The Effect of the Prepolymer Composition of Amino-Hardened Epoxy Resins on the Water Sorption Behavior and Plasticization

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Synopsis

The main role of the amino hydrogen bonding in the plasticization of water-penetrated epoxy resins has been tested on a diglycidyl ether of bisphenol-A (DGEBA) epoxy cured with different amounts of triethylenetetramine (TETA). Samples were characterized both by calorimetric and moisture diffusion techniques. The increased water solubilities and glass transition temperature depressions observed for the samples cured with an increased content of amino hardener were attributed to the high hydrophilic character of the amine. Theoretical models, based on the analysis of the free volume and entropy of the water saturated polymer, have been used to test the nature of the polymer–diluent interactions. The comparison between the experimentally determined and theoretical values of the wet glass transition temperatures indicates how the free volume better describes the behavior of the low amino content resins while the entropy model become effective at increasing amino contents. Moreover, the actual water solubilities have been determined by thermal cycling of water-saturated samples of different composition and used in the cited models.

INTRODUCTION

Epoxy resins are usually employed as glassy matrices for structural composite materials. Since these materials are used at different temperature and humidity conditions, the knowledge of the polymer structure parameters affecting the water sorption and transport behavior is needed in order to predict short-term as well as long-term performance in service. It has been widely described how sorbed moisture plasticizes the epoxy resin depressing the glass transition temperature of the polymer; however, the nature of the association process between the water and the polymer is not clearly understood. The free volume theory,[1] in fact, satisfactorily applies to polymer–diluent systems whose glass transition temperatures and thermal expansion coefficients are well defined, but fails not only for systems and temperature ranges where uncertain evaluations or arbitrary assignments of these parameters must be made but also for polymer–diluent couples which present strong molecular interactions. An alternative description of the wet glass transition, which designates configurational entropy rather than free volume as the temperature-dependent function, has been proposed[2] for epoxies and other polymers in which water may be absorbed by localization at a strongly polar molecular groups (hydrogen bonding). Evidence has been given, in fact, by broad line nuclear magnetic resonance analysis[3] that the plasticization effect of the water on a crosslinked epoxy may be related to the strong interactions between the dissolved water and segments or groups of the polymer, although the exact sorption sites to which water may be bonded are still uncertain.

Previous works[4,5] show that epoxy resins may undergo localized solvent crazing in the presence of sorbed moisture which alters the apparent water solubilities, depending on the temperatures and relative humidities to which the samples have been previously exposed. An analysis[6] of the effective diffusion coefficients based on the dual mode sorption theory[7] confirmed the cavitational nature of the damage associated with network inhomogeneities as regions of low and high crosslinking densities.

The dependence of the water sorption behavior as a function of the prepolymer composition is analyzed by testing with diffusion and calorimetrical techniques the polymer tendency to swell or to craze, to resolve the sorption process into effects arising from morphological (microcavitation) as well as chemical (hydrogen-bonding) origins.

The free volume and the entropy models have been used to evaluate the nature of the epoxy–water interactions by comparing the experimental and theoretically predicted values of the glass transition temperature depressions of epoxies crosslinked with different amounts of hardener and subsequently saturated at high temperature in liquid water. The actual values of the dissolved water to be used in the cited models were experimentally determined, as described in a previous work,[4] by liquid water sorption tests made at low and high temperatures.

EXPERIMENTAL

Materials

Specimens were prepared from Epikote 828 (kindly supplied by Shell It.) using triethylenetetramine (TETA)—Montedison SpA—as curing agent. A large excess, 25 phr, a stoichiometric, 14 phr, and a defect, 5 phr, of TETA was used in preparing the samples of different composition. Distilled water was used in the sorption experiments. The epoxy samples were made following the same procedures previously described.[4]

Differential Scanning Calorimetry

Large-diameter aluminum ermetically sealed pans were used in all runs. Measurements were made with a Perkin-Elmer DSC-2, equipped with an intracooler and using a nitrogen atmosphere. The instrument was calibrated for temperature and enthalpy with indium. Scans were made at 20°C/min heating rate.

Infrared Spectroscopy (IR)

Scans were made from 3800 to 450 cm^{-1} on thin films of 0.1 mm of the three resins by using a Perkin-Elmer Infrared Spectrometer Model 457.

Liquid Water Sorption Tests

Gravimetric liquid sorption measurements were performed by weighing 3.0 × 1.0 × 0.03 cm^3 samples on a four-digit analytical balance following immersion in water maintained at constant temperature. The samples were removed from
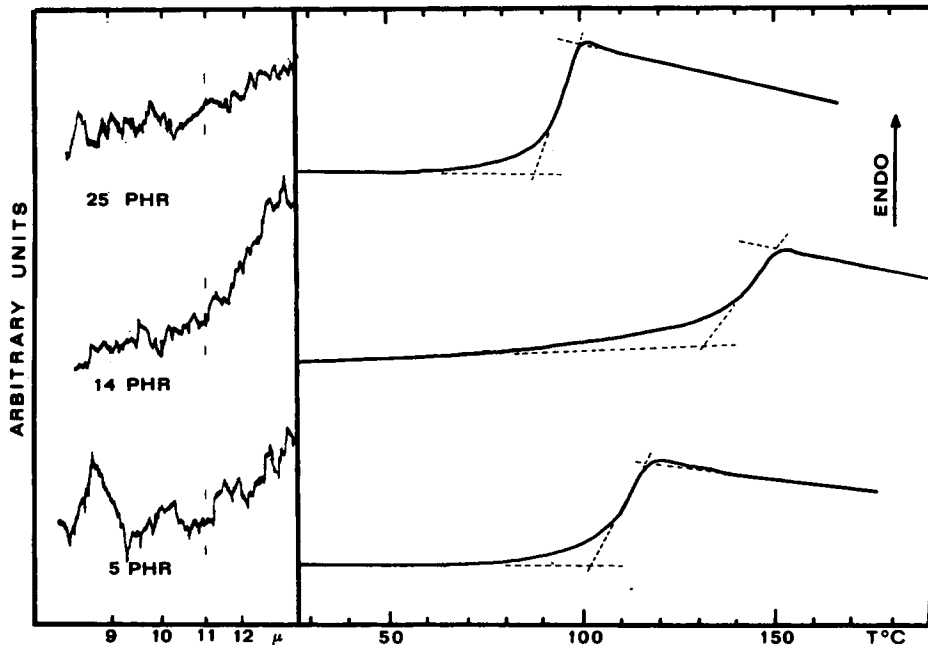
Fig. 1. Infrared spectra (left side) and DSC thermograms (right side) of the DGEBA epoxy resin cured with different amount of TETA.

the water, blotted, placed in a weighing bottle, weighed, and finally replaced in the constant temperature pool.

Sorption data are reported as percentage of weight gain referred to the dry weight and plotted as a function of $\sqrt{t}/l$, where l is the thickness of the samples, ranging from 0.2 to 0.4 mm. Sorption equilibria were achieved over 2–40 days, depending upon the test temperature.

RESULTS AND DISCUSSION

DSC traces and infrared spectra for the resin with different prepolymer compositions are reported in Figure 1. The glass transition temperatures, calculated at $\Delta C_p/2$, are 109°C, 142°C, and 95°C, respectively for the 5, 14, and 25 phr and are reported in the second column of Table I. The stoichiometric composition (14 phr) shows the highest glass transition temperature, while, for the resin made with an excess of hardener, it is the lowest. The densities at 20°C of the three resins, determined by gravimetric and volumetric measurements, are reported in the first column of Table I together with some other physical

TABLE I
Experimental Values of Some Physical Properties of DGEBA Epoxy Resin Cured with Different Amounts of TETA

Prepolymer composition	$\rho_{20°C}$ (g/cm^3)	T_g dry (°C)	T_g wet (°C)	S^{70} (%)	S^{20} (%)	S_{70}^{20} (%)	ΔS^{20} (%)	ΔC_p, (cal/g°C)
5 phr	1.174	109	105	1.92	1.50	2.42	0.92	0.11
14 phr	1.219	142	109	3.30	2.70	3.90	1.20	0.11
25 phr	1.107	95	59	8.66	10.80	10.80	0.00	0.13

properties which will be discussed later. As observed for the glass transition, the density of the resin of stoichiometric composition (1.219 g/cm^3) is higher than both the 5 phr (1.147 g/cm^3) and 25 phr (1.104 g/cm^3). This may be attributed to a higher and more homogeneous crosslinking density obtained for the better balanced amino–epoxy system in which diffusion controlled reactions are less favored.[8]

The only reaction which practically occurs when amines are present in excess or in stoichiometric concentration is the fast amino addition, but, if epoxide is present in excess, the secondary hydroxyl groups, formed in the previous reaction, could add to the remaining epoxide rings[9] until the glass transition temperature of the forming network exceeds the curing temperature and the unfavored reaction becomes diffusion controlled. The glass transition temperature of the 5-phr hardener resin is, in fact, only slightly higher than the curing temperature (100°C). Infrared spectra, on the left side of Figure 1; show, at 11-μm wave length, the presence of epoxide rings more evident for the 5-phr than for the 14-phr composition, but not for the 25-phr in which they completely reacted with the large number of other amino groups. However, the partially unreacted amines plasticized the 25-phr system which, in fact, shows the lower glass transition temperature and density.

The liquid water sorption behavior at 20°C (O) and 70°C (●) for the three types of amino hardened epoxies are shown in Figures 2, 3, and 4. Water uptakes at 20°C are compared in the same figures for the "as cast" samples (O) and for the previously equilibrated at 70°C samples (▲). Equilibrium water uptakes at 70°C (S^{70}) and at 20°C for the "as cast" (S^{20}) and the previously exposed to 70°C (S^{20}_{70}) are reported, respectively, in the fourth, fifth, and sixth columns of Table I. The resin crosslinked with a large excess of hardener, when immersed in liquid water at 20°C and 70°C, sorbs 10.80% and 8.66% of water, which is much higher than for the other two compositions. The water uptakes for the 5 phr
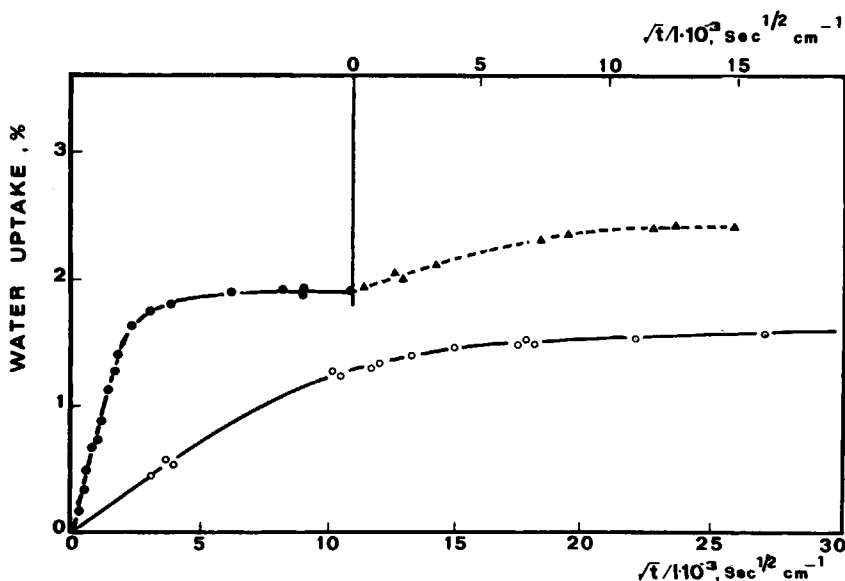

Fig. 2. Water uptake kinetics at 20°C (O, ▲) and 70°C (●) of the 5 phr TETA prepolymer composition epoxy resin.

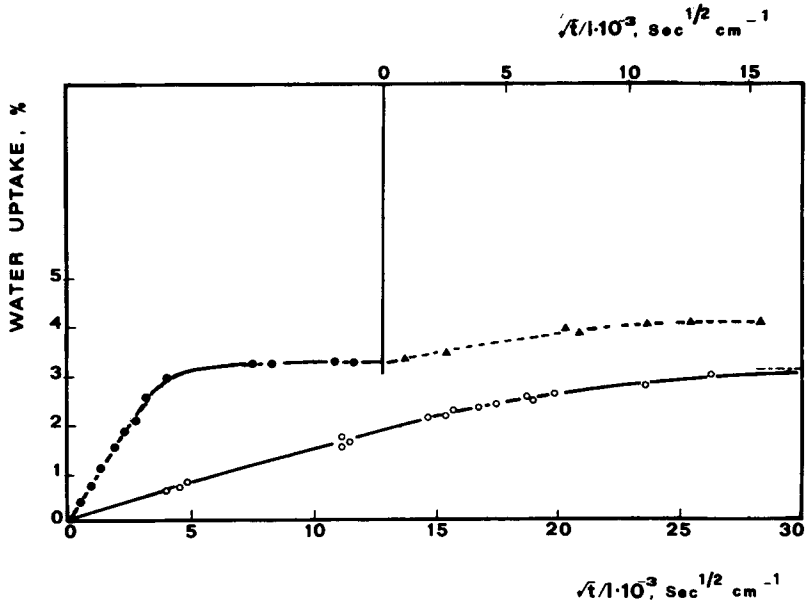$\sqrt{t}/I \cdot 10^{-3}$, sec$^{1/2}$ cm^{-1}

Fig. 3. Water uptake kinetics at 20°C (O, ▲) and 70°C (●) of the 14 phr TETA prepolymer composition epoxy resin.

are, in fact, of only 1.50% and 1.92% at 20°C and 70°C while they are of 2.20% and 3.30%, respectively, for the 14 phr.

The strong influence of the prepolymer composition on the equilibrium water uptakes at both temperatures may be related to the increase of the number of hydrogen bonding sites due to the presence of unreacted amines where water may be sorbed.

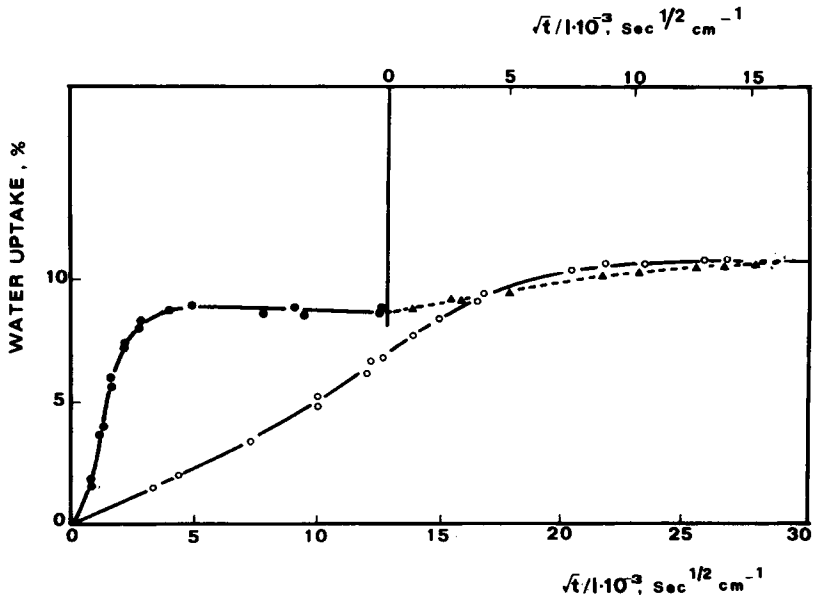$\sqrt{t}/I \cdot 10^{-3}$, sec$^{1/2}$ cm^{-1}

Fig. 4. Water uptake kinetics at 20°C (O, ▲) and 70°C (●) of the 25 phr TETA prepolymer composition epoxy resin.

The sorption kinetics for the 5- and 14-phr compositions are apparently Fickian in character both at 20°C and 70°C, while appear anomolous for the 25 phr; they are, in fact, upward when reported as a function of the square root of time.

The samples equilibrated at 70°C, which showed water solubilities higher than those equilibrated at 20°C in the case of 5 phr and 14 phr but lower for 24 phr, were brought down to 20°C and weight changes were followed (upper right part of Figs. 2, 3, and 4). As described in previous works for the stoichiometric composition,[4,5] when the sample is previously equilibrated in water at a higher temperature, the water uptakes reached at a lower temperature are greater than those of a sample equilibrated directly at low temperature. Such differences in the apparent equilibrium have been associated with a microcavitational damage[5] which may occur for the synergistic action of the sorbed moisture and the high temperature in the regions of different crosslinking densities. Microcavitation leads to higher apparent solubilities since void filling increases the water uptakes. The values of the water actually dissolved in the resin at 70°C should take into account the excess of water due to the damage. Actual solubilities at 70°C (reported in the first column of Table II) have been obtained by subtracting from the apparent solubility S^{70} the difference, ΔS^{20}, between the water uptakes at 20°C found for the undamaged (S^{20}) and the damaged resin (S_{70}^{20}). Previous studies[4,5] indicate how, for the epoxy resin examined, one can refer to an undamaged state for temperatures lower than 20°C. The calculated actual solubilities at 70°C are 1.00%, 2.10%, and 8.66% for the three types of resin of increasing amino content and are, respectively, lower than the corresponding solubilities at 20°C, according to the slight exothermic process associated with the water sorption.[5] The value at 70°C of the water uptake for the 25-phr epoxy is unchanged since the thermal cycling from 70°C to 20°C gave the same final value reached by the "as cast" sample directly at 20°C, indicating that no microcavitational damage is present at that temperature. The wet glass transition of that resin, obtained by scanning a sample saturated at 70°C in the DSC, is, in fact, of 59°C, well below the testing temperature. At this condition, the polymeric system is in the rubbery state, and the crazes, which have been indicated as responsible for the increased apparent solubilities, disappear.

The experimental values of the wet glass transition temperatures of the three epoxy resins equilibrated in liquid water at 70°C, T_{gw}, are reported in the third column of Table I. The wet 5-phr epoxy shows the lower depression of the glass transition temperature, from 109°C to 105°C, while were from 142°C to 109°C for the 14 phr and from 95°C to 59°C for the 25 phr.

TABLE II
Apparent (S_{app}) and Actual (S_{act}) Water Solubilities in DGEBA Epoxy Resin Cured with Different Amount of TETA. Comparison between Experimental Wet Glass Transition Temperatures and Values Calculated According to Entropy and Free Volume Models by Using Apparent and Actual Water Solubilities

Prepolymer Composition	S_{app}^{70} (%)	S_{act}^{70} (%)	Entropy model		Free volume model		$T_g$wet, (°C)
			$T_g(S_{app})$ (°C)	$T_g(S_{act})$ (°C)	$T_g(S_{app})$ (°C)	$T_g(S_{act})$ (°C)	
5 phr	1.92	1.00	81	92	92	100	105
14 phr	3.30	2.10	100	110	104	115	109
25 phr	8.66	8.66	57	57	52	52	59

The apparent (S_{app}^{70}) and the actual (S_{act}^{70}) water solubilities have been used to predict the glass transition temperatures of the plasticized resins by means of theoretical free volume[1] and entropy models.[2] The values of the physical parameters to be used are reported in Tables I and II.

Free Volume Model

The expression used to correlate the variation of the glass transition temperature of a plasticized polymer is

$$T_{gw} = [\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd}]/[\alpha_p V_p + \alpha_d (1 - V_p)] \qquad (1)$$

where V_p is the volume fraction of the resin in the resin–water mixture and T_{gp} and α_p are the dry glass transition temperature and the difference between the volume expansion coefficients of the polymer in the rubbery and glassy state, while T_{gd} and α_d are the characteristic transition temperature and the volume expansion coefficient of the water. Previous authors[10,11] identified T_{gd} and α_d with a temperature near the freezing point of water and the corresponding expansion coefficient: 4°C and 3.66×10^{-3} °C^{-1}.

Entropy Model

The expression derived assuming the configuational entropy as the temperature dependent function is[2]

$$T_{gw} = T_{gp}[1 - Ry(r)/(M_s \Delta c_p)] \qquad (2)$$

with $y(r) = r \ln(1/r) + (1 - r) \ln 1/(1 - r)$ and $r = (M_s/M_w)f$, where R is the universal gas constant, M_w is the molecular weight of the water, $M_s = N_A/N_s$ is the effective formula weight of the hydrogen bond sites with N_A the Avogadro's number (mol^{-1}) and N_s the number of hydrogen bond sites for grams of resin and, finally, f are the grams of moisture per gram of dry resin. ΔC_p is the change of the specific heat at the glass transition.

The experimental and theoretical wet glass transitions, calculated by using the actual and apparent solubilities in the cited models, are reported in Table II.

The values of the wet glass transition temperature obtained from the free volume model using the actual solubility, $T_{gw}(S_{act})$, match better the effective wet glass transition temperature, T_{gw}, of the resin made with a defect of hardener. Conversely, the entropy model adequately describes both the plasticizations observed for the resin made with a large excess of hardener and of stoichiometric composition, when the actual values of the solubilities are used.

The effectiveness of two distinct models in describing the plasticization due to the water sorption indicates that different types of polymer–diluent interactions may be present: strong polymer–diluent interactions lead to a mechanism driven by hydrogen bond formation while, in the opposite case, the free volume changes become effective.

Furthermore, the main role of the amino–hydrogen bonds compared to the hydroxyl–hydrogen bonds in the plasticization of moisture-penetrated epoxy resins is confirmed both by the analysis based on the entropy model and by the strong sensitivity on the amino content of the water solubilities.

In conclusion the data of Table II indicate that the water sorption in the polymer containing a large number of potential hydrogen-bonding sites is driven by the strong interactions between the water molecules and particular segments or groups present in the polymer. The water actually dissolved in the three resins at 70°C, in fact, progressively increases from 1.00% to 8.66% as the highly hydrophilic amino content is increased from 5 phr to 25 phr. Moreover, the data of the water solubilities to be used in both models to better match the experimental wet glass transition temperatures are those obtained in the hypothesis of the presence of an excess of water trapped in the crazed regions. Independent mechanical tests gave the same information,[4] showing an increase in the degree of plasticization for the samples equilibrated in liquid water at low temperatures also if a lower water uptake than at higher temperatures was reached.

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