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Mechanisms of moisture absorption by cyanate ester modified epoxy resin matrices: the clustering of water molecules

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Abstract

One of the important factors, which determine the concentration of moisture that a polymer will absorb, is the effect of non-random mixing whereby water-clustering is said to occur. The Flory–Huggins theory cannot predict the isotherms observed for highly polar polymers since the theory assumes complete random mixing. The complementary model of Brown [Brown GL. In: Rowland SP, editor. Water in polymers. Washington, DC: American Chemical Society; 1980. p. 441. [1]] considers the moisture distribution in polar polymers, consists of components associated with random mixing (Flory–Huggins theory) and clustering of the water molecules. Moisture sorption isotherms of cyanate ester/epoxy blends at different relative humidities have been analysed by the clustering theory of Brown [Brown GL. In: Rowland SP, editor. Water in polymers. Washington, DC: American Chemical Society; 1980. p. 441. [1]] and the dual mode sorption theory of Zimm [Zimm BH. J Chem Phys 1953;21:934. [2]]. Clustering was found to occur in cyanate ester/epoxy blends conditioned at relative humidities of 40% and higher. The Cluster size indicates that the majority of the absorbed water in a cured cyanate ester/epoxy blend was not clustered but present in monomeric form through hydrogen bonding to polar sites. It is postulated that the phenomenon of thermal spiking enhanced moisture absorption can be explained by an equilibrium between cluster formation and declustering associated with network relaxation at the spike-temperature.

Keywords: Cyanate ester resins; Moisture absorption; Water clustering

1. Introduction

Glassy polymers, when exposed to a range of relative humidities, show differing absorption behaviour at low and high relative humidities (i.e. low or high activities of the penetrant species). At low activities, sorption of gases and vapours into glassy polymers is successfully described by a dual mode sorption theory, which assumes a combination of Langmuir-type trapping within pre-existing holes and Henry's law type dissolution of penetrant into the glassy matrix. At high activities, strong positive deviations from Henry's law were observed, which indicated that the sorbed molecules diffuse through the macromolecular array according to a different mechanism [3].

If the penetrant is water, both transport and sorption is much more complex than for inert gases. In fact, the high cohesive energy of water leads to the phenomenon of clustering in the polymer. The water molecule is relatively small and in the liquid and solid states is strongly associated through hydrogen bond formation. This combination of features distinguishes it from the majority of organic penetrants. Whereas, the diffusion coefficient generally increases with concentration for organic vapors, marked decreases have been observed with water in several polymers [4]. Values for the enthalpy of formation of the hydrogen bond in the range of 3.4–6.6 kcal/mol have been obtained [4]. As a result, strong localized interactions may develop between the water molecules and suitable polar groups in the polymer. On the other hand, in relatively non-polar materials, clustering or association of the sorbed water is encouraged.

Both clustering and plasticisation may give a curvature to the water vapour isotherm depending on the probability that

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hydrogen bonds will form between the water molecules and the hydrophilic groups in the polymer [5]. Carfagna and Apicella [6] have used clustering theory and polymer–solvent interactions to explain the water absorption characteristics of cured epoxy resins at different temperatures and relative humidities. They claimed that cluster formation is favoured at high relative humidities. The cluster analysis of Zimm and Lundberg [7] has been used to explain the moisture absorption kinetics of polyimides, polyacrylates, polymethyl methacrylate, polyhydroxy ethyl methacrylate and polyvinyl pyrollidone [8–10]. Rodriquez et al. [9] suggested that polymers with a strong interaction with water have negligible degrees of water clustering, while the more hydrophobic polymers exhibit a higher degree of clustering. Dlubek et al. [8] have used positron annihilation lifetime spectroscopy to study the nature of water present in the free volume of a polymer structure and compared it to the cluster analysis of Zimm and Lundberg [7]. A number of investigators have also used various spectroscopic techniques such as Fourier transform infrared spectroscopy and broadband dielectric relaxation spectroscopy for studying the water cluster formation in the polymer structure [11,12]. The degree of clustering has an important impact on the prediction of moisture absorption in high humidity environments and on the effect of thermal spiking during conditioning. In recent publications [13–16], the effects of blend composition on the enhancement of moisture absorption during thermal spiking have been investigated. The enhancement phenomenon is associated with relaxations within the 3D network in the presence of absorbed moisture because it is also observed when there is no evidence of hydrolytic degradation [15]. It has also been shown that the swelling of the resins during moisture absorption is only additive in volume at the latter stages of the process [14]. This is indicative that diffusant clustering is an important aspect of moisture absorption in cyanate ester resins. The phenomenon of the reverse thermal effect in moisture absorption also indicates of a complex mechanism of network relaxation and redistribution of the sites where water molecules are located. To probe these mechanisms, the moisture sorption isotherms of two cyanate ester/epoxy blends at different relative humidities have been analysed in terms of a dual mode sorption theory and the clustering analysis proposed by Zimm [2] and Brown [1].

2. Experimental

The two resin systems used in this study were blends of an epoxy with a cyanate ester. The cyanate esters used were the dicyanate AROCY L-10 available from Ciba–Geigy and the tri-functional novolac cyanate ester Primaset PT-30 which is available from Allied-Signal. The epoxy resin was the approximately tri-functional epoxy phenolic novolac resin DEN 431, which is reported to contain 2.8 glycidyl groups and is available from Dow chemicals. Equal weight fractions of the epoxy and cyanate ester were used and are designated as AROCY L-10/DEN 431 (50:50) and PT-30/DEN 431 (50:50). The curing cycle was recommended by the manufacturer and involved 2 h, at 180 °C followed by post-curing for 4 h, at 250 °C. For conditioning, resin coupons were cut to dimensions of $55\times25\times1\ \mathrm{mm}^3$ using a water-cooled diamond wheel and dried in vacuum at 50 °C to constant weight.

The dried samples were placed on racks above a range of saturated salt solutions in distilled water, which gave relative humidities from 11 to 100% in sealed chambers in an air-circulating oven at 50 °C [17,18]. Coupons were removed intermittently, weighed and returned to the humidity chamber.

3. Results

Fig. 1 gives the isothermal absorption curves for AROCY L-10/DEN 431 (50:50) after conditioning for 5000 h in environments of differing humidity. From Fig. 1 it can be seen that even after conditioning for 5000 h, equilibrium has not been reached with samples continuing to absorb moisture at a low rate. This was particularly true for the high relative humidity environments, such as 96 and 100%. Therefore, it was difficult to define exactly the equilibrium moisture content. The initial region of the absorption curves was found to be linear, which is one of the characteristics of fickian diffusion. Both resins absorbed 80–85% of their final moisture content in the first 100 h. After this initial rapid uptake, the continuing absorption process was very slow.

Table 1 gives the moisture contents (M_{5000}) for AROCY L-10/DEN 431 (50:50) and PT-30/DEN 431 (50:50) resin samples respectively, after conditioning at 50 °C in seven different relative humidities for 5000 h. From this data, absorption isotherms of M_{5000} against the partial vapour pressure of water in the environment were constructed, as shown in Fig. 2.

BET type II [19] isotherms, which cannot be fully

Table 1
Maximum moisture contents of AROCY L-10/DEN 431 (50:50) and PT-30/DEN 431 (50:50) resin samples exposed to various hygrothermal environments for 5000 h at 50 °C

Relative humidity (%R.H.)	Moisture content (M_{5000}) (wt%)	
	PT-30/DEN 431 (50:50)	AROCY L-10/DEN 431 (50:50)
11	0.48	0.41
16.5	0.70	0.48
31	1.04	0.71
46	1.44	1.06
75	2.19	1.63
96	2.96	2.16
100	3.19	2.18

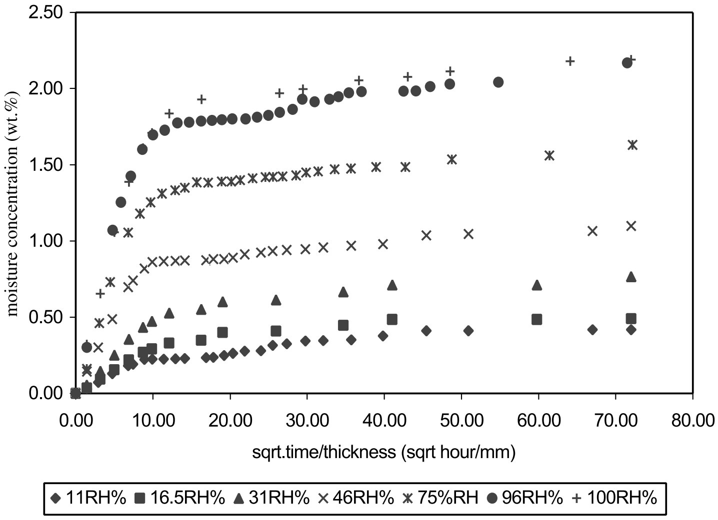

Fig. 1. Isothermal absorption curves for AROCY L-10/DEN 431 (50:50) resin samples conditioned for 5000 h in different humid environments at 50 °C.

explained by dual mode sorption theory [20], were obtained for both resin systems. Therefore, the linear portion of the isotherm at low pressures (i.e. up to 40% R.H.) was examined by the dual mode sorption theory. The clustering analysis developed by Zimm [2] and Brown [1] was used to examine the high humidity data.

3.1. Dual-mode sorption at low activities

The quantitative description of penetrant diffusion in to micro-heterogeneous media has evolved over the last three decades and has become known as the dual mode sorption theory. Based on Meares [21] concept of microvoids in the glassy state, Barre [22] suggested two concurrent mechanisms of sorption, ordinary dissolution and 'hole-filling'. It has been shown by Michaels et al. [23] that highly non-linear isotherms from the sorption of inert gases into glassy polymers can be divided into a combination of a Henry's law and a Langmuir components. In order to explain some of the sorption phenomena, Veith and Sladek [20] postulated that only the penetrant molecules associated with the Langmuir diffusion component were immobilised, so that a mathematical formulation of the diffusion could be achieved. This has become known as the dual mode sorption theory.

As shown in Fig. 2, at low vapour activities, the slope of the sorption isotherm, which is concave to the pressure axis is consistent with the dual-mode sorption model. The equilibrium component of the theory is expressed by Eq. (1) [20]:

$$C = C_D + C_H = K_D P + \frac{C'_H bP}{1 + bP} \tag{1}$$

where C is the total solubility in cc (STP)/cc polymer. C_D is the contribution from Henry's law-type mode, and C_H is the contribution from Langmuir-type mode. K_D is Henry's law

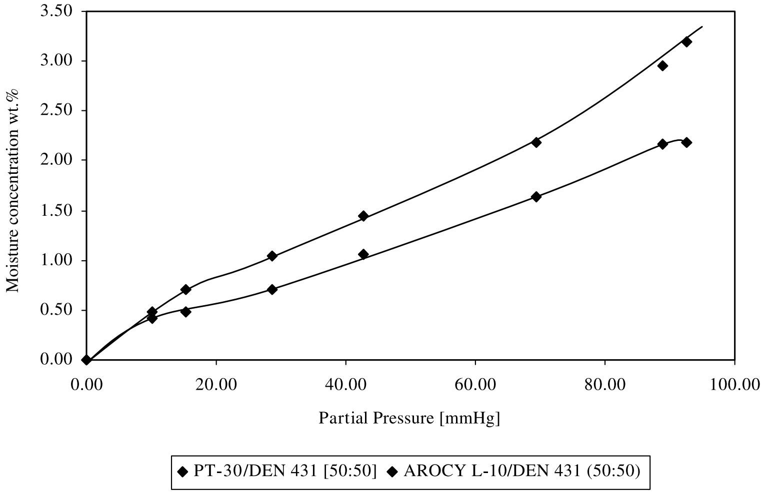

Fig. 2. Moisture concentration at 5000 h (M_{5000}) as a function of partial pressure of water for AROCY L-10/DEN 431 (50:50) and PT-30/DEN 431 (50:50) resin samples conditioned at 50 °C.

dissolution constant in cc (STP)/cc polymer mm Hg, b is the hole affinity constant in mm Hg^{-1}, P is the pressure in atm., C'_{H} is the hole saturation constant in cc (STP)/cc polymer.

The first term C_{D}, represents sorption of normally diffusible species while the second term, C_{H}, represents sorption in microvoids or 'holes'. The hole affinity constant, b, represents the ratio of rate constants of sorption and desorption of penetrant in the holes.

The dual-mode sorption parameters, b, K_{D} and C'_{H} were estimated from the absorption data at low vapour pressures (up to 40% R.H.) using the method proposed by Vieth and Sladek [20]. Table 2 gives the values of the dual-mode sorption parameters obtained using this method. However, this theory cannot describe the entire BET type II isotherm, which is produced from the experimental data. This can be seen by differentiating C with respect to P twice in Eq. (1), which gives:

$$\frac{\delta_2 C}{\delta P^2} = \frac{2C^1_{\mathrm{H}}b^2}{(1+bP)^3} \tag{2}$$

The assumption in this analysis is that, a plot of M_∞ against P is linear. However, b is always positive. The deviation from linearity can be explained by clustering of the diffused water.

3.2. Clustering analysis

3.2.1. Zimm's analysis

The clustering function, G_{11}/V_1, a monotonic, increasing function of the probability of finding molecules of the same kind close to one another, proposed by Zimm [2] is described quantitatively by Eq. (3):

$$G_{11}/V_1 = -(1-\phi_1)\left[\frac{\delta(a_1/\phi_1)}{\delta a_1}\right]^{-1}_{\mathrm{T,P}} \tag{3}$$

In Eq. (3), ϕ_1 is the volume fraction of penetrant and a_1 is the penetrant activity (usually equated to relative humidity/100).

The volume fraction of penetrant (ϕ_1) was calculated from the densities, which were found by Archimedian principle to be 1.26 and 1.25 g cm^{-3} of the PT-30/DEN 431 and AROCY L-10/DEN 431, respectively.

For a random solution the activity (a_1) is proportional to the volume fraction (ϕ_1) and so:

$$G_{11}/V_1 = 1 \tag{4}$$

The cluster function is a measure of the tendency of like molecules to form aggregates. If $G_{11}/V_1 > -1$ like molecules tend to cluster. If $G_{11}/V_1 < -1$, there is a tendency for like molecules to segregate, that is, for the system to form alternating arrays of unlike molecules. When the clustering function equals zero the degree of clustering is just sufficient to overcome the excluded volume of the polymer molecule.

Table 2
Dual mode sorption parameters for cyanate ester/epoxy resin blends. K_{D} in mm^3(STP)/mm^3-mmHg, C'_{H} in mm^3 and b in mmHg^{-1}

Resin	K_{D}	b	C'_{H}
AROCY L-10/DEN 431	0.030	0.15	0.78
PT-30/DEN 431	0.016	0.47	0.21

In order to solve the differential in Eq. (3), a_1/ϕ_1 was plotted against a_1. The experimental data was fitted to a second order polynomial, which was differentiated. The results of the Zimm's analysis for AROCY L-10/DEN 431 and PT-30/DEN 431 resin are shown in Tables 3 and 4, respectively. In this analysis, a small term for the compressibility of component 1 in a binary mixture was ignored.

Zimm and Lundberg [7] have provided a more useful index in the quantity $\phi_1 G_{11}/V_1$. This quantity is the number of type 1 molecules in excess of the mean concentration of type 1 molecules in the vicinity of a given type 1 molecule, and is $-\phi_1$ for a random solution. This definition of $\phi_1 G_{11}/V_1$ specifies the excess solvent molecules in the vicinity of the central solvent molecule, but does not include the central solvent molecule. Using this definition, Starkweather [24] has suggested that the average number of solvent molecules in a cluster, N_{C} (cluster number), can be calculated from the equation:

$$N_{\mathrm{C}} = \frac{\phi_1 G_{11}}{V_1} + 1 \tag{5}$$

For a random solution the activity coefficient, a_1/ϕ_1 is invariant with concentration, and from a combination of Eqs. (3) and (5), this would give:

$$N_{\mathrm{C}} = 1 - \phi_1 \tag{6}$$

If the central solvent molecule is included then the cluster number should be given by the equation:

$$N_{\mathrm{C}} = \phi_1[(G_{11}/V_1) + 1] + 1 \tag{7}$$

$$N_{\mathrm{C}} = -\phi_1(1-\phi_1)\left[\frac{\delta(a_1/\phi_1)}{\delta a_1}\right] + 1 \tag{8}$$

3.2.2. Brown's analysis

Brown [1] has proposed a method of interpreting the sorption of water into certain polar polymers, in which the conventional Flory–Huggins solution theory and cluster theory are combined. In his analysis, the total water sorbed by a polymer is viewed as the sum of the fractions of randomly distributed water molecules (Flory–Huggins theory), and those associated or clustered. Brown [1] has noted that for a large number of polymers, a plot of the reciprocal of water sorption against the reciprocal of partial pressure of water exhibits near linear behaviour, which can be described by the equation:

Table 3
Moisture absorption data for the PT-30/DEN 431 (tri-functional cyanate ester blend) resin for Zimm-type analysis of the cluster function (G_{11}/V_1)

Relative humidity (%)	a_1	P (mmHg)	M_∞ (wt%)	ϕ_1 (×100)	a_1/ϕ_1	G_{11}/V_1
11	0.11	10.19	0.48	0.608	18.08	104.6
16.5	0.165	15.28	0.70	0.887	18.60	104.7
31	0.31	28.71	1.04	1.319	23.50	104.2
46	0.46	42.60	1.44	1.825	25.20	103.5
75	0.75	69.46	2.19	2.770	27.07	103.2
96	0.96	88.91	2.96	3.754	25.60	102.8
100	1.00	92.61	3.19	4.043	24.73	102.7

$$\frac{1}{\phi_1} = (K_1/P) - K_2 \tag{9}$$

when $K_2 = 0$, this equation represents sorption according to Henry's law. When K_2 is negative the isotherm is considered to be a Langmuir or of an attenuated type, whereas when K_2 is positive it is an enhanced clustered isotherm. As P approaches zero, the limiting, infinite dilution isotherm is given by the inverse of Henry's law expression:

$$\frac{1}{\phi_H} = \frac{K_1}{P} \tag{10}$$

This analysis allows a unique definition of the Flory–Huggins interaction parameter, χ. Through the use of the limiting (Henry's law) approximation of the Flory–Huggins theory, χ can be defined according to equations:

$$P \approx \phi_1 \exp(1+\chi) \approx K_1\phi_1 \tag{11}$$

and

$$\chi \approx \ln K_1 - 1 \tag{12}$$

At any relative pressure, the experimental sorption can be compared to that predicted by the Henry's law isotherm to provide a ratio, N_e, which is defined as the 'enhancement number', and can be calculated from Eqs. (9) and (10):

$$N_e = \frac{\phi_1}{\phi_H} = \frac{K_1}{K_1 - K_2 P} = 1 + K_2\phi_1 \tag{13}$$

The enhancement number is a measure, of the extent to which the sorption of water is increased by the abnormalities of the process, which result from non-random mixing. Using the partial pressure of water (P) as an adequate approximation to the activity, it can be seen from Eq. (9) that the derivative within the brackets in the equation used to calculate the cluster number (Eq. (8)) is equal to $-K_2$. The cluster number for this case is given by the equation:

$$N_C = 1 + K_2\phi_1 - K_2\phi_1^2 \tag{14}$$

and comparing this to the enhancement number from Eq. (5):

$$N_C = N_e - K_2\phi_1^2 \tag{15}$$

Brown applied this analysis to sorption data for four different polymers and found an orderly decrease in χ with increasing polymer hydrophilicity, and as moisture concentration reached saturation. However, no trend in cluster number was found. Thus, clustering appears to be related to the nature of the water molecule and quite probably to the hydrogen-bonding propensity of the polar groups on the polymer, but not to any appreciable extent to the concentration of polar groups.

Brown [1] concluded that at low partial pressures or relative humidities, water is distributed uniformly throughout the polymer, but probably preferentially where hydrogen bonding is possible. At higher pressures, chains of water molecules form at hydrogen bonding sites. The initial sorption process can be described by a conventional solution theory and the enhancement process can be viewed as one of occupancy of sites.

The analysis of Brown [1] was applied to the experimental sorption data for the cyanate ester/epoxy blends. A plot of the reciprocal of volume fraction of water (ϕ_1) against the reciprocal partial pressure of water (see Fig. 3) resulted in a curve, which exhibited near-linear behavior for

Table 4
Moisture absorption data for AROCY L-10/DEN 431 (di-functional cyanate ester blend) resin for Zimm-type analysis of the cluster function (G_{11}/V_1)

Relative humidity (%)	a_1	P (mmHg)	M_∞ (wt%)	ϕ_1 (×100)	a_1/ϕ_1	G_{11}/V_1
11	0.11	10.19	0.41	0.513	21.44	106.7
16.5	0.165	15.28	0.48	0.600	27.50	106.5
31	0.31	28.71	0.71	0.888	34.90	106.4
46	0.46	42.60	1.06	1.330	34.96	105.9
75	0.75	69.46	1.63	2.040	36.76	105.8
96	0.96	88.91	2.16	2.704	35.50	105.4
100	1.00	92.61	2.18	2.729	35.35	105.4

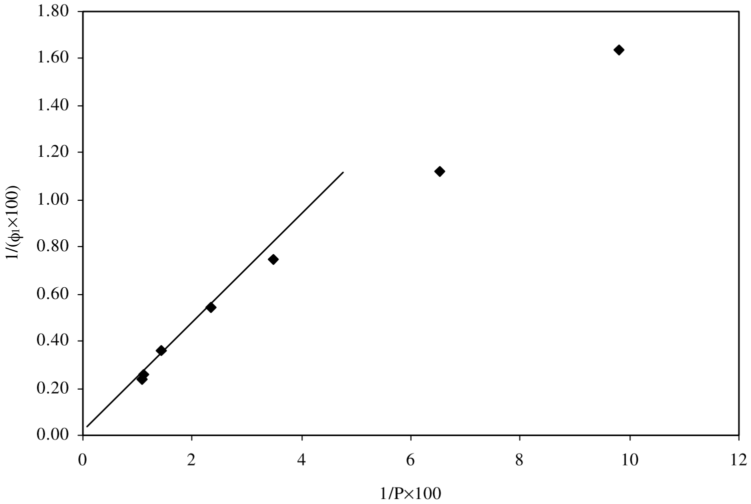

Fig. 3. Brown cluster analysis of the moisture absorption by the PT-30/DEN 431 (50:50) resin at differing partial water pressures.

the data obtained at high pressures (i.e. high relative humidities). However, the curve deviates from linearity at low pressures. The results of Brown analysis are given in Table 5.

In Table 5, K_1 and K_2 are constants, χ is interaction parameter, ϕ is volume fraction of penetrant, N_e is enhancement number, and N_c is cluster number.

4. Discussion

The cluster function, G_{11}/V_1 obtained using Zimms [2] model is greater than 1, which clearly indicates that water is clustered in both the resins. The positive values for K_2 obtained from the Brown [1] analysis also indicates that the isotherms are clustered for these resins. At low relative humidities, the dual mode sorption theory can describe the isotherms. At high relative humidities, the dual mode sorption theory can no longer describe the sorption isotherms, but the clustering analysis indicates that penetrant clustering is occurring. The point of inflection in the sorption isotherm (see Fig. 2) occurs at a relative humidity of 40% and above, at which the dual mode sorption theory no longer applies, and the isotherm is considered to be clustered. This is also the point at which the curve produced from the Brown analysis also ceases to be linear (see Fig. 3) and below which the isotherm is not considered to be clustered. There is, therefore, good agreement between the two analyses as to the partial pressure of water at which the isotherm becomes clustered. In these resin blends, clustering does not occur below 40% R.H.

However, the average cluster size for the cyanate ester/epoxy blend is only 1.02, where as for poly(methyl methacrylate) [5] the cluster size is 2.9, for polyester resins [3] the cluster size is 2. However, the cluster size in a relatively polar epoxy (XD7342/TMAB) is 1.23 [1]. This indicates that in more polar polymers the majority of the water is not clustered but hydrogen bonded at favorable sites on the polymer chain. The clustering may occur at polar centers or in microcavities existing in the polymer matrix. Water bonded to polar sites can act as a nucleus for the cluster formation. Cluster growth within the polymer will be determined by the potential field and the relative size of the microcavity in the surrounding polymer and because of steric factors, which effectively limit the size of a cluster to that of the microcavity. However, in polymers of high segmental mobility, association of the water may occur in a completely random manner throughout the polymer. From the results, it can be seen that changing the di-functional cyanate AROCY L-10 in the blend for a tri-functional cyanate ester PT-30 has no effect on the size of clusters formed even though it has absorbed more moisture.

Furthermore, the thermodynamic tendency for clustering of water molecules at high humidities but not below 40% R.H. helps explain the thermal spiking phenomenon

Table 5
Brown analysis of the cluster isotherm

Resin	K_1	K_2	χ	Values at $P=1$		
				ϕ	N_e	N_c
PT-30/DEN 431	21.53	0.47	2.06	0.046	1.02	1.02
AROCY L-10/ DEN 431	30.14	0.35	2.4	0.033	1.04	1.03

K_1 and K_2 are constants. χ is the Flory–Huggins interaction parameter, ϕ is volume fraction of penetrant, N_e is enhancement number, and N_c is cluster number.

observed for resins used as matrices for advanced composites. During conditioning, clusters will tend to form at polar sites within the network leading to an increased moisture content especially in nanovoids. During a thermal spike in a 0% R.H. environment, the local humidity within the network will cause the water molecules to decluster and be redistributed. Depending on the ability of the polymeric network to relax at the thermal spike temperature, on reimmersion in the humid environment, the reabsorbed penetrant molecules will be located as clusters in regions of sufficient volume, without impact on the glass transition temperature. With 'low' thermal spike temperatures, where network relaxation is slow, an enhanced moisture absorption will be observed. However, at 'high' spike temperatures, the network will relax reducing the number of sites where clustering can occur. In the extreme, this will lead to a reduction in the equilibrium moisture concentration.

5. Conclusions

Clustering of water occurs in cyanate ester/epoxy blends, as can be seen by the clustered absorption isotherm. At low activities, the sorption data can be described by the dual-mode sorption model, while clustering of the penetrant was evident at higher activities. The point at which clustering first occurs can be identified by both the dual mode sorption theory and the Brown analysis, and there is good agreement between the two methods. In the resin blends studied, clustering does not occur below 40% R.H. This observation provides a mechanism for understanding of the enhancement of moisture absorption through thermal spiking and the presence of a maximum enhancement temperature [13].

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