Physical Degradation by Water Clustering in Epoxy Resins

C. CARFAGNA, *Istituto G. Donegani C. R. Napoli, 80100 Naples, Italy*, and
A. APICELLA, *Polymer Engineering Laboratory, University of Naples,
80125 Naples, Italy*

Synopsis

Water uptakes in sorption experiments on thin sheets of epoxy resins have been explained on the basis of theoretical models. The occurrence of an irreversible void formation process at higher humidities induces strong deviations from the Flory–Huggins analysis. This phenomenon can be successfully explained on the basis of cluster formation.

INTRODUCTION

In the last few years an increasing interest has been devoted to the understanding of the phenomena related to liquid and vapor sorptions and diffusion in polymers. The attention of researchers mainly pointed to the different behavior of glassy polymers exposed to low or high activities of different penetrant species.

In fact, at low activities, sorption of gases and vapors in glassy polymers is successfully described by a dual mode sorption, which assumes a combination of Languimir-type trapping with preexisting gaps plus a Henry's law solution of penetrants in the glassy matrix.[1] Quantitatively, it may be written

$$C = k_D a + C'_H ba/(1 + ba) \tag{1}$$

where C is the total sorbed molecules concentration, k_D is the effective Henry's law solubility constant, C'_H is the Languimir capacity constant, b an affinity parameter, and a the activity of the penetrant.

At high activities, strong positive deviations from Henry's law indicate that sorbed molecules diffuse through the macromolecules according to a different mechanism.[2]

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. Both plasticization and clustering may cause curving water vapor isotherms depending on the possibility of forming hydrogen bonds between water and hydrophilic groups, or only among water molecules.[3]

The clustering theory developed by Zimm[4] from statistical mechanics in 1953 and then applied by Zimm and Lundberg in 1956 to sorption of vapors by polymers was used to interpret positive deviations from Henry's law related to the clustering of penetrant in polymeric rubbers.[5]

In this communication water sorption by glassy epoxy resins at different

CCC 0021-8995/83/092881-05$01.50

temperatures and relative humidities are explained in terms of solvent–polymer interactions and cluster formation.

EXPERIMENTAL

Specimens were prepared from Epikote 828 (kindly supplied by Shell Italiana Co.) using commercial triethylenetetramine (TETA) (Montedison S.p.A.) as curing agent. Distilled water was used in the sorption experiments. Dissolved gases were removed by repeated freeze–thaw cycling, under vacuum, using liquid nitrogen as refrigerant. The epoxy samples were prepared following the same procedures previously described.[6]

THEORETICAL

The analysis derived by Zimm and Lundberg[5] provides us a useful method to evaluate the tendency of water to cluster in a polymer network. If i and j are two water molecules, the probability that they are each at the coordinate i and j and in the range of these coordinates $d(i)$ and $d(j)$ is

$$(1/V^2)F_2(i,j)d(i)d(j)$$

where V is the volume of the system and $F_2(i,j)$ is a molecular pair distribution function.

The cluster integral is

$$G_{11} = \frac{1}{V} \iint [F_2(i,j) - 1]d(i)d(j)$$

In 1953, using Mayer and McMillan's power series, Zimm[4] derived a relationship between the cluster integral G_{11}, the penetrant activity (a_1), its volume fraction (ϕ_1), and its partial molecular volume ($\bar{v}_1$)

$$\frac{G_{11}}{\bar{v}_1} = -\phi 2 \left[\frac{\partial(a_1/\phi_1)}{\partial a_1}\right]_{P,T} - 1 = -\frac{\phi_2}{\phi_1} + \frac{\phi_2}{\phi_1}\frac{a_1}{\phi_1}\left(\frac{\partial\phi_1}{\partial a_1}\right)_{P,T} - 1 \quad (2)$$

$G_{11}/\bar{v}_1$ represents the tendency of water molecules to aggregate. High positive values of $G_{11}/\bar{v}_1$ denote a tendency for penetrant to cluster. $\phi_1 G_{11}/\bar{v}_1$ is the excess of the penetrant molecules over the mean concentration found in the close vicinity of a given penetrant molecule.

Solvent equilibrium uptake for noninteracting polymer-penetrant molecules may be described by the Flory–Huggins theory[7]

$$\ln a_1 = \ln v_1 + v_2 + \chi_1 v_2^2 \quad (3)$$

where the subscripts 1 and 2 refer to the solvent and polymer, respectively, v is the volume fraction, and χ_1 is the interaction parameter. Equations (2) and (3) represent the two limiting cases, for strongly and poorly mutually interacting components, respectively.

The Flory–Huggins model successfully describes poorly interacting swollen systems, such as polystyrene/n-hexane at varying activities,[6] by using a simple concentration-independent interaction parameter. This approach faults for the epoxy–water system in the condition investigated here.

Epoxies, in fact, show differently shaped isotherms when analyzed at different
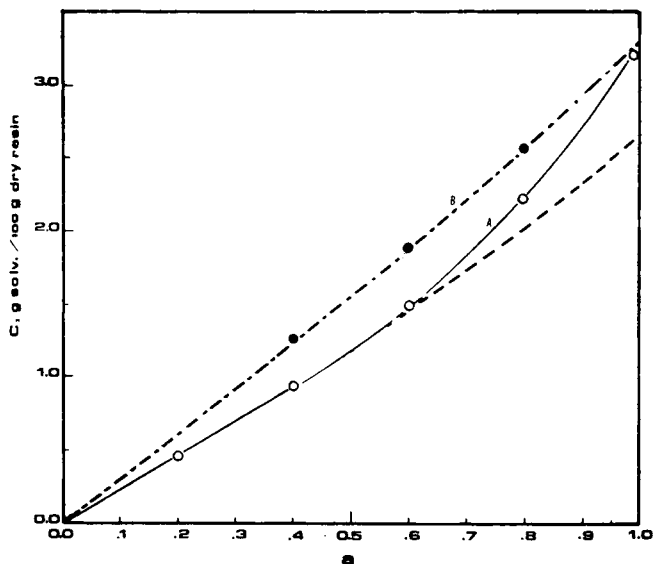
Fig. 1. Water uptakes at 75°C for the DGEBA–TETA epoxy system at different values of the external activities. (O) First sorption cycle; (●) second sorption cycle; (– – –) Henry's law; (· · ·) eq. (2), $\chi_1 = 2.652$; (–·–) eq. (2) + damage.

temperatures or for different previous conditioning histories.[8] Such history dependency has been phenomenologically explained in terms of microvoid nucleation during the sorption process, which was favored at high relative humidities by the tendency of water to cluster and at higher temperature by the lower energy required for the craze formation.[9] The occurrence of an irreversible void formation process induces strong positive deviations from the Flory–Huggins analysis using a single interaction parameter (curve a in Fig. 1).

After the conditioning of the sample at higher relative humidities and temperatures, the analyzed polymer was irreversibly microdamaged (crazed) only by the tendency of water to aggregate, without modifying the molecular water–polymer interaction (χ_1 = const). In this hypothesis, the overall water uptakes (curve b) in the equilibrium damaged state can be assumed as the sum of two terms,[8] namely from eqs. (1) and (3). The value of χ_1 can be experimentally determined from the initial portion of the curve a (when the damage was absent[8]), while the hole capacity constant C_H^1 can be calculated from the difference between the actual and the theoretical values of the water uptakes at activity equal to 1.

The clustering integral can be used to describe the damaging phenomenon during the water sorption.

Figures 1 and 2 show typical isotherms at $T = 75°C$ and $T = 45°C$, respectively, for the system water–Epikote crosslinked by TETA. The dotted curve (Fig. 1) represents the behavior of the water sorption as calculated by the Flory–Huggins eq. (3), while the straight line represents the limiting Henry's law calculated at low activities. The experimental curve is no more represented by the Flory–Huggins theory only for values of water activity higher than 0.6. In these conditions the water–water interactions are not limited to those predicted by the Flory–Huggins random mixing model. In fact the values of χ are not constant
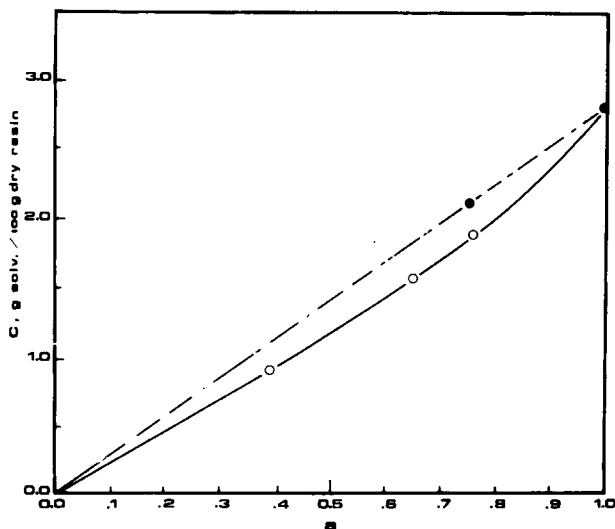
Fig. 2. Water uptakes at 45°C for the DGEBA–TETA epoxy system at different values of the external activities. (O) First sorption cycle; (●) second sorption cycle.

over the entire range of activities.   This deviation suggests that for activity higher than 0.6 a random mixing model is no more valid.   This behavior was also observed by other authors[2] for the system water–polyacrylonitrile.   In our case the vapor sorbed at low activities may act as nuclei for cluster formation at high activity.

The previous observations on swelling and microvoiding hold to the evaluation of the cluster formation by using the eq. (2), in which the effective value of water uptake is the experimental value minus the difference between the value calculated from the Flory–Huggins theory and the value estimated by the Henry's law $\phi_{\text{eff}} = \phi_{\text{exp}} - (\phi_F - \phi_H)$.   The term in parentheses accounts for the swelling. In this way we intend to take into account the effect of water plasticization of the polymer which is described by the Flory–Huggins theory not only in the limiting case of the Henry's law but also at higher activity of penetrant.   The $\phi_{\text{eff}} G_{11}/\bar{v}_1$ so calculated functions are reported in Figure 3 for data reported in a previous publication.[8]

The function is strongly dependent on temperatures, thus suggesting that (at increasing temperatures) water aggregation increases.   This is in agreement with a previous paper,[6] where water-induced microvoids formation in the polymer was found to be an endothermic process.   The fact that at 45°C the value of $\phi_{\text{eff}} G_{11}/\bar{v}_1$ is almost zero may indicate that the cluster formation is kinetically not favored and not observed in the times of the experiment.   At lower temperatures, translational freedom of water molecules can be strongly affected by the stiffness of the segments of chain molecules.   In this condition water does not easily aggregate.

The hypothesis that, at lower activity, water is bonded at polar sites and can act as nucleus for the cluster formation is supported also by other authors.[10] NMR analysis showed that, at low concentrations, water may be interacting with adjacent bond sites so that not only translational but also rotational movements become hindered.
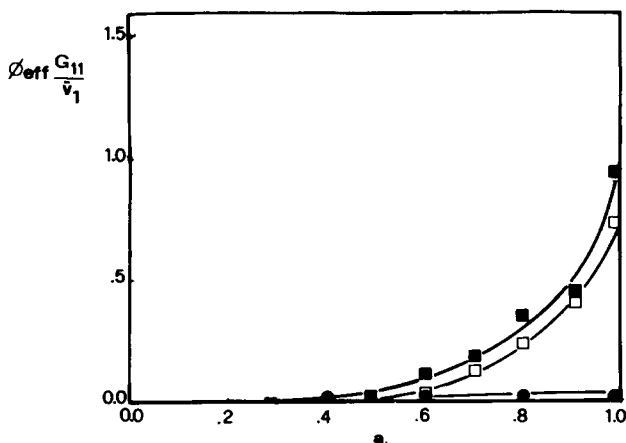
Fig. 3. Cluster integral functions at 75°C (■), 60°C (□), and 45°C (●).

As previously found,[8] the synergistic effect of high humidity and temperature can induce irreversible damage in the epoxies. Microvoids formation can be successfully explained on the basis of cluster formation induced by clustering in the matrix. This phenomenon is particularly evident in the epoxies, in which the glassy and crosslinked stiff structure does not allow the matrix to relax after the microvoids due to the cluster have been formed.

References

1. W. R. Vieth and K. J. Sladek, *Colloid Sci.*, **20,** 1014 (1965).

2. V. Stannet, M. H. Haider, W. J. Koros, and H. B. Hopfenberg, *Polym. Eng. Sci.*, **20,** 300 (1980).

3. V. T. Stannet, W. J. Koros, D. R. Paul, L. K. Lonsdale, and R. W. Baker, in *Advances in Polymer Science*, H. J. Cantow, G. Dall'Asta, K. Dusek, J. D. Ferry, H. Fujita, M. Gordon, W. Kern, S. Okamura, C. G. Overberger, T. Saegusa, G. V. Shultz, W. P. Slichter, J. K. Stiller, Eds., Springer-Verlag, Berlin, 1979.

4. B. H. Zimm, *J. Chem. Phys.*, **21,** 934 (1953).

5. B. H. Zimm and J. L. Lundberg, *J. Phys. Chem., Wash.*, **60,** 425 (1956).

6. A. Apicella and G. Sarti, Europhysics Conference Abstracts, W. J. Mertz, Ed., European Physical Society, Geneva, Switzerland, 1980, Vol. 44, p. 116.

7. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.

8. A. Apicella and L. Nicolais, *Ind. Eng. Chem., Prod. Res. Dev.*, **20,** 138 (1981).

9. E. H. Andrews and L. Bevan, *Polymer*, **13,** 337 (1972).

10. P. Moy and F. E. Karazs, *Polym. Eng. Sci.*, **20,** 315 (1980).