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 theory assumes complete random mixing. The complementary model of Brown[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[1] and the dual mode sorption theory of Zimm[2]. Clustering was found to occur in cyanate ester/epoxy blend conditioned at relative humidities of 40% R.H. and higher. The Cluster size indicates that the majority of the water in a cured cyanate ester/epoxy blend was not clustered but is present as monomeric form presumably hydrogen bonded to polar sites.

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 in to glassy polymers is successfully described by a dual mode sorption theory, which assumes a combination of Langmuir-type trapping within pre-existing gaps and a Henry's law of dissolution of penetrant in to the glassy matrix. At high activities, strong positive deviations from Henry's law were observed, which indicates 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 to 6.6 kcal/mol have been obtained[4]. As a result, strong localized interactions may develop between the water molecule 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 water vapour isotherm depending on the probability that hydrogen bonds between itself and between water and hydrophilic groups will form[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 theory has important implications for the effects of thermal cycling during moisture absorption and a high humidity environments. In four preceding publications[7-10] the effects of blend composition, thermal spike-time, and dry spiking on moisture absorption under thermal spiking have been investigated. The phenomenon of the reverse thermal effect on cyanate ester modified epoxy resin has also been studied. In the current study, 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 AROCYL-10 available from Ciba-Geigy and the tri-functional Novolac cyanate ester PT-30 which is available from Allied-Signal. The epoxy resin was the di-functional epoxy phenolic novolac resin DEN 431, which is available from Dow chemicals. Equal weight fractions of the epoxy and cyanate ester were used to form the resin blend. Two resin blends used in this study are designated as AROCYL-10/DEN431 (50:50) and PT30/DEN431 (50:50). The curing cycle was recommended by manufacturer and involved 2 hours, at $180^0 C$ followed by post-curing for 4 hours, at $250^0 C$. For conditioning, resin coupons were cut to dimensions of $55 \times 25 \times 1$ mm using a water-cooled diamond wheel and dried in vacuum at $50^0 C$ 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 $50^0 C$ [11,12]. Coupons were removed intermittently, weighed and returned to the humidity chamber.
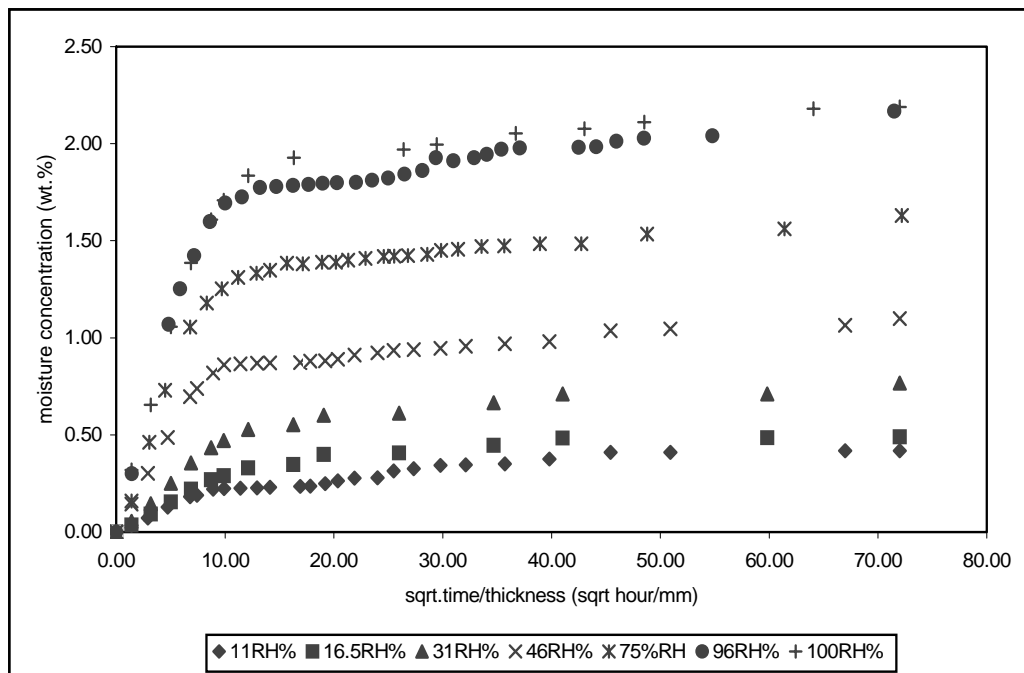
3. Results

Figure 1 Isothermal absorption curves for AROCYL 10/DEN 431 (50:50) after conditioning for 5000 hours in different humid environments.

From Figure 1 it can be seen that even after conditioning for 5,000 hours, 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% R.H. Therefore it was difficult to define exactly the equilibrium moisture content. Initial region of the absorption curves was found to be linear, which is one of the fickian diffusion characteristics. Both the resins have absorbed 80-85% of total moisture content in first 100 hours, and after this initial rapid uptake absorption process was very slow.

Table 1

Maximum moisture contents of AROCYL 10/DEN 431 (50:50) and PT 30/DEN 431 (50:50) resin samples exposed to various hygrothermal environments for 5,000 hours at 50 ^{0}C.

Relative Humidity (%R.H.)	Moisture content (wt.%)	
	PT30/DEN431 (50:50)	AROCYL10/DEN431 (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

Table 1 gives the moisture contents for AROCYL 10/DEN 431 (50:50) and PT 30/DEN 431 (50:50) resin samples respectively, after conditioning at $50\,^0$C in seven different relative humidities for 5,000 hours. From this data, absorption isotherms of M_t against the vapour pressure of water to which the resin samples had been exposed were constructed (see Fig. 2).
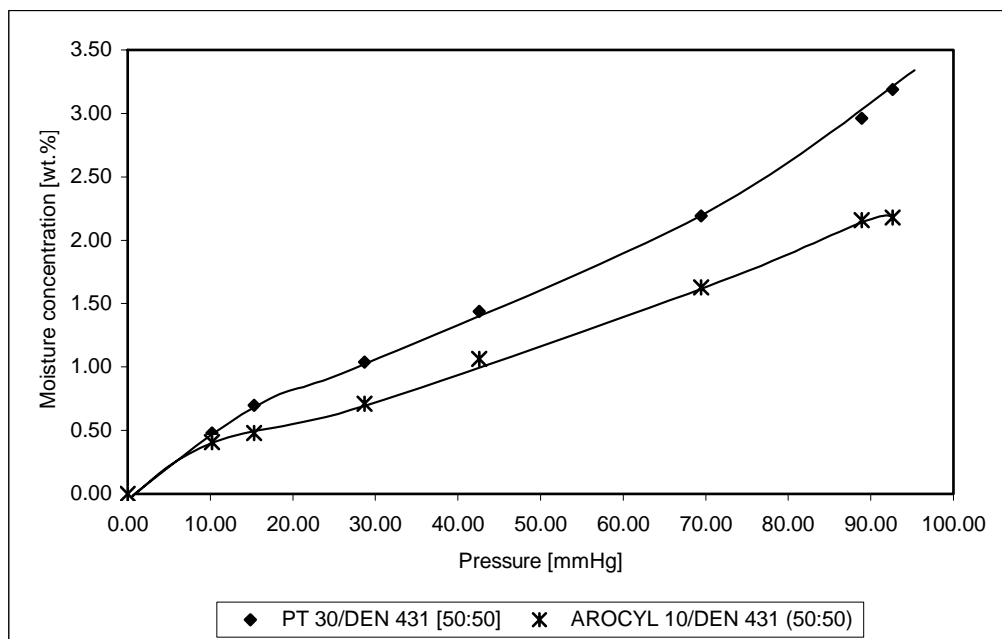

Figure 2 Moisture absorption isotherms for AROCYL 10/DEN 431 (50:50) and PT 30/DEN 431 (50:50) resin samples conditioned at $50\,^o$C.

BET type II[13] isotherms were obtained for both the resin systems, which cannot be explained fully by dual mode sorption theory[14] alone. Therefore the linear portion of the isotherm at low pressures (i.e. up to 40% R.H.) is examined by the dual sorption theory. The clustering analysis developed by Zimm[2] and Brown[1] is used to examine the high humidity component.

3.1. Dual-mode sorption at low activities

Quantitative description of penetrant diffusion in micro-heterogeneous media has evolved over the last three decades and has become known as the dual sorption theory. Based on Meare's[15] concept of microvoids in the glassy state, Barres[16] suggested two concurrent mechanisms of sorption: ordinary dissolution and "hole-filling". It is shown by Veith et al[17] that highly non-linear isotherms obtained for sorption of inert gases in glassy polymers can be divided into a combination of a Henry's law part and a Langmuir part. In order to explain some of the peculiarities of the kinetics of sorption, Veith and Sladek[14] in 1965 postulated that only penetrant molecules associated with Langmuir diffusion component are immobilised, allowing mathematical formulation of the diffusion process as well. This overall quantitative description has become known today as the dual sorption theory.

At low vapor activities, the sorption isotherm shapes, concave to the pressure axis as shown in Fig. 2, are consistent with the dual-mode sorption model. The equilibrium part of the theory is expressed by equation 1 for the isotherm[14];

$$C = C_D + C_H = K_D p + \frac{C_H' b p}{1 + bp} \qquad (1)$$

Where, C is solubility, K_D is Henry's law dissolution constant, b is hole affinity constant, p is pressure

The dual-mode sorption parameters, b, K_D and C_H' were estimated from the absorption data at low vapor pressures (up to 40% R.H.) using the method proposed by Vieth and Sladek[14]. Table 2 gives the values of the dual-mode sorption parameters obtained using this method.

Table 2

Dual mode sorption parameters.

K_D in $cm^3(STP)/cm^3 - cmHg$, C_H' in $cm^3(STP)/cm^3$ and b in $cmHg^{-1}$.

Resin	K_D	b	C_H'
AROCYL 10/DEN 431	0.030	0.15	0.78
PT 30/DEN 431	0.016	0.47	0.21

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 Equation 1, which gives:

$$D\frac{\partial^2 C_D}{\partial x^2} = \frac{\partial C_D}{\partial t}\left[1 + \frac{C_H'\left(b/K_D\right)}{\left(1+\left(b/K_D\right)C_D\right)^2}\right] \quad (2)$$

The assumption in this analysis is that, a plot of M_t 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 Equation 3

$$G_{11}/V_1 = -(1-\phi_1)\left[\frac{\delta(a_1/\phi_1)}{\delta a_1}\right] - 1 \quad (3)$$

where ϕ_1 is the volume fraction of penetrant and a_1 is the penetrant activity.

The volume fraction of penetrant (ϕ_1) was calculated using the values of 1.26 and 1.25 g cm^{-3} for the density of PT30/DEN431 and AROCYL10/DEN431 respectively obtained experimentally using the Archimedian principal. In order to calculate the differential in Equation 3, a_1/ϕ_1 was plotted against a_1 (Fig. 3).
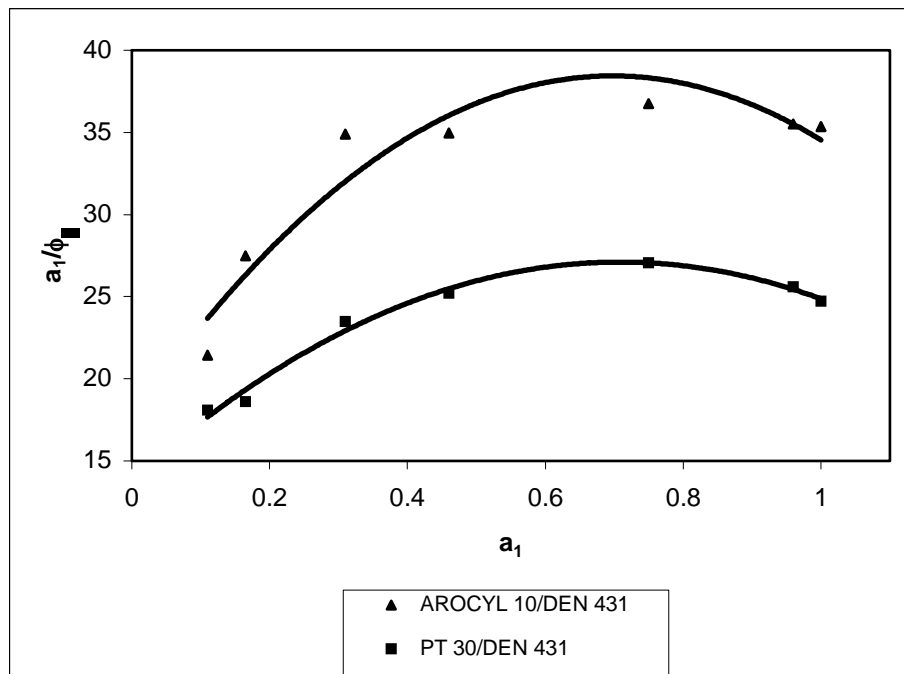

Figure 3 : Plot of penetrant activity/volume fraction against penetrant activity for AROCYL 10/DEN 431 and PT 30/DEN 431 resin at $50^0 C$.

The experimental data was fitted to a second order polynomial which was differentiated. The results of the Zimm's analysis for AROCYL 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.

Table 3
Moisture absorption data for PT 30/DEN 431 resin for Zimm-type analysis of cluster function (G_{11}/V_1).

Relative Humidity (%)	a_1	p (mmHg)	M_∞ (wt.%)	ϕ_1 ($\times 100$)	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

Table 4
Moisture absorption data for AROCYL 10/DEN 431 resin for Zimm-type analysis of cluster function (G_{11}/V_1).

Relative Humidity (%)	a_1	p (mmHg)	M_∞ (wt.%)	ϕ_1 ($\times 100$)	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

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.

3.3.2. Brown's analysis
Brown has proposed[1] a method of interpreting the sorption of water into certain polar polymers, in which 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;

$$\frac{1}{\Phi_1} = (K_1/p) - K_2 \qquad (4)$$

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;

$$\frac{1}{\Phi_H} = \frac{K_1}{p} \qquad (5)$$

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 6 and 7;

$$p \cong \Phi \exp(1 + \chi) \cong K_1 \Phi \qquad (6)$$

And $\chi \cong \ln K_1 - 1$

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, termed as "enhancement number", calculated from Equations 5 and 6 as follows;

$$N_e = \frac{\Phi}{\Phi_H} = \frac{K_1}{K_1 - K_2 p} = 1 + K_2 \Phi \qquad (7)$$

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. For many purposes, an estimation of the average number of solvent molecules in a cluster is useful. This is termed as cluster number, N_C. Starkweather[18] has suggested that, the cluster number, N_C can be provided by the expression;

$$N_C = \frac{\Phi_1 G_{11}}{V_1} + 1 \qquad (8)$$

For a random solution, the activity coefficient, a_1/Φ_1, is invariant with concentration, and from a combination of Equations 4 and 8, this gives;

$$N_C = 1 - \Phi \qquad (9)$$

However, in this case there is no clustering. So that the cluster number should be one. In Zimm's analysis of the cluster function $\Phi G_{11}/V_1$, specifies the excess of solvent molecules in the neighborhood of the central solvent molecule but not the central one. Brown considered this central solvent molecule and proposed the modified equation for N_C.

$$N_C = \Phi_1 \left(\frac{G_{11}}{V_1} + 1 \right) + 1 \qquad (10)$$

$$N_C = -\Phi_1 (1 - \Phi_1) \left[\frac{\partial \left(\frac{a_1}{\Phi_1} \right)}{\partial a_1} \right] + 1 \qquad (11)$$

Values of N_C calculated from Equations 10 and 11 exceed those calculated from equation 4 by the quantity Φ_1. This difference between N_C is negligible for glassy polymer. Using the partial pressure of water (p) as an adequate approximation to the activity, it can be seen from equation 4 that the derivative within the brackets in the equation used to calculate the cluster number [Equation 11] is equal to $-K_2$. The cluster number for this case is given by the equation;

$$N_C = 1 + K_2\Phi_1 - K_2\Phi_1^2 \qquad (12)$$

By comparing equations 7 and 12 a relationship between the enhancement number and cluster number can be obtained;

$$N_C = N_e - K_2\Phi_1^2 \qquad (13)$$

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 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 form on the 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 water sorption against the reciprocal partial pressure of water (1/(R.H./100)) (see Fig. 4) resulted in a curve which exhibited near-linear behavior for 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.
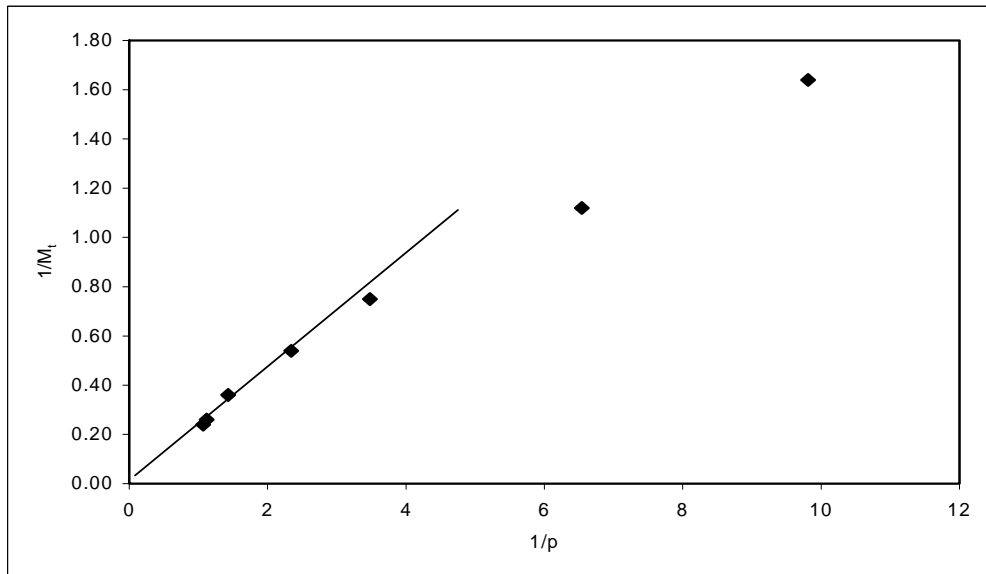

Figure 4 : Plot of the reciprocal of water absorption (M_t) against the reciprocal partial pressure of the water (1/(R.H./100)) for PT 30/DEN 431 (50:50) resin samples.

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.

Table 5
Data from the cluster analysis according to Brown (1).
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.

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
AROCYL 10/DEN 431	30.14	0.35	2.4	0.033	1.04	1.03

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 Brown's[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. 4) 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. 4) 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 the resin blends studied, 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 resin[3] 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 AROCYL-10 in blend by tri-functional cyanate ester PT 30 has no effect on size of clusters formed even though it has absorbed more moisture.

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's analysis, and there is good agreement between the two methods. In the resin blends studied, clustering does not occur below 40% R.H.

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