

Mechanism of thermal spiking-enhanced moisture absorption by cyanate ester cured epoxy resin matrices

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Summary: The moisture absorption of blends of cyanate ester resin with epoxy resin, has been studied under constant hygrothermal condition and with a series of thermal spikes, in an attempt to understand the so-called enhanced moisture absorption phenomenon. Various resin blends of differing composition were studied, so that the effect of resin structure on moisture absorption could be assessed. It was found that intermittently applied thermal spikes can cause enhanced moisture absorption by cyanate ester and blends with epoxy resin in humid environment. The equilibrium moisture concentration was found to increase with the concentration of cyanate ester in the blend. The results of the desorption study on both control and spiked specimens showed that some of the water molecules remain entrained in the resin, probably as a result of hydrolysis of the polymer matrix. The glass transition temperature was reduced by absorbed moisture.

Keywords: cyanate ester, moisture absorption, thermal spiking, glass transition temperature

Introduction

Epoxy resins are the most common matrices for high performance carbon-fibre composites, which are used to make structural artefacts for the aerospace industry. One of the concerns for successful practical application is the extent of degradation which occurs on exposure to a moist environment. The moist environment may be especially damaging if the temperature is not constant but varies rapidly over a wide range. Sudden, large temperature changes, referred to as “thermal spikes”, are encountered for example by aircraft flying at supersonic speeds. Thermal spikes may alter significantly the moisture absorption as well as the performance of the composite materials.

Reflecting the state of the technology, previous investigations concentrated on epoxy resin matrix composites. As a result, the hydrophilic nature of epoxy resin as composite matrices has been well documented. Since many applications in the aerospace industry cannot accept the moisture sensitive nature of epoxy resin matrix composites, intensive research work has been undertaken to identify new thermosetting resins with reduced moisture absorption but without compromising its processibility. One important example of this achievement was the synthesis of the polycyanurates or cyanate ester resins for the use as matrices in composites.

The co-reaction of a cyanate ester with epoxy resin changes both the branching density and the chemical composition of the resulting network [1]. In this paper, we report an investigation aimed at studying the effect of changes in chemical structure of cyanate ester / epoxy blends by varying the composition of the blend on its moisture absorption behaviour.

Experimental Work

Materials

The four cyanate ester / epoxy blends were used in this study. The cyanate ester used was the dicyanate DCBA (AROCYL 10), and the epoxy resin, DEN 431 which is a Phenolic Novolac resin. Table 1 shows the four cyanate ester / epoxy blends used in this study and the ratio of cyanate group : epoxy group.

Table 1: Resin blends with varying AROCYL 10 concentration.

Resin system designation	AL10 (P)	A/D (70:30)	A/D (50:50)	A/D (30:70)
AROCYL 10 (wt.%)	100	70	50	30
DEN 431 (wt.%)	0	30	50	70
AROCYL 10:DEN 431 (molar ratio)		2.12:1	0.9:1	0.38:1

Sample Preparation

The component resins were first preheated to 120⁰C to reduce their viscosity and allow complete mixing with glass stirrer. The resin blend was degassed at 120⁰C for 2 hours in a vacuum oven to remove entrapped air bubbles and volatilise to ensure that defect-free samples were formed. The resin was poured into silicon rubber moulds which had been preheated to 180⁰C. The recommended curing cycle involved 2 hours, at 180⁰C followed by post-curing for 4 hours, at 250⁰C. For conditioning, the resin samples were cut to dimensions of 55×25 mm using a water-cooled diamond wheel. For DMTA analysis the resin samples were cut to dimensions 40×10×1 mm. The specimens were then milled down to a thickness of 1mm, and all of the faces polished to a 1200 grit finish. Before conditioning, all of the samples were dried in a vacuum oven at 50⁰C until a constant weight was attained.

Conditioning

After drying samples were placed on racks above a saturated salt solution of potassium sulphate (K₂SO₄) in distilled water, which has a relative humidity of 96% in a sealed humidity chamber in an air-circulating oven at 50⁰C. Resin samples were removed intermittently, weighed and returned to the humidity chamber (control samples) or subjected to thermal spike (spiked specimens). Once a spike had been performed, the samples were re-weighed and placed back in the chamber. This allowed sorption curves to be plotted as moisture content (expressed in weight percent) against $\sqrt{\text{time}}/\text{thickness}$. The moisture absorbed was determined using an Electro-balance accurate to 10⁻⁵ g. The moisture content was calculated using the following equation;

$$M_t = 100 \times \left(\frac{m_t - m_o}{m_o} \right) \quad (1)$$

Where m_o and m_t are the dry sample weight and wet sample weight at time t respectively.

The desorption of the previously moisture saturated samples was carried out in a vacuum oven maintained at 50^oC and 1000 mbar. Samples were removed at suitable time intervals, weighed and replaced in the vacuum oven.

Thermal spike programme

The Table 2 lists the spiking times for resin specimens determined by Xiang et al (2).

Table 2: Spiking times at different temperatures for the resin specimens.

Temp. (°C)	100	120	140	160	180	200	220
Time (min.)	3.5	4	4.5	5	5.5	6	6.5

Thermal spiking was carried out in an air-circulating oven: Checkmate 320/TS/S. The spiking specimens were vertically placed in a steel frame during spiking processes to allow uniform heating of the two major surfaces. In all cases the first spike was applied after conditioning the specimen in hygrothermal environment for approximately one day. The moisture content in the specimens was measured before and after applying the thermal spike. The specimens were subsequently removed from the oven and allowed to air-cool before being returned immediately to the humidity chamber until the next thermal spike should be applied. This routine was subsequently repeated at regular intervals.

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^oC to 300^oC.

Results

Fig. 1 and 2 show the effect of thermal spiking temperature on the moisture absorption for AL10 (P) and A/D (30:70) resin samples respectively.

From the absorption curves it can be seen that resin specimens had not achieved equilibrium moisture content even after conditioning for over 4,000 hours and 26 thermal spikes. Even after 4,000 hours of conditioning resin samples continued to absorb moisture at a low rate. This suggests that moisture absorption is non-fickian in nature. Thermal spiking to 120^oC had caused noticeable enhancement in the moisture absorption for all the resin blends. The A/D (30:70) blend was found to absorb lowest moisture than other three resin blends at all spiking temperatures studied. While AL10 (P) had absorbed more moisture than the other three resin blends, the moisture content was found to decrease with decrease in cyanate ester concentration in the blend.

Highest moisture enhancement was shown by A/D (70:30) resin blend (44%) at 180^oC -spike temperature, while the lowest enhancement was shown by A/D (30:70) resin samples (25%) at 180^oC -spike temperature. The maximum moisture enhancement spike temperature was found to be different for each resin blend. Maximum moisture enhancement temperature shifted to a higher temperature (from 140^oC to 180^oC) as the composition of the blend was changed from A/D (30:70) to cyanate ester (AL10 (P)). In the thermal spike temperature

range used (120°C - 180°C), the moisture content of A/D (70:30) resin samples continued to increase. For A/D (50:50), and A/D (30:70) resin samples the maximum enhancement temperature occurred at 140°C . The results suggest that for A/D (70:30) blend a phase similar to the AL10 (P) was present which was controlling the moisture absorption. The chemical structure of A/D (30:70) blend was apparently different. Table 4 shows the residual weight obtained after drying of the resin samples in vacuum oven for 3,500 hours at 50°C .

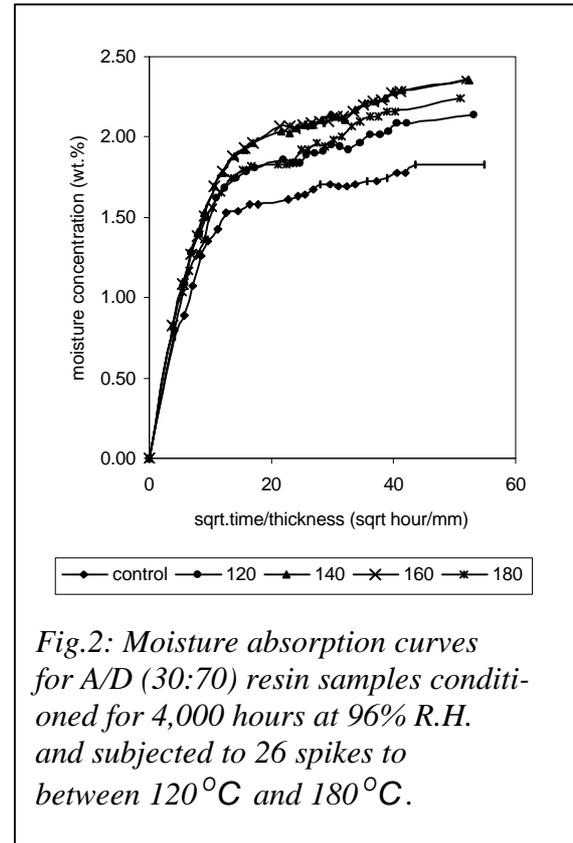
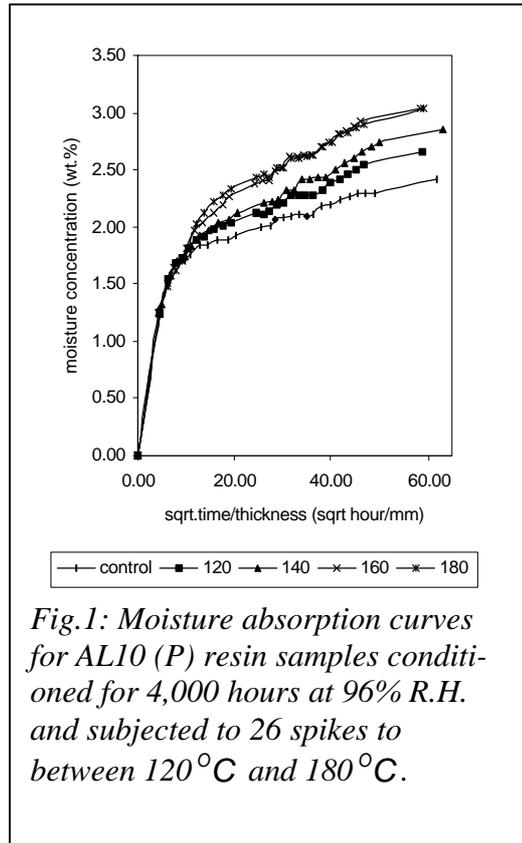


Table 3: Moisture concentrations for AL10 (P), A/D (70:30), A/D (50:50), and A/D (30:70) resin samples, after 4,000 hours conditioning at 96% R.H./ 50°C and 26 thermal spikes.

Spike temperature ($^{\circ}\text{C}$)	Final moisture concentration (wt.%)			
	AL10 (P)	A/D (70:30)	A/D (50:50)	A/D (30:70)
Control/50	2.42 (± 0.015)	2.04 (± 0.005)	2.04 (± 0.016)	1.82 (± 0.005)
120	2.65 (± 0.014)	2.32 (± 0.008)	2.45 (± 0.023)	2.13 (± 0.009)
140	2.85 (± 0.015)	2.59 (± 0.009)	2.74 (± 0.028)	2.35 (± 0.008)
160	3.03 (± 0.005)	2.81 (± 0.005)	2.70 (± 0.031)	2.35 (± 0.009)
180	3.03 (± 0.018)	2.93 (± 0.015)	2.60 (± 0.005)	2.24 (± 0.048)

The residual weight increased with increasing spike temperature for all four resin systems. The maximum moisture enhancement spike temperature was 180°C , 180°C , 140°C , and 140°C for AL10 (P), A/D (70:30), A/D (50:50), and A/D (30:70) resin samples respectively. However after desorption, the residual weight was directly related to the maximum temperature employed.

The highest residual weight was observed for the AL10 (P) resin samples at all spike temperatures, while the lowest residual weight was observed for A/D (30:70) resin samples. The residual weight was found to increase with increasing weight fraction of

cyanate ester (AROCYL 10) in the resin blend. The residual weight of the A/D (30:70) blend were much lower (0.035% to 0.095%) in comparison to the 0.23% to 0.63% for the pure cyanate ester (AL10 (P)). (Note: The residual weight of the A/D (50:50) resin samples cannot be directly compared with the that of the other blends because they were conditioned for a large period of 5,000 hours and subjected to several more (29) thermal spikes.)

Table 4: Residual weight in AL10 (P), A/D (70:30), A/D (50:50) (conditioned for 5,000 hours), and A/D (30:70) resin samples, after drying in vacuum at 50°C for 3,500 hours.

Spike Temp. (°C)	Residual weight M_{dry} (wt.%)			
	AL10 (P)	A/D (70:30)	A/D (50:50)	A/D (30:70)
Control/50	0.23 (± 0.018)	0.11 (± 0.007)	0.21 (± 0.014)	0.035 (± 0.001)
120	0.33 (± 0.009)	0.16 (± 0.004)	0.27 (± 0.028)	0.068 (± 0.002)
140	0.41 (± 0.007)	0.22 (± 0.002)	0.31 (± 0.023)	0.074 (± 0.006)
160	0.52 (± 0.007)	0.31 (± 0.021)	0.33 (± 0.005)	0.093 (± 0.023)
180	0.63 (± 0.014)	0.45 (± 0.014)	0.37 (± 0.015)	0.095 (± 0.014)

Fig. 3 and 4 show the $\tan \delta$ spectra for AL10 (P) and A/D (70:30) resin samples, which had been conditioned at 96% R.H. and subjected to intermittent thermal spikes to 180°C.

From the Fig. 3 it can be seen that for the 160°C -spiked specimens of AL10 (P) main $\tan \delta$ peak is split in to two peaks. The second peak appeared at 178°C (T_{g2}). For the specimens spiked to higher temperature, this second peak was shifted to 160°C. From the Fig. 4 it can be seen that thermal spiking of the A/D (70:30) samples to 180°C caused the main $\tan \delta$ peak to split into two. The second peak appeared at 162°C. No splitting of main $\tan \delta$ peak was observed for the A/D (50:50) and A/D (30:70) resin samples. If the splitting of the $\tan \delta$ peak is the result of a two phase resin structure with differing sensitivity to plasticization during spiking, it is possible to suggest that the absorbed moisture has a large suppression-effect on the glass transition temperature of one phase, and lesser effect on the glass transition temperature of the second phase.

Table 5: Thermomechanical data for AL10 (P), A/D (70:30), A/D (50:50), and A/D (30:70) resin samples, conditioned at 96% R.H., and intermittently spiked to between 120°C and 180°C.

Spike Temperature (°C)	AL10 (P)		A/D (70:30)		A/D(50:50)	A/D (30:70)
	T_{g1} , °C	T_{g2} , °C	T_{g1} , °C	T_{g2} , °C	T_{g1} , °C	T_{g1} , °C
As-cured	248	-	214	-	201	186
Control	218	-	202	-	185	169
120	219	-	194	-	176	171
140	219	-	193	-	163	170
160	214	178	188	-	193	169
180	215	160	184	162	186	166

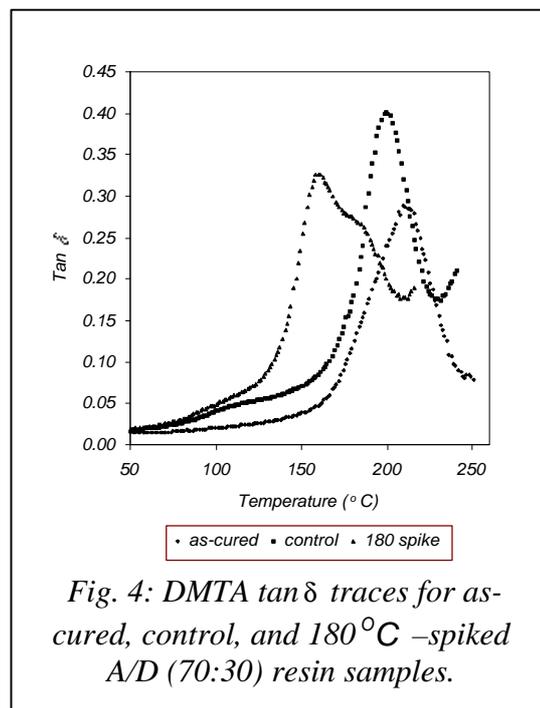
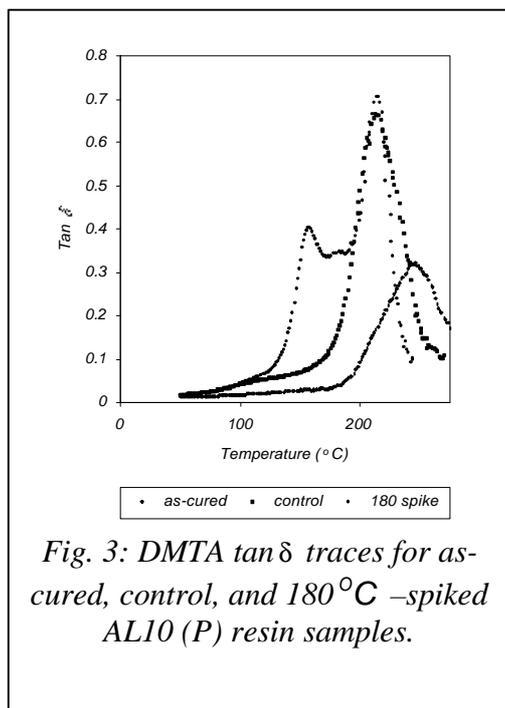


Table 6: Thermomechanical data for AL10 (P), A/D (70:30), A/D (50:50), and A/D (30:70) resin samples, which had been previously spiked and subsequently dried in a vacuum oven to constant weight.

Spike Temperature, °C	AL10 (P)		A/D (70:30)	A/D (50:50)	A/D (30:70)
	T_{g1} , °C	T_{g2} , °C	T_{g1} , °C	T_{g1} , °C	T_{g1} , °C
As-cured	248	-	214	201	186
Control	237	-	211	195	184
120	234	-	210	194	184
140	224	-	209	193	184
160	214	-	205	193	184
180	219	196	196	186	183

Discussion

With isothermal conditioning the moisture content (after 4,000 hours) increased with increasing concentration of cyanate ester in the blend (see Table 3). The blend with the lowest concentration of cyanate ester (30% wt.) absorbed the least moisture while the blend containing highest concentration of cyanate ester (70% wt.) absorbed the most. Spiking to 120°C enhanced the moisture content of the A/D (50:50) blend by 20%, but only 9% for the cyanate ester. At 180°C, the A/D (70:30) resin exhibited greatest enhancement (by 44%). Moisture content continued to increase with spike temperature up to maximum spike temperature studied (180°C) for AL10 (P), and A/D (70:30) resin samples, but for other two blends after maximum moisture enhancement spike temperature (160°C) the moisture content fell (see Table 3).

Fig. 5 compares the effect of cyanate ester concentration in the blend on the final moisture content (after 4,000 hours) achieved under isothermal conditioning with the maximum moisture absorbed after spiking (spike-temperature varies-see the Fig. 5 for details) and the residual weight after drying for samples spiked to 180 °C.

It can be seen that the moisture content and residual weight increases as the concentration of cyanate ester in blend increases.

M. Bauer and J. Bauer [1] have shown that for the reaction between DCBA and corresponding glycidyl ether BADGE, within the range from R=0 to R=0.7 (where R is the initial fraction of the epoxy groups) the network structure changes from pure polycyanurate to a almost completely oxazolidinone. This data cannot be used directly to predict the final chemical composition of the resin blends studied here, but it can be used as a guide to predict the chemical groups which dominate the final composition of the cured blend.

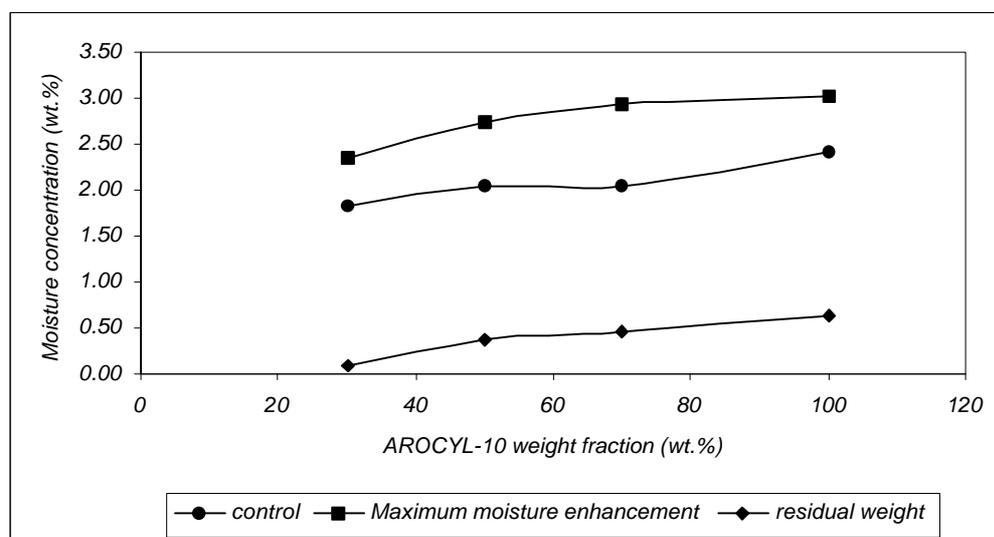


Fig. 5: Effect of the weight fraction of cyanate ester (AROXYL-10) on the final moisture content achieved at control conditioning, maximum moisture enhancement spike temperature (the maximum moisture enhancement spike temperature was 180 °C for AL10 (P) and A/D (70:30), and 160 °C for A/D (50:50) and A/D (30:70) blend), and residual weight obtained after drying for 180 °C spiked samples.

Thus AL10 (P), which is thermally cured without addition of a catalyst, will have a polycyanurate structure, with the maximum number of triazine rings. The cured A/D (70:30) blend will have a structure consisting of triazine rings and small concentration of isocyanurate and oxazolidinone groups. The structure of the A/D (50:50) blend will contain the maximum number of isocyanurate groups followed by triazine and oxazolidinone groups. The A/D (30:70) blend will give a cured resin with the highest concentration of oxazolidinone groups. The FTIR results given elsewhere [3] support these conclusions. Therefore it appears that as the moisture content decreases the number of oxazolidinone groups increases. On other hand, when the number of triazine rings increases the moisture content increases.

Thus it can be argued that the triazine rings are hydrolytically less stable than the oxazolidinone groups. This is also supported by the results of the desorption experiments. The residual weight after drying in vacuum, indicated that partial hydrolysis of the polymer matrix has occurred. Residual weight increased with increase in spike temperature (see Table 4). The residual weight for 180 °C -spiked samples increased with increase in concentration of cyanate ester in blend. However the residual weight for the A/D (30:70) blend was very small showing that only limited hydrolysis had occurred. Increasing the weight fraction of the

cyanate ester (AROCYL 10) in the epoxy resin blend from 30% to 100% increased Tg from 186 °C to 248 °C. Thermal spiking of AL10 (P) resin samples to 160 °C caused the main $\tan \delta$ peak to fall from 248 °C to 214 °C with the formation of a second peak at 178 °C. It was found that spiking to 180 °C had no further effect on Tg₁, but Tg₂ dropped by 20 °C to 160 °C. But there was no incremental increase in moisture content. Thus it can be inferred that thermal hydrolysis at the spike-temperature was responsible for the fall in Tg₂ and not the plasticization by absorbed moisture.

After drying, Tg₂ for the 160 °C-spiked samples was not present whereas it remained in the 180 °C-spiked sample. Isothermal moisture absorption by AL10 (P) leads to a residual weight of 0.23% and a reduction in the dry-Tg from 248 °C to 237 °C. At a thermal-spike of 180 °C, the Tg₂ appeared at 160 °C, which on drying remains as a separate peak at 196 °C. Therefore, it can be concluded that partial hydrolysis leads to a phase of differing water sensitivity. Higher the thermal-spike temperature the greater the degree of the degradation and moisture sensitivity of the partially hydrolysed network.

Splitting of the $\tan \delta$ peak also occurred for A/D (70:30) resin samples spiked to 180 °C. On drying Tg₂ was not present. Thus the mechanism responsible for the splitting of the $\tan \delta$ peak appears completely reversible for A/D (70:30) resin samples spiked to 180 °C. This is consistent with the above argument since the enhanced moisture sensitivity of a degradation product means that it would shift by a higher amount than the undegraded network on drying. In this case the two peaks would overlap. Because of the reduced concentration of “homopolymer” curing structure, the presence of a shoulder to the main peak would be difficult to detect. Peyses and Bascom [4] examined the effect of moisture on the Tg of highly cross-linked, high temperature epoxy resin (Narmco 5208) using DMA. They identified two $\tan \delta$ peaks in the relaxation spectra. They suggested that second peak was indicative of degradation of the resin molecular structure. This degradation was believed to be assisted by moisture and was “both partially reversible and partially permanent”.

Splitting of the $\tan \delta$ peak was not observed for A/D (50:50) and A/D (30:70) resin samples. The effect of thermal spiking on Tg for A/D (30:70) resin samples was not significant, because Tg fell only by an additional 5 °C when the spike-temperature was increased from 120 °C to 180 °C. After drying the Tg returned to its original value showing that moisture absorption was reversible despite a small residual weight of 0.03%.

E'_R (rubber storage modulus) is dependent on the average molecular weight between cross-links, E'_R and can thus be used to monitor changes in the cross-link density. Fig. 6 plots the effect of spiking on rubber storage modulus obtained from DMTA experiment of AL10 (P) and A/D (30:70) resin. E'_R was found to decrease for AL10 (P), A/D (70:30), and A/D (50:50) resin blends with spiking temperature. This confirms that thermal spiking leads to chain scission or degradation of the cross-links. The values of E'_R after drying suggests that the cross-link scission reaction is permanent. For the A/D (30:70) blend moisture absorption and thermal spiking had no effect on E'_R . Therefore cross-link density of A/D (30:70) resin samples has been shown to be unaffected by moisture absorption and spiking. This is further confirmation of the hydrolytic resistance of the oxazolidinone structure formed during cure. Furthermore the formation of a Tg₂ peak in the other blends can be attributed to a degradation product with higher water sensitivity.

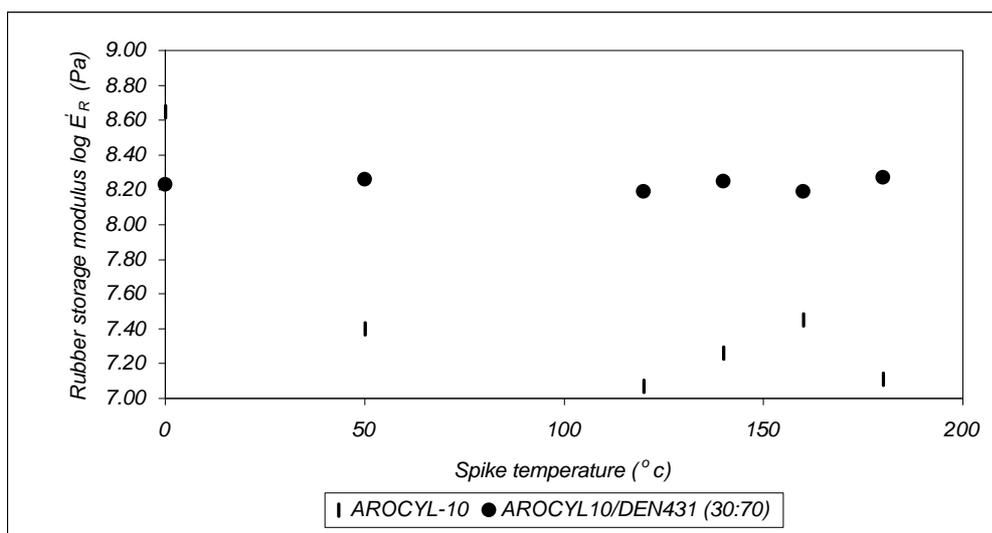


Fig. 6: Effect of spiking temperature on rubber storage modulus of AL10 (P) and A/D (30:70) resin samples conditioned at 96% R.H.

Conclusions

Regularly and intermittently applied thermal spikes during the conditioning causes higher moisture absorption by all of the resin systems studied. Spiking of the samples below or above the maximum moisture enhancement temperature resulted in lower moisture content. This can result from the molecular relaxation of the polymer matrix during conditioning and thermal spiking. This was confirmed by the demonstrated moisture reversibility of epoxy resin blend containing 30% cyanate ester. Where complete reaction of the epoxy groups with the cyanate ester can probably occur. On increasing the weight fraction of the cyanate ester the moisture absorption increased. The residual weight and the rubber storage moduli after conditioning suggests that combined effect of moisture and thermal spiking is causing scission of cross-links.

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