thermal spiking conditions. Enhanced moisture absorption has been observed at spike-temperatures above 120 °C. The results of the desorption studies on both control specimens and the spiked specimens showed that some of the water molecules remained entrained in the polymer. It is postulated that this water could be associated with that which is hydrogen bonded or from the hydrolysis of isolated residual cyanate ester groups because the concentration of entrained water remains constant at spike-temperatures below 180 °C. Above 180 °C a thermally activated process, leading to chain scission as indicated by a reduced recoverability of the glass transition temperature (T_g) on drying.

On isothermal resorption, the moisture concentration was found to be similar to that achieved through thermal spiking, showing that the entrained water at the lower spike-temperatures can also be achieved under mild conditions. The T_g is reversibly recovered to within 5 °C, which indicates a degree of relaxation rather than degradation. The moisture diffusion coefficient estimated from the resorption curves is lower than those estimated from the absorption and desorption curves. The isothermal resorption diffusion coefficient also decreased with increasing spike temperature. It is proposed that thermal spiking induced a relaxation of the network but as the spike-temperature approaches the transition region of the wet polymer, further hydrolytically induced relaxation events become feasible. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cyanate ester resins; Thermal spiking; Diffusion coefficient

1. Introduction

High modulus graphite/epoxy composites have been the materials of choice for aerospace applications. However, the use of conventional epoxy systems has drawbacks as a result of high water absorption. Cyanate ester act as a hardener for the curing of epoxy resin. The co-reaction of cyanate esters with epoxies modifies the crosslink density of the network and increases the extent of reaction of the individual functional groups which can improve the hot/wet performance of the cured resin. This moisture absorption can be attributed largely to the moisture affinity of specific functional groups of a highly polar nature in the cured resin. The absorbed moisture is normally considered to be present in the free-volume of a polymer matrix, acting as plasticiser, there by degrading its mechanical performance especially at elevated temperatures. The extent of this reduction in performance is directly related to the concentration of moisture absorbed by the polymer matrix [1]. The environment may be especially damaging if the temperature is not constant but varies rapidly over a wide range [2]. Sudden, large temperature changes, referred to as ‘thermal spikes’, are encountered, for example, by aircraft flying at supersonic speeds [3]. Thermal spikes may alter significantly the moisture absorption as well as the mechanical properties of cured polymer resin. Recent studies have shown that under such regular and rapid heating and cooling, or thermal spikes, polymer resins can absorb significantly more moisture than under normal constant hygrothermal conditions [4].

Cyanate ester composites provide superior performance in each of these areas, with hydrophobicity being especially important because it translates into significantly greater dimensional stability.

The objective of this investigation was, to evaluate the

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relationships between material behaviour and variables such as maximum and minimum temperatures during a thermal spike, the duration of the spike, dry spiking and number of spikes.

2. Experimental work

2.1. Materials

An uncatalysed cyanate ester cured epoxy resin was used in this study. The cyanate ester was the tri-functional Primaset PT30 resin, which is based on cyanated phenol–formaldehyde oligomers with a molecular weight of 320–420 g mol^{-1} and cyanate equivalent weight of 103, and is available from Allied-Signal. The epoxy resin was an epoxidised Phenolic Novolac resin (DEN431) with an epoxy equivalent weight of 172–179, which is available from Dow Chemicals.

To prepare the blend equal weight fractions of cyanate ester and epoxy resin were used. The curing cycle, which was recommended by the manufacturer, involved 2 h, at 180 °C followed by post-curing for 4 h, at 250 °C. Representative structures for the resin which form during cure, are given in Table 1 [5–8].

2.2. Conditioning

For conditioning, the resin samples were cut to dimensions of $55 \times 25\ \text{mm}^2$ using a water-cooled diamond wheel. The samples were then milled down to a thickness of 1 mm, and all of the faces polished to the 1200 grit. The samples were dried to constant weight in a vacuum oven at 50 °C, and placed on racks above a saturated salt solution of potassium sulphate (K_2SO_4) in distilled water, which has a relative humidity of 96% in a sealed humidity chamber in an air-circulating oven at 50 °C [9]. A set of four resin samples was used at each spiking-temperature. Resin samples were removed intermittently, weighed and returned to the humidity chamber (control samples) or subjected to thermal spikes (spiked-specimens). Isothermal diffusion experiments were also conducted on a range of differing relative humidities at a temperature 50 °C using the appropriate saturated salt solutions; lithium chloride (11%); calcium chloride (16.5%), magnesium chloride (31%); magnesium nitrate (46%); sodium chloride (75%) and immersion (100%). The desorption of the previously moisture saturated samples was carried out in a vacuum oven maintained at 50 °C and 1000 mbar. Isothermal resorption of previously conditioned and subsequently dried samples was carried out in a range of relative humidities as described above.

2.3. Thermal spike program

Three thermal spiking programs were used as shown in Table 2. Spike-program I was developed by Xiang and Jones [2]. t_s in Table 2 is the time spent by the samples in the oven after reaching the planned spiking-temperature at the centre of the cross-section of the samples. The three spike-programs were chosen so that the t_s, at the spike-temperature was 1, 3 and 5 min. Resin samples were placed in an oven preheated to the spike-temperature in metal racks, to ensure both major surfaces were heated evenly.

2.4. Glass transition temperature

Dynamic mechanical thermal analysis (DMTA) was performed in dual cantilever bending mode using a Polymer Laboratories Mk II analyser. This allowed the effect of thermal spiking and enhanced moisture absorption on the viscoelastic properties, such as the glass transition temperature to be measured. A frequency of 1 Hz was used 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

Fig. 1 plots the absorption curves for controlled unspiked resin samples and for the samples spiked to 160 °C using spike-program I given in Table 2. The peaks in 160 °C-spiked curve correspond to the moisture concentration prior to a thermal spike and troughs correspond to the moisture concentration after a thermal spike. Moisture was lost during the thermal spike. For simplicity the moisture concentration after a thermal spike is omitted from subsequent plots of moisture absorption. The increase in the concentration of absorbed moisture in the spiked-specimens relative to the control is clear, and the difference is termed the enhanced moisture absorption.

Figs. 2–4 show the moisture absorption curves for resin samples subjected to 29 spikes between 100 and 220 °C using spike-program I, and 5000 h conditioning.

From Table 3 it can be seen that thermal spiking to 100 °C

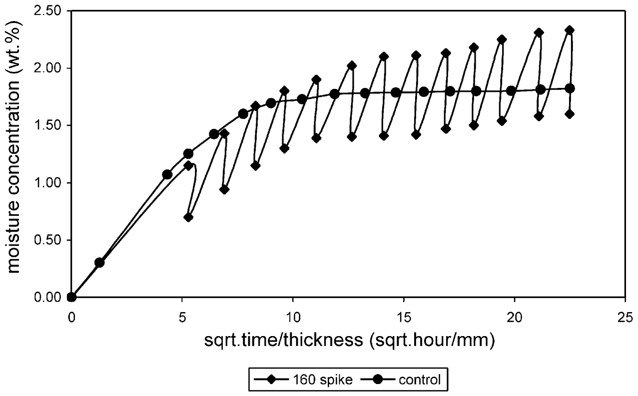
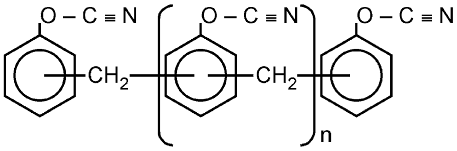
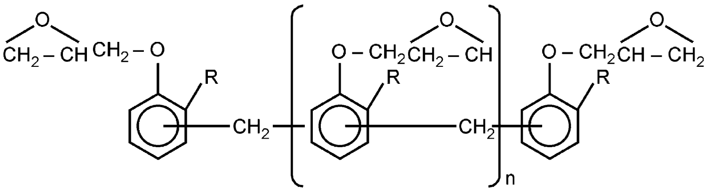
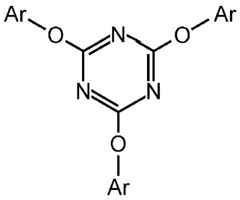
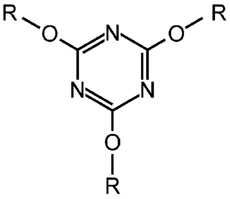
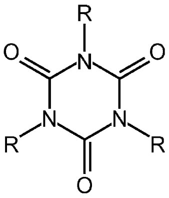
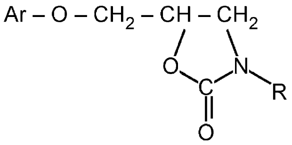
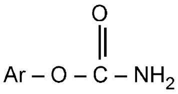


Fig. 1. The effect of 13 thermal spikes to 160 °C (as per spike-programme I given in Table 2) on the moisture absorption of resin samples conditioned at 96% RH/50 °C.

Table 1
Chemical structures of resins and representative chemical structures in the cured resin

Sr. No.	Chemical structure	Trade name
(i)		Primaset cyanate ester PT30 (cyanate equivalent weight = 103)
(ii)		Dow epoxy Novolak resin DEN 431 (epoxy equivalent weight = 172–179)
(iii)		Aryl cyanurate (triazine ring)
(iv)		Alkyl cyanurate
(v)		Alkyl isocyanurate
(vi)		Oxazolidinone
(vii)	 $\mathrm{Ar-O-\overset{\overset{\Large O}{\|}}{C}-NH_2}$	Carbamate

had very little enhancing effect on the moisture absorption for the resin system. Maximum moisture enhancement occurred at a spike-temperature of 180 °C. Above this temperature the absorption fell with increase in spike-temperature.

3.1. Moisture desorption and resorption studies

Absorption studies under spiking conditions have shown that thermal spiking (Table 3) causes enhanced moisture absorption by the resin samples. Based on this data, it could be argued that the enhancement is a direct result of physical changes to the resin. In order to check whether these changes are irreversible, desorption followed by resorption was carried out on the resin specimens which had been conditioned under 96% RH at 50 °C and regularly spiked using spike-program I. The desorption curves are given in Fig. 5 where it can be seen that even after prolonged drying in vacuum, a certain quantity of moisture still remains in the

Table 2
Three different thermal spike-programs used to spike the resin samples

Spike temperature (°C)	Spike time (min)					
	Spike I	t_s	Spike II	t_s	Spike III	t_s
120	4	1	6	3	8	5
140	4.5	1	6.75	3	9	5
160	5	1	7.5	3	10	5
180	5.5	1	8.25	3	11	5
200	6	1	9	3	12	5
220	6.5	1	9.75	3	13	5

specimens. The residual weight is compared to moisture contents after 5000 h (M_{5000}) conditioning in Table 3.

From this data, it can be seen that the isothermal control samples exhibited the lowest residual weight whereas those spiked at 220 °C had the largest residual weight. However, although the residual weight was found to increase with thermal spike-temperature, the concentration of water absorbed reached a maximum at a spike-temperature of 180 °C. On isothermal reabsorption, the weight increase after 3500 h also achieved a maximum value at that temperature.

After drying in a vacuum at 50 °C, the specimens were returned to their original conditioning environment (96% RH/50 °C). The moisture content in these specimens was then measured as before as a function of time by regular weighing without applying any thermal spikes. These isothermal resorption curves were found to be approximately Fickian reaching equilibrium moisture concentrations similar to that obtained after the first cycle of absorption and thermal spiking, as shown in Fig. 6 and Table 3.

The new moisture concentrations after resorption are calculated from the starting weights after desorption. Therefore, direct comparison should be done after adding the residual weight to the new moisture concentration (Table 3). The differences imply that further quantities of entrained water are induced on reconditioning. However, from Table 3 it can be seen that during resorption, the thermally spiked samples return approximately to their original enhanced moisture contents. During resorption, the 180 °C-spiked resin samples absorbed highest amount of moisture followed by 160 °C-spiked samples.

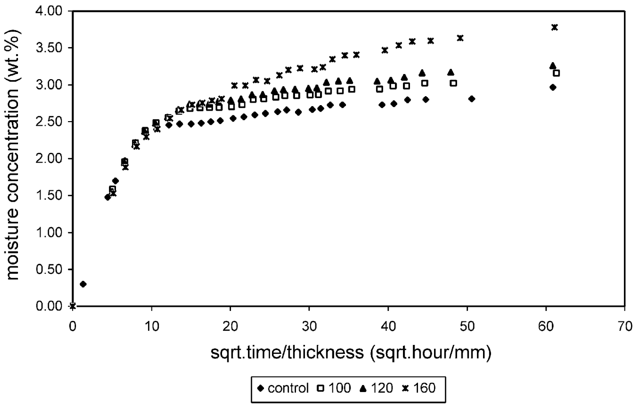


Fig. 2. Moisture absorption curves for resin samples conditioned for 5000 h at 96% RH/50 °C and subjected to 29 thermal spikes between 100 and 160 °C using spike-program I given in Table 1.

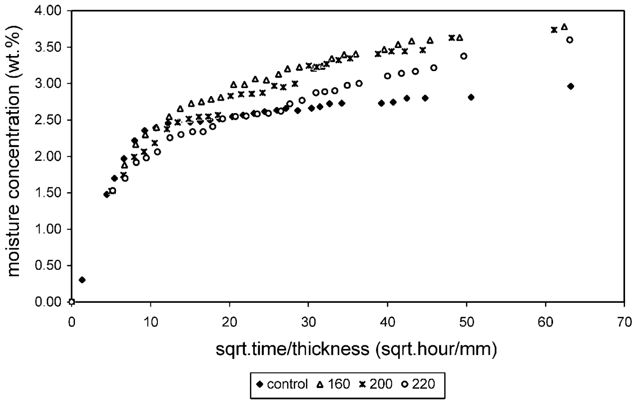


Fig. 3. Moisture absorption curves for resin samples conditioned for 5000 h at 96% RH/50 °C and subjected to 29 thermal spikes between 160 and 220 °C using spike-program I given in Table 1.

3.2. Diffusion coefficients

For the calculation of diffusion coefficients, the absorption data was plotted as moisture concentration against $\sqrt{t}$, where t is time in seconds. The diffusion coefficient was calculated using Eqs. (1) and (2) [10,11].

$$D = \pi\left(\frac{sd}{4M_\infty}\right)^2 \tag{1}$$

where s is the initial slope of the plot of M_t against $\sqrt{t}$ (t, the time), d the sample thickness and M_∞ is the moisture content at equilibrium. Since the specimens used to determine D were normally of finite dimensions, a correction for the effect of diffusion through the edges can be made according

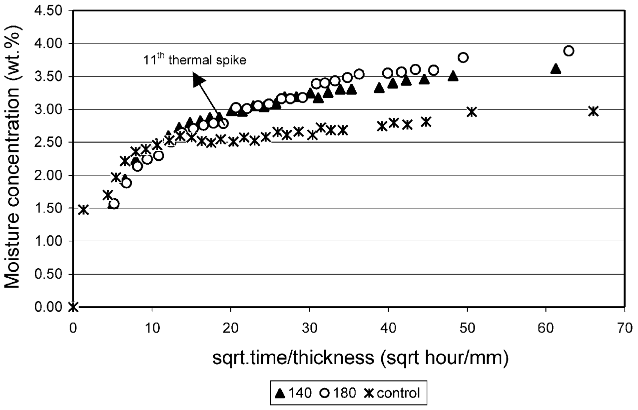


Fig. 4. Moisture absorption curves for resin samples conditioned for 5000 h at 96% RH/50 °C and subjected to 29 thermal spikes to 140 and 180 °C using spike-program I given in Table 1.

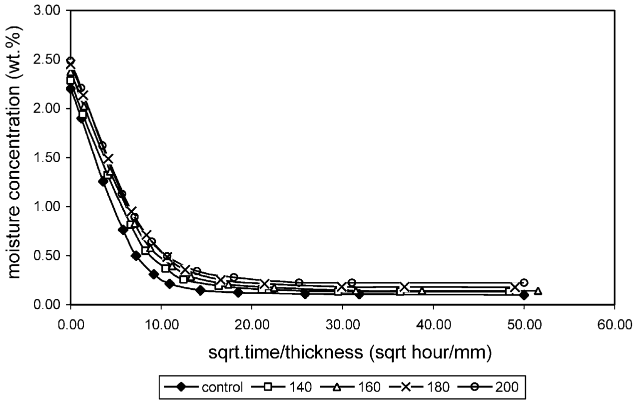


Fig. 5. Desorption curves for resin samples under vacuum at 50 °C for 3500 h after conditioning at 96% RH for 5000 h, and thermal spiking between 100 and 160 °C using thermal spike-program I given in Table 1.

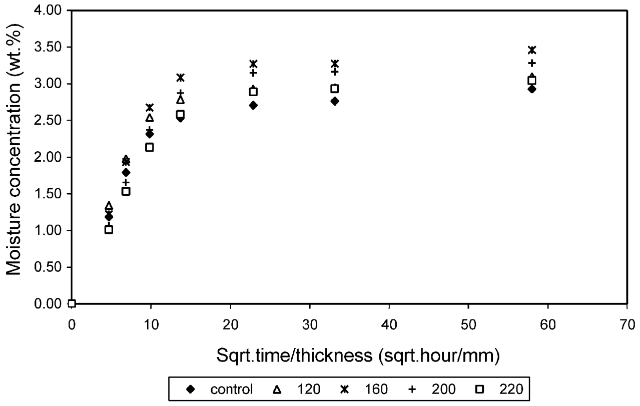


Fig. 6. Isothermal resorption curves for the resin samples conditioned for 3500 h at 96% RH/50 °C after absorption under thermal spiking conditions (from 100 to 220 °C) and subsequent drying in the vacuum oven.

to

$$D_C = D\left(1 + \frac{d}{h} + \frac{d}{w}\right)^{-2} \tag{2}$$

where h and w are sample length and width, respectively. Eq. (2) is based on the assumption that the rates of diffusion are the same in all directions. The maximum moisture content after 5000 h was used for the sorption calculation. The error in D_C was calculated from the standard deviation in M_∞. Table 4 shows the calculated data for the isothermally conditional samples.

The sorption plots obtained for samples conditioned at 50 °C in 96% RH with intermittent thermal spikes between 100 and 220 °C were clearly non-Fickian as shown in Figs. 2 and 3 so that an equilibrium moisture content was not reached. The isothermal control appeared to reach equilibrium at a concentration of 2.5% by weight after 225 h. After 9000 h, further moisture absorption was observed which implied that a 'structural' change may have recurred. At lower humidities, similar trends were observed but at lower moisture concentration, with approximate Fickian behaviour over the first 1000 h [12]. Sorption curves obtained for all specimens during drying (Fig. 5) and resorption stages (Fig. 6) showed Fickian behaviour. Slight deviation from Fickian behaviour was only evident after 3500 h on resorption. For calculating the diffusion coefficient, moisture concentration achieved after 5000, 3500 and 3500 h during absorption (M_{5000A}), desorption (M_{3500D}), and resorption (M_{3500R}), respectively is used as M_∞. However, the moisture concentrations achieved under thermal spiking were not used for the calculation of a diffusion coefficient. From Table 5 it can be seen that values of D_C for the resorption of moisture are significantly lower than those for isothermal absorption and desorption. Also, they decrease with increasing thermal spike-temperature.

3.3. Effect of spike-time on moisture absorption

In order to understand the effect of spike-time on moisture absorption kinetics, three different spike-programmes were used to thermally spike the resin samples. The three spike-programmes used in this study are given in Table 1. Spike-programme I was developed by Xiang and Jones [2]. t_s in Table 1 is the time spent by samples in the

Table 3
Moisture contents for resin samples conditioned at 96% RH/50 °C, after 5000 h conditioning (M_{5000A}) and 29 thermal spike using spike-program I, residual weights in resin samples after conditioning/spiking and subsequent drying in vacuum at 50 °C for 3500 h (M_{3500D}), and moisture concentrations after isothermal resorption at 96% RH/50 °C, for over 3500 h (M_{3500R})

Spike temperature (°C)	Moisture concentration (wt%)			
	Absorption, M_{5000A}	Desorption, M_{3500D}	Isothermal resorption, M_{3500R}	Total moisture concentration after two sorption cycles
Control	2.81	0.21	2.92	3.13
100	3.02	0.23	3.00	3.23
120	3.17	0.26	3.09	3.35
140	3.51	0.31	3.24	3.55
160	3.63	0.33	3.46	3.79
180	3.78	0.44	3.57	4.01
200	3.62	0.50	3.28	3.78
220	3.37	0.53	3.04	3.57

Table 4
Diffusion coefficients of cyanate ester cured epoxy resin (PT30/DEN431) for isothermal conditioning in a range of humidities at 50 °C, and for desorption at 50 °C in vacuo

Relative humidity (%)	Absorption		Desorption	
	M_{5000A} (%)	D_c (10^{-13}m^2 s^{-1})	M_{3500D} (%)	D_c (10^{-13}m^2 s^{-1})
11	0.48 ± 0.015	5.99 ± 0.18	0.18 ± 0.007	9.27 (±0.46)
16.5	0.70 ± 0.029	5.46 ± 0.22	0.19 ± 0.021	8.13 (±0.46)
31	1.04 ± 0.014	6.12 ± 0.08	0.20 ± 0.014	5.03 (±0.17)
46	1.44 ± 0.014	6.34 ± 0.06	0.19 ± 0.007	5.90 (±0.06)
75	2.19 ± 0.017	4.85 ± 0.03	0.23 ± 0.011	7.72 (±0.05)
96	2.96 ± 0.021	3.62 ± 0.02	0.19 ± 0.007	4.86 (±0.03)
100	3.19 ± 0.045	3.19 ± 0.04	0.23 ± 0.021	4.21 (±0.06)

oven after reaching the planned spiking-temperature at the centre of the cross-section of the sample.

Table 6 gives the moisture concentrations for the resin samples after 17 thermal spikes and 2000 h of conditioning at 96% RH/50 °C. From Table 6 it can be seen that the enhancement in moisture absorption, through spiking was found to decrease with increased spike-time for all spiking-temperatures.

3.4. Effect of dry-spiking on moisture absorption

To investigate the effect of dry-spiking on moisture absorption and to examine whether dry-spiking also causes an enhancement in moisture absorption, as observed for the wet resin samples. Resin samples were spiked at 180 and 200 °C prior to isothermal conditioning using spike-program I. This process is termed dry-spiking, while the samples which were spiked during the conditioning are described as wet-spiked. 15 dry-spikes were applied to the resin samples at 180 and 200 °C and then they were isothermally conditioned at 96% RH/50 °C, for over 3500 h.

Table 7 gives the final moisture concentrations achieved for resin samples dry and wet-spiked to 180 and 200 °C. From the results obtained it can be seen that dry-spiking to 180 and 200 °C has no effect on isothermal moisture absorption. An enhancement in moisture absorption was not observed. The concentration of moisture absorbed by the dry-spiked and the control samples were the same within experimental error. Thus the enhancement in moisture absorption is only observed when resin samples containing moisture are thermally spiked.

Table 5
Isothermal desorption and resorption diffusion coefficients at 50 °C of the cyanate ester cured epoxy resin samples after conditioning at 96% RH/50 °C, for 5000 h and 29 thermal spikes using spike-program I

Thermal spike temperature (°C)	Isothermal moisture diffusion coefficient D_C (10^{-13} m^2 s^{-1})		
	Absorption	Desorption	Resorption
Control/50	3.62	4.86	3.52
100	–	4.47	3.92
120	–	4.83	3.97
140	–	4.56	3.81
160	–	4.47	3.47
180	–	4.02	3.12
200	–	3.49	2.71
220	–	2.55	1.89

Desorption in vacuum at 50 °C was monitored for 3500 h, and isothermal resorption for over 3500 h at 96% RH/50 °C.

4. Discussion

4.1. Effect of thermal spiking temperature

The effect of thermal spiking temperature on the moisture contents of resin samples after sorption, desorption, and resorption is shown in Fig. 7. Conditioning of the resin samples at 96% RH with intermittent thermal excursions or spikes, in a dry oven, caused an enhancement in the moisture absorption. The moisture content reached a maximum at a specific temperature referred to as, the maximum moisture enhancement temperature (T_{max}). As shown in Fig. 7, above or below this temperature the enhancement was much less. The final moisture concentration M_∞, is not normally affected by the temperature of

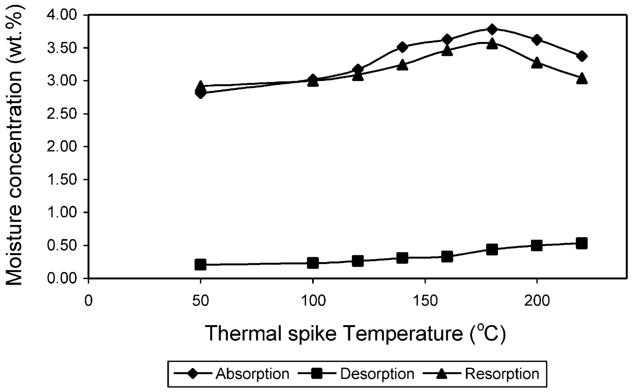


Fig. 7. Moisture contents for resin samples conditioned at 96% RH/50 °C, after 5000 h conditioning and 29 thermal spike using spike-program I, residual weights in resin samples after conditioning/spiking and subsequent drying in vacuum at 50 °C for 3500 h, and moisture concentrations after isothermal resorption at 96% RH/50 °C, for over 3500 h.

Table 6
Moisture concentrations for resin samples, after 2000 h of conditioning at 96% RH/50 °C, and 17 thermal spikes using three different spike-programmes given in Table 2

Spike temperature (°C)	Final moisture concentration (wt%)		
	Spike I $t_s = 1$ min	Spike II $t_s = 3$ min	Spike III $t_s = 5$ min
Control	2.73	2.73	2.73
120	3.06	2.98	2.70
140	3.44	3.11	2.98
160	3.58	3.24	3.03
180	3.60	3.25	3.05
200	3.44	3.11	2.91
220	3.09	3.00	2.79

Table 7
Moisture concentrations achieved for resin samples initially dry-spiked to 180 and 200 °C using spike-programme I given in Table 1 and then conditioned at 96% RH/50 °C, for over 3500 h and for resin samples wet-spiked to 180 and 200 °C using spike-programme I given in Table 1

Spike temperature (°C)	Moisture concentration (wt%)	
	Dry spike	Wet spike
Control	2.81	2.81
180	2.80	3.88
200	2.78	3.73

the conditioning environment, since it is a thermodynamic property associated with the polarity of the molecules. Therefore, the moisture enhancement through spiking implies that more polar sites are becoming accessible. The most likely explanation is that the thermal event makes these sites available through scission of strong dipole–dipole or hydrogen bonds or through hydrolysis of crosslinks. For samples conditioned at 96% RH (Table 3) when samples are spiked above or below T_{max}, they absorbed less moisture. The reduction in moisture absorption above T_{max} can be attributed to a hygrothermally induced molecular relaxation of the polymer network. T_{max} is found to be a function of the conditioning time (number of spikes). The effect of number of spikes on moisture content for resin samples spiked to 140 and 180 °C is shown in Fig. 4. The samples were subjected to 29 spiking cycles. Over the first 11 spikes, T_{max} for the resin samples was 140 °C, but after 11 spikes 180 °C-spiked samples have shown higher enhancement than any other spiking temperature.

4.2. Residual weight after desorption

The desorption study shows that the moisture absorbed either by the controls or by the spiked resin samples cannot be totally removed even after drying at 50 °C in a vacuum oven over an extended period of time (see Fig. 5 and Table 3). This might indicate that either the water is strongly hydrogen bonded and/or partial hydrolysis (a chemical interaction between the water molecules and the resin structure) has occurred under the hygrothermal conditions employed. Zhou and Lucas [13,14] and Soles and Yee [15] have recently reported the retention of water in epoxy resins after desorption, and attributed it to differing degrees of hydrogen bonding. Table 4 shows that isothermal conditioning generally leads to the retention of weight, after desorption, of 0.18–0.23% over a range of humidities. Whereas on spiking to higher temperatures during conditioning the residual weight appears to increase linearly

Table 8
DMTA data for resin samples, conditioned at 96% RH/50 °C, and intermittently spiked between 100 and 220 °C and subsequently dried in a vacuum oven at 50 °C for 3500 h

Spike temperature (°C)	Moisture content (wt%)	$T_{\mathrm{g\ wet}}$ (°C)		$T_{\mathrm{g\ dry}}$ (°C)		$T_{\mathrm{g}E'(\mathrm{wet})}$ (°C)	$T_{\mathrm{g}E'(\mathrm{dry})}$ (°C)
		1	2	1	2		
As-cured	–	272		272		227	227
Control	2.96	250		269		217	224
100	3.15	250		269		219	224
120	3.26	248		268		220	225
140	3.61	244		268		210	226
160	3.77	242		267		206	226
180	3.88	238		267		186	216
200	3.73	235		262		170	200
220	3.59	233	149	262	194	123	169

$T_{\mathrm{g\ wet}}$ and $T_{\mathrm{g\ dry}}$ are the glass transition temperatures after absorption and desorption, respectively. $T_{\mathrm{g}E'(\mathrm{wet})}$ and $T_{\mathrm{g}E'(\mathrm{dry})}$ are from the onset of the reduction in storage modulus.

with temperature (Fig. 7) reaching 0.53% with intermittent spikes to 220 °C. In Table 3, the total moisture absorbed after two cycles is consistent with a non-desorbable concentration of water of ≈0.2%. The remaining 0.3% at 200 °C would appear to be associated with a separate mechanism.

From Table 8 it can been seen that the glass transition temperature of the samples spiked up to 180 °C is recoverable within 5 °C of the as-cured resin after drying. The 5 °C difference between as-cured and dried samples could be attributed to experimental batch to batch variation or from the small amount of hydrogen bonded water which is incorporated during the first cycle of absorption. However, with thermal excursions, above that temperature, the glass transition only returns within 10 °C. Furthermore, the onset of the reduction in storage modulus ($T_{gE'}$) occurs at significantly reduced values of 216–169 °C indicating a broadening of the relaxation peak. In addition, at 220 °C a secondary relaxation peak forms at 194 °C (Table 8). Since these temperatures exceed the value of T_g determined from the reduction in storage modulus, the network can relax facilitating hydrolytic degradation.

We conclude that below a spike-temperature of 180 °C the residual weight after drying can be attributed mainly to water which is either hydrogen bonded to and/or reacted with the resin structure without chain scission (≅ 0.25%). Above 180 °C, when network chains achieve some mobility a small degree of hydrolysis can account for the additional >0.25% retained weight.

Attempts to examine this hypothesis by FTIR analysis [12] of wet and dry samples were unsuccessful, showing no significant changes in the spectra of samples spiked to 220 °C. However, it should be remembered that the number of network bonds required to be ruptured to create a mechanism for relaxation is very small and may not be detectable by IR spectroscopy. However, a thermally cured PT30 cyanate ester resin exhibited small peaks in the FTIR spectrum at 2263, 2235, and 2200 cm^{-1} which can be attributed to residual –OCN groups. The former two peaks were absent after moisture conditioning. A peak at 1700 cm^{-1}, which can be attributed to a carbamate, appeared [12]. It is therefore entirely reasonable to assume that an undetectable concentration of –OCN groups is present in the thermally cured cyanate ester/epoxy blend.

Elsewhere we reported [16] that the hydrolytic stability of uncatalysed cyanate ester/epoxy resin networks was strongly dependent on the fraction of cyanate ester in the blend. Table 1 shows the structures of the groups formed during cure [5–8]. The cure is believed to proceed via trimerisation of the cyanate ester groups to an arylcyanurate or triazine (iii) which reacts with the glycidyl or epoxy groups to form an alkyl cyanurate (triazine ring (iv)) which isomerises into an alkyl isocyanurate (v) which can further react with the glycidyl groups to form an oxazolidinone (vi). Incomplete reaction with the epoxy groups can lead to residual cyanate ester groups which can react with water to form a carbamate (vii) [17]. Incomplete reaction of the epoxy groups is less probable because of the higher stoichiometric concentration of the PT30 resin. It can be concluded that residual cyanate ester groups and/or the ‘triazine rings’ in different states of reaction may be responsible for the sensitivity to water.

It has been reported that arylcyanates are stable to water at room temperature in the absence of catalysts. For example, only 5% hydrolysis of a bisphenolIA dicyanate was observed at room temperature after 6 months [18]. Thus the small quantity of retained water after isothermal conditioning could be explained by hydrogen bonded water or by reaction with isolated cyanate ester groups. The hydrolysis product of the latter is a carbamate ((vii) in Table 1) which can readily hydrogen bond water. Since at low relative humidities (Table 4) and temperatures up to 120 °C, the residual weight after desorption is constant at ≅ 0.25%, it follows that small quantities of residual cyanate groups, which hydrolyse and then hydrogen bond water are responsible for the moisture sensitivity in the absence of observable degradation, however, at spike-temperatures in excess of 180 °C where the network achieves some mobility some more permanent hydrolytic mechanism appears to be induced, as shown by changes in the thermomechanical response (Table 8). At intermediate thermal spiking temperatures, there appears to be a change from the low temperature to the high temperature mechanism.

4.3. Resorption

The resorption data suggest that any change taking place in the network structure of the polymer matrix during first stage of absorption/thermal spiking is irreversible. After desorption, the polymer would exhibit a network structure with ‘frozen in’ segmental conformations. The resorption process would thus be different from the sorption process because after a cycle of sorption and desorption the network structure has already been modified by relaxation effects. Apicella et al. [19] suggested that water absorption will cause an irreversible expansion of the polymer network. Thus, a larger rate of desorption of the dissolved water molecules from the expanded structure compared to that for network relaxation will lead to a higher free volume within the resin.

The resorption curves were found to be closely Fickian in nature. Equilibrium was reached after conditioning for over 3500 h. If relaxation of the resin network in the presence of absorbed moisture and interactions between water molecules and polar sites in resin network are responsible for the non-Fickian diffusion during the first stage of absorption, then the Fickian nature of the resorption curves suggests that molecular relaxation events and additional interactions between water molecules and polar sites present in resin structure are not significant during resorption.

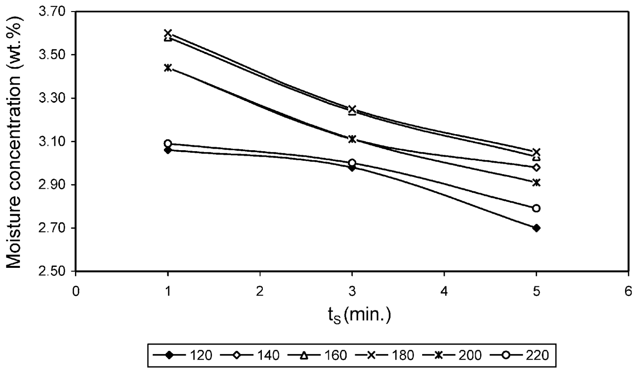


Fig. 8. Effect of spike-time on moisture concentrations for resin samples, after 2000 h of conditioning at 96% RH/50 °C, and 17 thermal spikes using three different spike-programs given in Table 1.

4.4. Diffusion coefficient

As shown in Table 5 the values of D_C estimated using resorption data were found to be lower at all spiking-temperatures than those estimated from the desorption data. D_C was found to decrease with an increase in spike-temperature. For the control samples, the value of D_C estimated from the resorption data is lower than that calculated from the initial isothermal conditioning data.

If moisture diffusion can be considered to be a process of 'hole filling', the reduction in D_C could indicate an apparent reduction in the molecular size of the holes in the polymer network. This may only be achieved through relaxation and a redistribution of the unoccupied volume within the polymer matrix. For the resin samples conditioned in the same hygrothermal environment, the degree of relaxation is expected to be larger for those thermally spiked to higher temperatures and therefore the reduction in D_C would also be correspondingly larger. Mijovic and Lin [20] suggested that the higher diffusion coefficient observed during moisture desorption is partly due to the release of the swelling strains formed during absorption.

In addition to the relaxation mechanism, the presence of residual water molecules which cannot be removed by desorption and become entrained in the polymer network, probably as a result of partial hydrolysis of residual functional groups in the polymer matrix, may also restrict the moisture diffusion during resorption, leading to a reduction in D_C.

4.5. Effect of thermal spike-time on moisture absorption

From the data in Table 6 it can be seen that the enhancement in moisture absorption, through spiking was found to decrease with increased spike-time for all spiking-temperatures. The data in Fig. 8 and Table 6 could be interpreted by an incomplete recovery of the additional desorption which occurs during a longer spike-time. An alternative explanation could be that more time is available for relaxation of network at high values of t_s resulting in a lower moisture absorption.

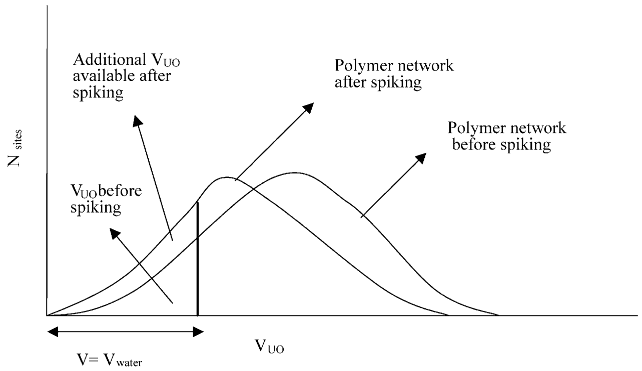


Fig. 9. Relationship between number of sites (N_{sites}) and unoccupied volume (V_{uo}) in the resin network at room temperature and when thermally spiked below wet glass transition temperature.

On spiking, reorganisation through skeletal rotational effects is required for the extra water to be absorbed. That is why the effect is strongly dependent on the proximity of T_g, (which is required for relaxation of the network to occur). The conformational reorganisation will be cooperative in nature.

Unoccupied volume in the crosslinked resin consists of free volume of molecular dimensions and of microvoids of larger dimensions [21,22]. The free volume, which leads to plasticisation 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 also present in highly crosslinked polymers because of the restrictions to conformational change of the network chains. Moisture which resides within these regions is a less effective plasticiser. Free volume theories have been used to explain an increase in unoccupied volume created during thermal spiking which can accommodate the extra moisture absorbed [23]. These theories rarely take into account the behaviour of the polymer network at temperatures in or approaching the glass transition region where the free volume is generally accepted to increase.

The distribution of the unoccupied volume (V_{uo}) in a resin network across the number of sites (N_{sites}) of differing dimensions is given schematically in Fig. 9. It is postulated that during a thermal spike, the unoccupied volume is redistributed to make available additional sites of molecular volume in to which the moisture can diffuse. Changes in the molecular conformation of the network chains are promoted at the spike-temperature as shown in Fig. 9. This redistribution will increase the unoccupied volume that is readily accessible to moisture which will result in a higher moisture content after conditioning following spiking. The distribution curve in Fig. 9 will become more and more uniform with spike-temperature, as equilibrium is approached. When the spiking-temperature is close to the T_g of the wet resin, relaxation through conformational change will tend to reduce the size of the microvoids and hence the concentration of water which can be held in the larger sized microvoids. This leads to a reduced value of M_∞ at higher spike-temperatures. Furthermore, the increased segmental mobility of the network will facilitate an increased rate of hydrolysis of sensitive groups. This in turn promotes the relaxation of the network.

5. Conclusions

Regular and intermittently applied thermal spikes during moisture conditioning can cause an enhanced absorption in cyanate ester modified epoxy resins. A maximum moisture enhancement spike-temperature exists for the resin. The spiking of samples below or above this temperature resulted in lower moisture content. This may result from the redistribution of the unoccupied volume available in the polymer network during conditioning and thermal spiking. The quantity of the entrained water (residual weight) increased with spiking-temperature. However, part of that was constant over a wide range of conditions and may be attributable to hydrogen bonded water or more likely to reaction with isolated cyanate ester groups.

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