

Clustering of Absorbed Water in Amorphous Polymer Systems

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INTRODUCTION

It is well known that amorphous polymers absorb solvents to limited extents. In some cases the solvent absorption follows Henry's law, that is, the solvent absorption is proportional to the vapor pressure of the absorbed solvent. In such cases the solvent molecules remain unclustered in the polymer matrix. On the other hand, in some cases the solvent absorption does not follow Henry's law and solvent uptake generally increases nonlinearly with the solvent vapor pressure and is greater than that predicted by Henry's law. In such cases it has been shown by Starkweather¹ that cluster formation by solvent molecules can account for the deviation.

The ability of solvent molecules to cluster depends upon the nature of polymer as well as the solvent. The theory of clustering of absorbed solvent molecules is based on solution thermodynamics as developed by Kirkwood and Buff². Later Zimm³ modified this to develop a relationship to determine the degree of clustering in terms of activity of the solvent, and studied the sorption of vapors by polymers.⁴ Several other workers⁵⁻¹⁰ have also presented evidence for the clustering of solvents in polymers. In addition some other relevant studies on the sorption of solvent in polymers have been cited.¹¹⁻¹⁵

In this paper we have studied the absorption of water in polymer systems based on a copolymer of poly(vinyl alcohol) and poly(vinyl butyral). In some cases it was found that at high levels of water absorption these copolymers became translucent, indicating the presence of two distinct phases with different refractive indexes. These observations have been analyzed using the cluster theory.¹⁻⁴

It is well known that light is scattered by inhomogeneities in a two-phase system,¹¹⁻¹⁴ provided that the size of the inhomogeneity is close to the wavelength of visible light. A physical effect of scattering of light in a polymer system is its hazy appearance. The size of scattering entities, which in our case are believed to be clusters of water, has been determined by analysis of light scattering patterns using the Debye-Bueche¹⁶ theory. A correlation between the clustering of absorbed water and light scattering has been presented

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THEORETICAL BACKGROUND: CLUSTERING OF ABSORBED SOLVENT

According to the cluster theory¹⁻⁴ the average number of solvent molecules, n , in the neighborhood of a solvent molecule in excess of the mean concentration of solvent is given by

$$n = c_1 G_{11} = (1 - v_1) \left(\frac{\partial \ln v_1}{\partial \ln a_1} \right)_{p,T} - 1 \quad (1)$$

where G_{11} is the cluster integral, c_1 is the molar concentration of solvent, v_1 is the volume fraction of solvent, and a_1 is the activity of solvent. Thus the average number of solvent molecules per solvent cluster C_n is

$$C_n = n + 1 \quad (2)$$

Furthermore, the relative number of clusters, N_c , can be determined as a function of weight fraction solvent absorbed, w , by the relationship

$$N_c = (w/C_n) \times 100 \quad (3)$$

In the present paper the solvent is water which is absorbed by the polymer systems under investigation to different extents at different relative humidity (RH) conditions. The activity of the solvent is simply given as $a_1 = (P/P_0)$, where P is the partial pressure of the solvent over the polymer and P_0 is the vapor pressure of the pure solvent.

Light Scattering

It is well known that light is scattered by inhomogeneities in a two-phase system¹⁶⁻¹⁹ as long as the size of scattering entities are close to the wavelength of light and if there is a significant refractive index difference between the two phases. A physical effect of scattering of light in any sample is its hazy appearance. Debye and Bueche¹⁶ first developed a relationship for scattering intensity from a spherically symmetrical system. Intensity I at a distance r from the center of spherical symmetry is given as

$$I = 4 \times K_4 \langle n^2 \rangle_{av} \gamma(r) [\sin(hr)/(hr)] r^2 dr \quad (4)$$

where K_4 is a constant, $\langle n^2 \rangle_{av}$ is the mean square refractive index,

$$h = (4\pi/\lambda) \sin(\theta/2) \quad (5)$$

λ is the wavelength of light = λ_{air}/n , n is the refractive index of the scattering sample, θ is the scattering angle, and $\gamma(r)$ is a correlation function which characterizes the size and shape of heterogeneities. For a perfectly

uniform system $\gamma(r)$ is constant while for a totally random system $\gamma(r)$ is given as

$$\gamma(r) = \exp(-r/a) \quad (6)$$

where a is the correlation distance, a measure of the size of the heterogeneity. For this correlation function, I reduces to²⁰

$$I = K_5 \langle n^2 \rangle_{\text{av}} \frac{a^3}{(1 + h^2 a^2)^2} \quad (7)$$

Now if $I(h)^{-1/2}$ is plotted as a function of h^2 , then

$$a^2 = (\text{slope}/\text{intercept}) \quad (8)$$

For small θ , $\sin(\theta/2) \sim \theta/2$. Therefore,

$$h = \frac{2\pi\theta}{\lambda} \quad (9)$$

With this simplification, $I(\theta)^{-1/2}$ may be plotted as a function of θ^2 (where θ is in radians). The correlation distance would then be given as

$$a = \left(\frac{\lambda}{2\pi}\right) \left(\frac{\text{slope}}{\text{intercept}}\right)^{1/2} \quad (10)$$

Several people have used a similar approach and different correlation functions.²¹⁻²³ Stein and co-workers²⁴⁻²⁷ have presented methods for measuring scattering intensities and for correcting the measured intensity.

Now if l is the average size of scattering homogeneity and the volume fraction of the polymer, (v_2), is close to 1, then the value of l can be determined as

$$l = a/v_2 \quad (11)$$

EXPERIMENTAL

Materials

The polymer used in this study was a random copolymer of vinyl alcohol (VA) and vinyl butyral (VB) with a 45-55 mole ratio. The copolymer was then plasticized with about 30 parts by weight of dihexyl adipate per hundred parts of polymer. The plasticized copolymer was then modified by the addition of an ionic salt. Studies were carried out on the above three systems, i.e., (a) copolymer of VA/VB, (b) plasticized copolymer, and (c) modified, plasticized copolymer.

Water Absorption

Constant relative humidity cells, with values ranging from 30 to 100%, were made by using aqueous solutions of calcium chloride at varying concentrations. Molded films were then hung in the constant RH chambers until equilibrium water absorption was attained. The level of water uptake was measured by near infrared (NIR). Weight percent of water absorbed was then plotted as a function of RH, and results were analyzed.

Small Angle Light Scattering

A standard photographic small angle light scattering (SALS) setup¹⁹ was used for observing the scattering developed in polymer systems exposed to different RH conditions. The SALS photographs (negative as well as positive) were obtained in the V_v mode in which the polarizer and the analyzer are parallel to one another.

The V_v mode is used since the scattering in our system is entirely due to density fluctuation with no anisotropic fluctuation. The variation of scattered light intensity (IV_v) as a function of scattering angle was measured on the negatives using a Joyce Loeb microdensitometer (Model MK III cs). IV_v was then plotted as a function of θ , and results were analyzed to obtain the size of scattering entities. It may be pointed out that samples exposed to low RH conditions were transparent and showed no scattering while samples exposed to high RH conditions were hazy and thus showed significant scattering.

RESULTS

Water Absorption

Figure 1 shows plots of wt % water absorbed as a function of RH for the following systems: (A) copolymer, (B) plasticized copolymer, and (C) modified and plasticized copolymer. In all three cases it can be clearly seen that the water absorption isotherms show a linear increase at low RH values which changes into a more rapid increase at high RH values. These isotherms are similar to type III absorption isotherms.²⁸ This suggests that polymer-water interactions are favored when the polymer is exposed to water, and the system follows the ideal Henry's law at low RH values but deviates from it in the positive direction at high RH values. It may be noted that the three systems show different levels of water absorption and in addition show different rates of deviation from ideal behavior. This latter point is further amplified in Figure 2, which is a plot of $\log v_1$ vs. $\log a_1$. The deviation from ideality is greatest for system C and least for system A, even though system A has the highest amount of water absorbed at equivalent RH values. The deviation from ideal behavior begins at about 0.95 wt % water for system A. For systems B and C the deviation begins at about 0.7 wt % water, which represents about 0.93 wt % of the copolymer since these two are plasticized. Thus we see that the amount of water relative to the amount of polymer is approximately the same irrespective of plastization and modification.

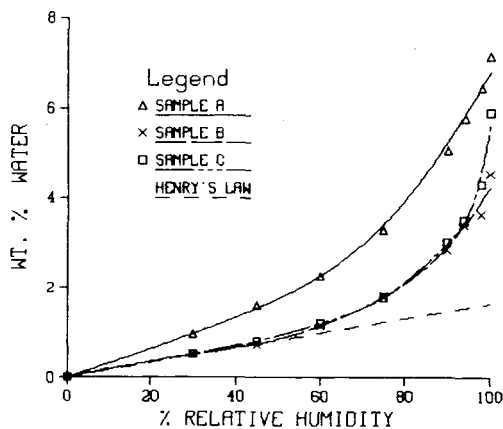


Fig. 1. Plot of weight percent water absorbed vs. relative humidity: (Δ) Sample A, PVB/PVOH copolymer; (\times) Sample B, plasticized copolymer; (\square) Sample C, plasticized copolymer modified.

Using the plots of Figure 2, values of $\partial \ln v_1 / \partial \ln a_1$ were determined at various values of v_1 and substituted in eq. (1). Subsequently, the average cluster size, C_n , was determined from eq. (2) and plotted as a function of v_1 for the three polymer systems in Figure 3. The value of C_n represents the average number of water molecules at the polymer sites where water is associated. In our polymer system it is natural to assume that the water molecules absorbed would be associated with the hydroxyl (OH) groups in the polymer. According to the cluster theory,¹ deviation from ideal behavior would occur when all the water absorption sites in the polymer are saturated. After this point, the additional water absorbed goes to sites which already have a water molecule, thus giving rise to "clustering" of water. The average number of water molecules per "cluster" would be 1 until all the sites are saturated and would rise to values greater than 1 beyond this point. As can be seen from the plots in Figure 3, C_n has a value of 1.0 for $v_1 = 0$ to 0.005 and increases for higher values of v_1 . The rate of increase

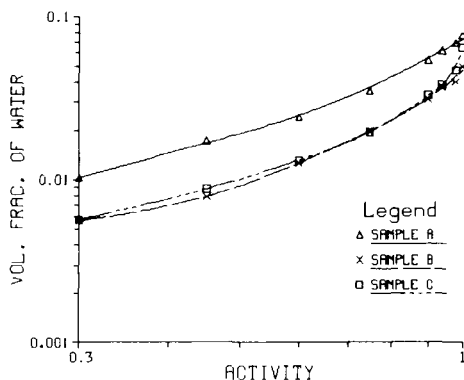


Fig. 2. Plot of n (volume fraction water v_1) vs. n (activity a_1): (Δ) Sample A, PVB/PVOH copolymer; (\times) Sample B, plasticized copolymer; (\square) Sample C, plasticized copolymer modified.

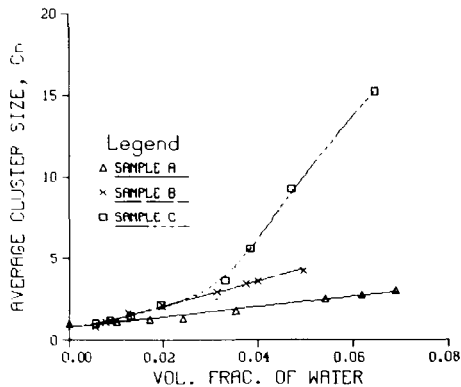


Fig. 3. Plot of average cluster size, c_n , vs. volume fraction water, v_1 : (Δ) Sample A, PVB/PVOH copolymer; (\times) Sample B, plasticized copolymer; (\square) Sample C, plasticized copolymer modified.

is greatest for C and lowest for A with B being intermediate. The ultimate value of C_n is significantly different for all three systems.

Finally the values of N_c , relative number of clusters, are determined by eq. (3) and plotted as a function of wt % water, w , for the three polymer systems as shown in Figure 4. Here it can be observed that for systems A and B the values of N_c rise steeply at first and then tend to level off at higher absorbed water contents. The films for these two systems remain relatively transparent at all levels of water absorption (except that B shows a slight haze at RH close to 100%), implying that the clusters formed are not large enough to scatter visible light.

On the other hand, system C shows a maximum in the curve and the relative number of clusters actually decrease beyond a certain critical water content (2.2 wt %). This means that the sites of water clusters coalesce to form bigger clusters and in effect reduce the number of clusters that exist. The water content of 2.2 wt % represents an exposure to a RH of about 85% as seen from Figure 1. At this RH the system C, which is a modified

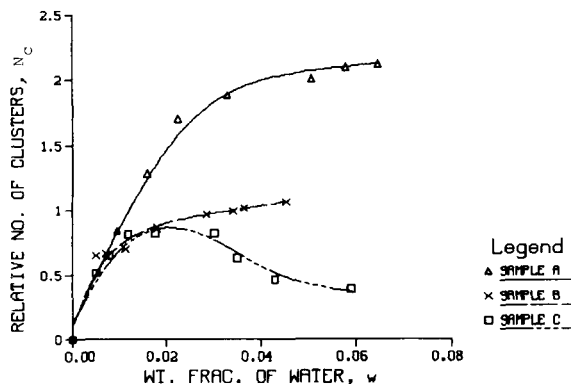


Fig. 4. Plot of relative number of clusters, N_c , vs. weight fraction water w : (Δ) Sample A, PVB/PVOH copolymer; (\times) Sample B, plasticized copolymer; (\square) Sample C, plasticized copolymer modified.

and plasticized copolymer, begins to turn hazy in appearance, implying that at this juncture the water clusters have a size big enough to scatter light. Thus the observation of coalescence of clusters to form bigger clusters is supported by the change in appearance. The section following describes the light scattering observation on hazy samples.

Small Angle Light Scattering

The copolymer of VB and VA is amorphous in nature and remains amorphous when plasticized and modified, thus providing no anisotropic contribution to light scattering. The plasticizer and the salt added to the base copolymer are compatible at the level of additions, providing no density fluctuation contributions to light scattering. Furthermore, the refractive index values of components are close to each other, thus providing no refractive index fluctuations either. Hence in all three cases the sample films with no water absorption are transparent and show no SALS in either the H_v mode (cross polars) or the V_v mode (parallel polars). In some cases the film becomes hazy upon water absorption due to density fluctuation provided by the clustering of water into inhomogeneities big enough to scatter light. This would contribute to V_v scattering only, and hence all experiments were carried out in the V_v mode as has been mentioned earlier. The refractive index of the copolymer is about 1.45 and that of water is about 1.33. The difference is large enough to give rise to light scattering if a water-rich phase separates from the polymer.

Upon water absorption, the films of the base copolymer remained transparent at all levels of RH and gave no significant V_v scattering. This implies that the water absorbed is well distributed in the polymer matrix and does not form clusters which are large enough to scatter light. This supports the results and analysis of the earlier section which predicted very little clustering in the copolymer by itself. Water absorption in the plasticized films showed no haze or V_v scattering at low RH levels but showed a slight haze and a slight increase in V_v scattering intensity at RH values of 98% and higher. This also is in agreement with previous results which predicted some clustering in plasticized copolymer. However, since the V_v intensities were low and the range of RH values showing scattering narrow, no detailed analysis was carried out in these samples.

Water absorption had the most marked effect on the appearance of plasticized and modified copolymer films. In these, haze began to develop at 90% RH and increased with increasing RH values. The V_v scattering intensity followed the same pattern. This implies that in system C water clustering becomes significant at a much lower RH and water content. The clusters are big enough to scatter light at 90% RH and either increase in size or in number or both at higher RH values. The photographic V_v patterns for system C were obtained at 90, 92, 94, 96, and 98% RH values under identical conditions and at equal exposure times. All the patterns were circularly symmetric on account of scattering from isotropic density fluctuations and showed maximum intensity at the center, decreasing monotonically with scattering angle. The photographic negatives were scanned on a microdensitometer and scattering intensity corrected by subtracting

the background intensity which was obtained by using a dry film sample which contained a negligible amount of moisture.

The background-corrected relative intensity, I_{V_0} , is plotted as a function of scattering angle θ in Figure 5 for three RH levels. Other RH levels were omitted for sake of clarity of data presentation in Figure 5. The films of system C at 100% RH exposure were too hazy, thus giving rise to excessive secondary scattering. The I_{V_0} vs. θ plots can now be analyzed, using the Debye-Bueche analysis to estimate the size of water clusters. For this $(I_{V_0})^{-1/2}$ is plotted as a function of θ^2 , and the slope and intercept of these plots are obtained. In the 90% RH sample, the intensity levels were too low and hence meaningful results could not be obtained. For 92, 94, 96, and 98% RH samples the plots of $(I_{V_0})^{-1/2}$ vs. θ^2 are given in Figures 6-9, respectively. All the plots show two distinct slopes, one at low values of θ^2 and one at high values of θ^2 . The slope at higher values is related to the short range correlation of the scattering inhomogeneity (water clusters in our case) and is related to the correlation distance a as defined in eqs. (6) and (7).

From the values of slope and intercept in each case the values of a were determined using eq. (10). Subsequently, the size of the scattering inhomogeneity l at different RH values was determined from eq. (11) and presented in Table I along with the values of a . These results show that the size of clusters does not change significantly for samples with RH values between 92 and 96%. The size of clusters for these samples is around 0.3 μm . The slight difference between the three samples in this range is within experimental error. The cluster size increases considerably for the 98% RH sample to 0.43 μm . This suggests that the coalescence of clusters around 98% RH is much more drastic than at lower RH values. This conclusion is also supported by the previous analysis of relative number of clusters as shown in Figure 4. From this we can see that the relative number of clusters N_c changes from a value of about 0.77 to about 0.67 as the RH changes from 90 to 96% (using Fig. 1 and 4). However, the value of N_c changes from 0.67 to about 0.3 as we go from 96 to 98% RH. This sudden reduction in the number of clusters obviously results in a sudden increase in cluster size as shown by the light scattering results. It may also be pointed out that

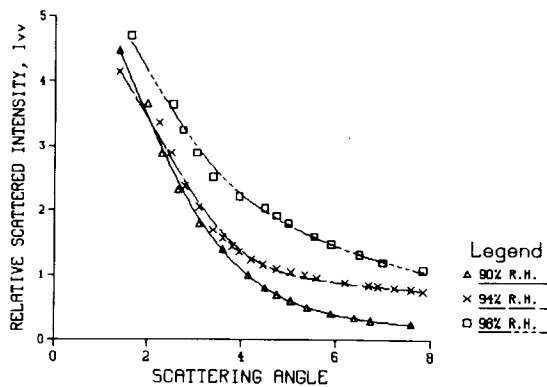


Fig. 5. Plot of scattered V_0 intensity (Δ) I_v vs. scattering angle for 90%, 94% (\times) and 98% (\square) RH exposed films of system C.

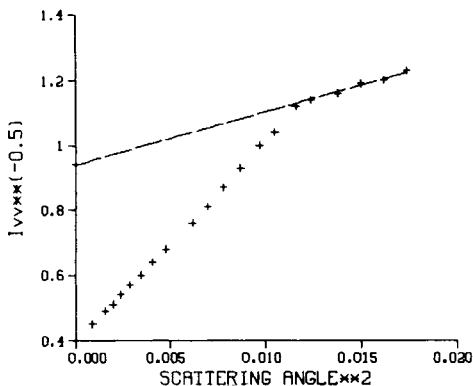


Fig. 6. Plot of $I^{-1/2}$ vs. θ^2 for films of system (C) exposed at 92% RH (Debye-Bueche¹⁶ analysis).

the clustering analysis showed a decrease in N_c only for system C, thus supporting the SALS results.

DISCUSSION

In the above analysis, a correlation between the clustering theory and the light scattering results has been shown. Both methods provide similar information and are complimentary to each other. It may be pointed out that the shape of the curve after the maximum point in the N_c vs. wt % water curve (Fig. 4) is of importance. A sharp dropoff after the maximum in the curve would represent a sudden development of visual haze while a gradual decrease would represent a gradual buildup of haze with increasing RH. This then could be verified by light scattering studies of samples with different shapes of N_c vs. wt % water curves.

Referring back to the intensity equation (7), it can be seen that at low values of h (i.e., at low scattering angle) the intensity is much more dependent upon a . Thus a higher value of a would result in higher scattering

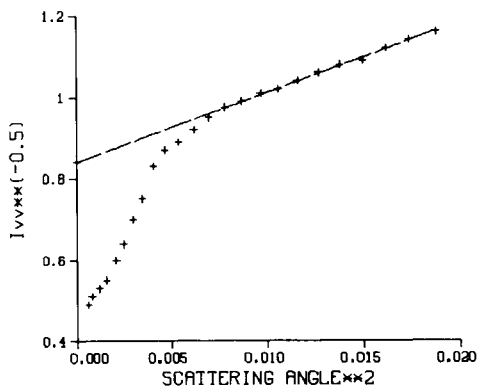


Fig. 7. Plot of $I^{-1/2}$ vs. θ^2 for films of system (C) exposed at 92% RH (Dedye-Bueche¹⁶ analysis).

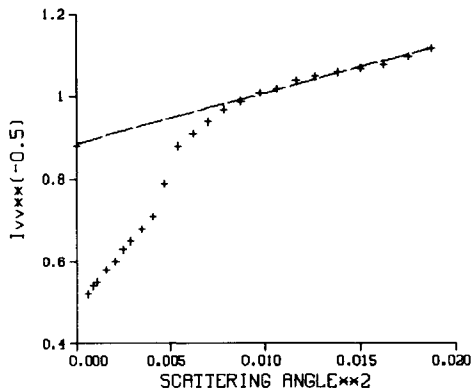


Fig. 8. Plot of $I^{-1/2}$ vs. θ^2 for films of system (C) exposed at 96% RH (Debye-Bueche¹⁶ analysis).

intensity, as is the case with the 98% sample. Moreover, the larger the correlation distance, the more rapidly will the scattering intensity decrease with increasing scattering angle. This is also seen in Figure 5 for values of θ greater than 4° .

Based on the clustering analysis and SALS results, a model has been developed for the microscopic structure of the copolymer of VA/VB. It is proposed that the hydroxyl (OH) units of this copolymer form sites for the absorption of water molecules. The absorption curve of Figure 1 would be linear in accordance to Henry's law until all the sites are saturated after which clustering of water molecules would begin.¹ This happens at a water content of about 0.93–0.95 wt % based on copolymer level for all three systems. This value represents 1 mol of water for every 8 mol of vinyl alcohol repeat units. This suggests that OH units exist in "microdomains" consisting of an average of 8 OH groups per microdomain. These OH domains thus become the sites for initial water absorption. When all OH domains have at least 1 water molecule, the number of OH domains would be equal to the number of water clustering sites. Beyond 0.93–0.95 wt %

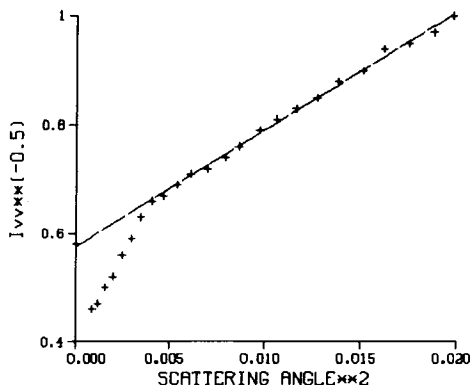


Fig. 9. Plot of $I^{-1/2}$ vs. θ^2 for films of system (C) exposed at 98% RH (Debye-Bueche¹⁶ analysis)

TABLE I

Exposure (% RH)	$w \times 100$	a (μm)	l (μm)
92%	2.70	0.28	0.29
94	2.85	0.30	0.31
96	3.10	0.29	0.30
98	3.40	0.41	0.43

water, the OH domains begin to have more than 1 molecule of water per OH domain, and the rate of water absorption increases asymptotically with increasing RH. In the base copolymer and the plasticized copolymer these OH domains remain more or less isolated, and the OH domains plus the water absorbed on them attain a size which is considerably smaller than the wavelength of light and hence do not scatter light. However, for the modified system the number of clusters, that is, the number of sites with water clustering, actually decreases beyond a critical water concentration w_c . This thus implies that the OH domains with the clustered water coalesce in system C at the value of w_c to form large domains. These domains are now big enough to scatter visible light and appear as haze in the films. The apparent reason for the coalescence is that in system C the water rich OH domains undergo phase separation due to the presence of an ionic salt. The ionic salt is water-soluble and thus significantly affects the solubility parameter of the water-rich phase such that at w_c this phase is incompatible with the vinyl butyral phase, resulting in phase separation. The phase separation manifests itself in the coalescence of OH domains with the ionic salt acting as sites for this coalescence.

The association of eight OH groups in the copolymers may be compared to the associations of metal ions in ionomers. Eisenberg and co-workers²⁹⁻³¹ have carried out theoretical calculations for the formation of ionic domains in ion-containing polymers and have postulated that the formation of a spherical domain can accommodate a maximum of eight ions. He has supported his theoretical analysis by strong experimental evidence. With an entirely different system and approach, our results also show evidence that eight OH groups are associated via hydrogen bonding to form microdomains. These OH domains, in a manner similar to the ionomers,²⁹ would have a correlation distance of about 100 Å, which is too small to scatter light. On the other hand, the mean radius of gyration of P(VA/VB) copolymer is estimated to be about 100 Å and hence the coalescence of two or more domains would form larger domains which could have a size on the order of 1000–2000 Å. This would explain the observation of similar sizes of inhomogeneities in system C as obtained by light scattering. It may also be noted that in system C the average size of scattering inhomogeneities increases with higher level of coalescence as the water content increases, i.e., leading to phase separation. Thus once again it can be seen that the water absorption is supportive of SALS results.

We are currently pursuing the investigation of domain sites by small angle neutron scattering. For this we are preparing deuterated copolymers and using deuterium oxide for absorption at different levels of RH. We hope to present our findings in a subsequent publication.

CONCLUSION

In conclusion we can say that water absorption (or in a general sense solvent absorption) in amorphous polymer systems provides an excellent insight into the microstructure of the polymer system. The theory of clustering of absorbed solvents is very effective for this purpose. Furthermore, when the solvent clusters begin to achieve a size comparable to the wavelength of light, the scattering of light can be analyzed to obtain the size of these clusters, thus complementing the cluster theory. The techniques presented in this paper can prove very effective in predicting the performance of polymer systems when exposed to different humidity conditions. Of special importance in some cases is the optical clarity required in systems under varying weather conditions.

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Received May 6, 1985

Accepted August 20, 1985