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# Diffusion of moisture into two-phase polymers

## Part 3 *Clustering of water in polyester resins*

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The equilibrium moisture absorption isotherm of a two-phase polyester resin system has been interpreted using both the dual mode sorption theory and an analysis proposed by Brown. Good agreement was found to exist between these two analyses as to the relative humidity at which clustering first occurs. The two-phase structure of the resin was found to have no significant effect on the equilibrium moisture isotherm. However, the average cluster number calculated for the resin is believed to result from larger clusters in the less dense phase of the resin and smaller clusters in the dense phase.

## 1. Introduction

The water molecule is relatively small, and in the liquid and solid states is strongly associated by hydrogen bond formation. This combination of characteristics distinguishes it from the majority of the organic penetrants. For polar polymers, strong localized interactions may develop between the water molecule and suitable polar groups. For relatively non-polar polymers, clustering or association of the absorbed water molecules may occur.

It has been suggested [1] that clustering may be initiated at polar centres or in microcavities existing in the polymer matrix. 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 way throughout the polymer.

Sorption isotherms can be used to obtain information on the interaction between a polymer and a penetrant. For water sorption by polymers, the experimental data is usually presented on the basis of some form of Henry's Law. That is, a measure of the quantity of water absorbed per unit quantity of substrate or substrate plus water, is plotted against the activity of water in the environment. Since data for water rarely exhibits linearity over any appreciable range of sorption, an alternative function is required. One of the most common approaches adopted for quantifying sorption isotherms has been the BET theory. Isotherms of the BET type II classification have been found for hydrophilic polymers such as wool and silk, while type III isotherms, and even linear isotherms, have been observed for less hydrophilic polymers such as poly(methyl methacrylate) and polyethylene.

In the BET theory the penetrant is localized at specific sites and it has been suggested that the dual mode sorption theory is a more realistic approach for characterizing the sorption isotherms of polymers [2]. This theory considers that the absorbed moisture in a glassy polymer exists in the form of mobile water and bound water. The mobile water is believed to be distributed throughout the polymer and can be described by Henry's Law. The bound water is described by a Langmuir-type absorption at specific sites. The nature of these sites is unknown although microvoids or other, unknown immobilizing mechanisms have been suggested [3].

Brown [4] has proposed an alternative method of interpreting the sorption of water into certain polar polymers, in which conventional Flory–Huggins solution theory and cluster theory are combined. In this paper both the dual mode sorption theory and the method proposed by Brown are employed in an attempt to interpret the sorption isotherm of Crystic 272 polyester resin.

## 2. Experimental details

The resin used in this study was the isophthalic unsaturated polyester resin Crystic 272 (Scott Bader Co. Ltd). The resin was cold cured using 2phr (parts per hundred of resin) of a 50% methyl ethyl ketone peroxide solution (Catalyst M, Scott Bader Co. Ltd) and 0.3 phr of a cobalt naphthenate solution (Accelerator E, Scott Bader Co. Ltd).

Resin specimens suitable for accurate absorption measurements were prepared by casting the activated resin into polypropylene beakers. Cast resin discs were produced using this technique without the need for any release agents. The discs were ground to a thickness of approximately 12 mm and specimens 2 mm × 10 mm × 30 mm were then cut from the discs using a water cooled diamond saw. All the faces of each specimen were polished to a better than 1 $\mu$m finish using cerium oxide.

After cutting and polishing the specimens were post-cured in an air circulating oven at 130° C for 1.5 h. This schedule is considered to produce a fully post-cured structure, as further post-curing does not change the mechanical properties or the glass

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TABLE I Relative humidities over saturated salt solutions at 50° C

| Saturated salt solution | Relative humidity (%) |
|---|---|
| $LiCl \cdot H_2O$ | 11 |
| $CaCl_2 \cdot 2H_2O$ | 16.5 |
| $MgCl_2 \cdot 6H_2O$ | 31 |
| $Mg(NO_3)_2 \cdot 6H_2O$ | 46 |
| $NaCl$ | 75 |
| $K_2SO_4$ | 96 |

transition temperature of the resin. After slowly cooling from the post-curing temperature, specimens were placed in a vacuum oven at 50° C and dried to constant weight. This procedure ensures that the specimens are completely dry prior to testing.

The specimens were conditioned either by immersion in distilled water or by exposure to a specific relative humidity. All conditioning took place at 50° C as this increases the rate of moisture uptake over that at room temperature, but is below the glass transition region of the resin (70–150° C).

Specific relative humidities were created by means of saturated salt solutions. The reason for using saturated salt solutions is that they can liberate or absorb large quantities of water without changing the equilibrium humidity. Several lists of relative humidities over saturated salt solutions have been compiled [5–8]. From this data, salts whose equilibrium relative humidities have a low temperature dependence and a linear variation with temperature can be selected. From the relative humidity diagrams of Young [5], and other data from the literature, six saturated salt solutions, corresponding to six different relative humidities, were selected for use at the conditioning temperature of 50° C. The six salts selected are shown in Table I.

Specimens to be conditioned by humidity were suspended over the saturated salt solutions on glass racks, inside insulated glass tanks with sealed lids. Specimens to be conditioned by immersion were placed in glass screw-lid jars filled with distilled water. To maintain the temperature at 50° C both the humidity tanks and the jars were placed in an air circulating oven. Each specimen was exposed to a specific environment for a predetermined length of time, sufficient for the equilibrium moisture content ($M_\infty$) to be reached, prior to weighing the specimens to determine $M_\infty$.

From this data (Table II) an absorption isotherm for moisture absorption into Crystic 272 polyester resin was constructed (Fig. 1).

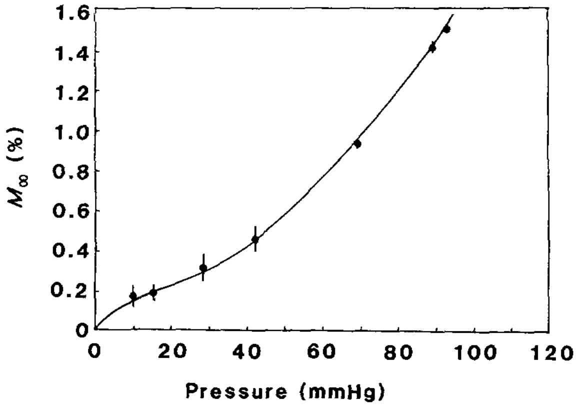

*Figure 1* Moisture absorption isotherm for Crystic 272 polyester resin at 50° C.

## 3. Results and discussion

The dual mode sorption theory of Vieth *et al.* [3] is quantitatively described by the following equation:

$$C = C_D + C_H = k_D P + \frac{C'_H bP}{1 + bP} \quad (1)$$

where $C$ is the total solubility ($M_\infty$), $C_D$ is the contribution from Henry's Law mode, $C_H$ is the contribution from Langmuir-type mode, $k_D$ is the Henry's Law dissolution constant, $b$ is the hole affinity constant, $C'_H$ is the hole saturation constant, $P$ is the pressure.

It has been suggested [2] that at low relative humidities experimental sorption isotherms can be described by the dual mode sorption theory. Using a curve fitting approach the best values for $k_D$, $C'_H$, and $b$ for a given system can be found.

Specimens of dry Crystic 272 polyester resin were exposed to a number of humid environments and allowed to reach their equilibrium moisture contents ($M_\infty$). An absorption isotherm of $M_\infty$ against the vapour pressure of water to which the specimens had been exposed was plotted (Fig. 1). The low pressure (i.e. < 40% r.h.) portion of the sorption isotherm was then characterized using the dual mode sorption theory (Table III). 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:

$$\frac{\delta^2 C}{\delta P^2} = \frac{2C'_H b^2}{(1 + bP)^3} \quad (2)$$

This implies that there is no point of inflection in a plot of $M_\infty$ against $P$ since $C'_H$ and $b$ are always positive. It is, therefore, necessary to invoke a clustering model to describe the isotherm from the point at

TABLE II Moisture absorption data for Crystic 272 polyester resin for a Zimm-type analysis of cluster function

| Relative humidity (%) | $a_1$ | $P$ (mm Hg) | $M_\infty$ (%) | $\phi_1$ ($\times$ 100) | $a_1/\phi_1$ | $G_{11}/v_1$ |
|---|---|---|---|---|---|---|
| 11 | 0.11 | 10.19 | 0.16 | 0.195 | 56.4 | 286.9 |
| 16.5 | 0.165 | 15.28 | 0.18 | 0.220 | 75.0 | 286.7 |
| 31 | 0.31 | 28.71 | 0.32 | 0.380 | 81.6 | 286.3 |
| 46 | 0.46 | 42.60 | 0.44 | 0.537 | 85.7 | 285.9 |
| 75 | 0.75 | 69.46 | 0.92 | 1.117 | 67.1 | 284.6 |
| 96 | 0.96 | 88.91 | 1.42 | 1.715 | 56.0 | 282.5 |
| 100 | 1.00 | 92.61 | 1.49 | 1.805 | 55.4 | 281.7 |

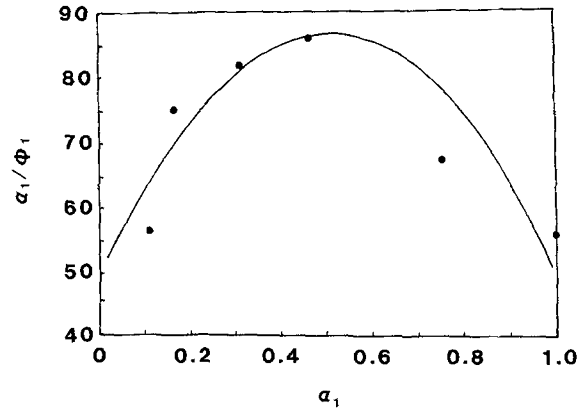

*Figure 2* Plot of penetrant activity/volume fraction against penetrant activity for Crystic 272 polyester resin at 50° C, (—) best second order polynomial.

which it begins to show a positive deviation from the dual mode sorption theory.

Clustering is the mechanism which is commonly used to explain positive deviations from the dual mode sorption theory and involves the aggregation of the penetrant molecules. The clustering function was determined from an analysis of the equilibrium sorption isotherm, and is described quantitatively by the equation proposed by Zimm [9]:

$$G_{11}/V_1 = -(1-\Phi_1)\left[\frac{\delta(a_1/\Phi_1)}{\delta a_1}\right]^{-1}_{T,P} \qquad (3)$$

where $G_{11}/V_1$ is the clustering function, $\Phi_1$ is the volume fraction of penetrant, $a_1$ is the penetrant activity (usually equated to r.h./100).

The volume fraction of penetrant ($\Phi_1$) was calculated using the manufacturer's value of 1.21 g cm$^{-3}$ for the density of the resin [10].

For a random solution the activity ($a_1$) is proportional to the volume fraction ($\Phi_1$) and so:

$$G_{11}/V_1 = -1 \qquad (4)$$

The extent to which $G_{11}/V_1 > -1$ indicates the extent of clustering in the solution.

In order to perform the differentiation as required in Equation 3, $a_1/\Phi_1$ was plotted against $a_1$ (Fig. 2). The experimental data was fitted to a second order polynomial and this was then differentiated. The results of this analysis are shown in Table III. It should be noted that in this analysis a small term involving compressibililty for component 1 in a binary mixture is ignored.

TABLE III Dual mode sorption parameters

| Resin | $k_D$ | $C'_H$ | $b$ |
|---|---|---|---|
| Crystic 272<br>(polyester)<br>[50° C] | $8.5 \times 10^{-3}$ | 0.07 | 0.5 |
| XD7342/TMAB<br>(epoxy)<br>[45° C]$^2$ | 7.77 | 1.57 | 4.6 |

$k_D$ in [cm$^3$ (STP)cm$^{-3}$-cm Hg, $C'_H$ [cm$^3$(STP) cm$^{-3}$] and $b$ [cm Hg$^{-1}$]. See text for definitions

Zimm and Lundberg [11] 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 (from Equation 4). This definition of $\Phi_1 G_{11}/V_1$ specifies the excesss solvent molecules in the vicinity of the central solvent molecule, but does not include the central solvent molecule. Using this definition Starkweather [12] has suggested that the average number of solvent molecules in a cluster, $N_c$ (cluster number), can be calculated from the equation:

$$N_c = \frac{\Phi_1 G_{11}}{V_1} + 1 \qquad (5)$$

For a random solution the activity coefficient, $a_1/\Phi_1$ is invariant with concentration, and from a combination of Equations 3 and 5, this would give:

$$N_c = 1 - \Phi_1 \qquad (6)$$

for such a solution. As Brown [4] points out, there should be no clustering in this case and the cluster number should therefore, be 1.

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

$$N_c = \Phi_1\,[(G_{11}/V_1) + 1] + 1 \qquad (7)$$

$$N_c = -\Phi_1\,(1-\Phi_1)\left[\frac{\delta(a_1/\Phi_1)}{\delta a_1}\right] + 1 \qquad (8)$$

Values of $N_c$ calculated from Equations 7 and 8 exceed those calculated from Equation 5 by the quantity $\Phi_1$. Now while this difference is negligible for glassy polymer systems it could become appreciable if this method were to be applied to other systems, for example dilute aqueous polymer solutions. This cluster number will be discussed again, in relation to the method proposed by Brown for the interpretation of sorption isotherms.

This author 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:

$$1/\Phi_1 = (k_1/P) - k_2 \qquad (9)$$

This equation represents Henry's Law sorption when $k_2 = 0$, a Langmuir or attenuated type of isotherm when $k_2$ is negative, and an enhanced or clustered isotherm when $k_2$ is positive. The limiting, infinite dilution isotherm, as $P$ approaches zero, is given by the inverse Henry's Law expression:

$$1/\Phi_H = k_1/P \qquad (10)$$

Using this limiting (Henry's Law) approximation of the Flory-Huggins theory the interaction parameter $\chi$ can be found.

$$P \approx \Phi_1 \exp(1+\chi) \approx k_1\Phi_1 \qquad (11)$$

and

$$\chi \approx \ln k_1 - 1 \qquad (12)$$

At any relative pressure the experimental sorption can be compared to that predicted for the Henry's Law isotherm to provide a ratio termed the enhancement number ($N_e$). From Equations 9 and 10 $N_e$ can be calculated:

$$N_c = \Phi_1/\Phi_H = k_1/(k_1 - k_2P) = 1 + k_2\Phi_1 \qquad (13)$$

$N_c$ is a measure of the extent to which the sorption of water is increased by the abnormalities of the sorption 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 Equation 9 that the derivative within the brackets in the equation used to calculate the cluster number (Equation 8) is equal to $-k_2$. The cluster is, for this case, given by the equation:

$$N_c = 1 + k_2\Phi_1 - k_2\Phi_1^2 \qquad (14)$$

and comparing this to the enhancement number from equation 5:

$$N_c = N_e - k_2\Phi_1^2 \qquad (15)$$

The approach proposed by Brown [4] was applied to the experimental sorption data for the polyester resin. A plot of the reciprocal of water sorption against the reciprocal of the partial pressure of water (1/(r.h./100)) (Fig. 3) resulted in a curve which exhibited near-linear behaviour for the data obtained at high pressures (i.e. high relative humidities). However, the curve deviates from linearity at low pressures. The results of this analysis are shown in Table IV.

A similar observation was made by Brown [4], for four acrylic polymers of varying hydrophilicity, where he concluded that at low relative pressures the water is distributed throughout the polymer, but probably preferentially where hydrogen bonding is possible. At higher pressures it was considered that clusters of water molecules on the hydrogen bonding sites predominate. These conclusions are consistent with the BET type II isotherm observed in Fig. 1.

The point of inflection in the sorption isotherm (Fig. 1) occurs at pressures above which the dual mode sorption theory does not apply, where the isotherm is considered to be clustered. This pressure is also the point at which the curve produced from the Brown analysis ceases to be linear (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 pressure at which the isotherm becomes clustered.

The dual mode sorption theory is temperature dependent, and $k_D$, $C'_H$ and $b$ should all decrease with increasing temperature [13]. This dependence is described by the equation:

$$x = x_0 \exp(-\Delta H_x/RT) \qquad (16)$$

where $x$ is $k_D$, $C'_H$ or $b$, $\Delta H_x$ is the appropriate enthalpy difference, $R$ is the gas constant, $T$ is the temperature, although in some instances $b$ does not follow this relationship. Bearing this in mind, it is noted that the measured values of the Henry's Law dissolution constant ($k_D$), the hole saturation constant ($C'_H$) and the hole affinity constant ($b$) for the polyester under investigation are much lower than, for example, an epoxy resin (XD7342/TMAB), as shown in Table III. In particular the contribution to the total solubility from the mobile water, described by Henry's Law dissolution ($C_H$), is much greater in the case of epoxy resin. This results from the readiness of the water molecules to cluster in the polyester resin. This is evidenced by the value of the interaction parameter ($\chi$), which indicates that the polymer is not very hydrophilic.

TABLE IV A comparison of the moisture absorption data for Crystic 272 polyester resin and poly(methyl methacrylate) using the Brown analysis

| Resin | $k_1$ | $k_2$ | $\chi$ | Values at $P = 1$ | | |
|---|---|---|---|---|---|---|
| | | | | $\phi$ | $N_e$ | $N_c$ |
| Crystic 272 (polyester) | 112.7 | 58.8 | 3.7 | 0.018 | 2.1 | 2.0 |
| Poly(methyl methacrylate) [4] | 119 | 80 | 3.8 | 0.025 | 3.0 | 2.9 |

See text for definitions

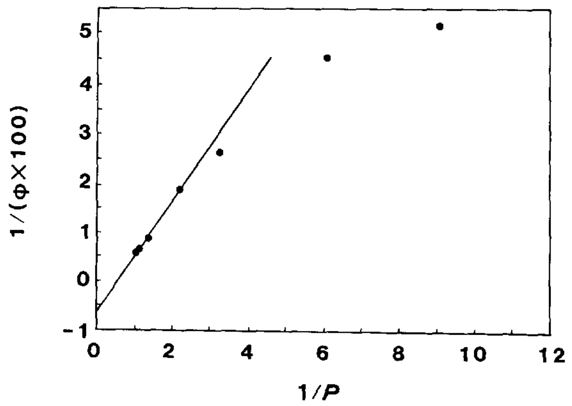

*Figure 3* Inverse plot of absorption of moisture by Crystic 272 polyester at 50° C.

Using the Zimm approach [9], the cluster integral, calculated from the sorption isotherm, indicates a highly clustered isotherm (i.e. $G_{11}/V_1 \ggg -1$). That the isotherm is clustered can also be seen from the analysis proposed by Brown. The positive value of $k_2$ in this analysis gives a clear indication that the isotherm is clustered, and is comparable to a value quoted in the literature for poly(methyl methacrylate) [4]. However, the average cluster size ($N_c$) for the polyester is only 2.0 whereas for poly(methyl methacrylate) the cluster size is 2.9. A value of $N_c$ calculated for the, relatively polar, epoxy resin (XD7342/TMAB) was 1.23, and would tend to indicate that in this case the majority of the water is not clustered but hydrogen bonded at favourable sites on the polymer chain.

In the analyses, the two-phase structure of the polyester resin [14–15] appears to have no effect on the equilibrium moisture absorption isotherm, whereas it does have a significant effect on the moisture diffusion characteristics of the resin [14]. However, this does not mean that the moisture is homogeneously distributed throughout the resin. It is more likely that larger clusters in the less dense phase and smaller clusters in the dense phase combine to give the calculated value of $N_c$ as 2.

## 4. Conclusions

Clustering of water occurs in two-phase polyester resins, as can be seen by the highly clustered equilibrium moisture absorption isotherm. The equilibrium moisture absorption isotherm appears to be unaffected by the two-phase structure of the resin. 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 system studied, clustering does not occur below 30% r.h.

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## References

1. J. A. BARRIE, "Diffusion in Polymers", edited by J. Crank and G. S. Park (Academic Press, London, 1968) p. 259.
2. M. T. ARONHIME, X. PENG and J. K. GILLHAM, *J. Appl. Polym. Sci.* **32** (1986) 3589.
3. W. R. VEITH, J. M. HOWELL and J. H. HSIEH, *J. Membrane Sci.* **1** (1976) 177.
4. G. L. BROWN, in "Water in Polymers", edited by S. P. Rowland (American Chemical Society, Washington, D.C., 1980) p. 441.
5. J. F. YOUNG *J. Appl. Chem.* **17** (1967) 241.
6. F. E. M. O'BRIEN, *J. Sci. Instruments* **25** (1948) 73.
7. ASTM, Designation: E104-51 (1971) "Standard Recommended Practice for Maintaining Constant Relative Humidity by means of Aqueous Solutions".
8. BS 3718: 1964. "British Standard Specification for Laboratory Humidity Ovens (Non-Injection Type)".
9. B. H. ZIMM, *J. Chem. Phys* **21** (1953) 934.
10. "Crystic 272 isophthalic resin for filament winding", Technical Leaflet No. 907, (Scott-Bader, 1975).
11. B. H. ZIMM and J. L. LUNDBERG, *J. Phys. Chem.* **60** (1956) 425.
12. H. W. STARKWEATHER, *Polymer Lett.* **1** (1963) 133.
13. G. RENADE, V. STANETT and W. J. KOROS, *J. Appl. Polym. Sci* **25** (1980) 2179.
14. P. M. JACOBS and F. R. JONES, *J. Mat. Sci.* **24** (1989) 233.
15. P. M. JACOBS and F. R. JONES, Moisture diffusion into two phase matrix resins for fibre composites, in "Developments in the Science and Technology of Composite Materials (ECCM 3)" edited by A. Massiah (Elsevier, Bordeaux, 1989) pp. 627–633.

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