Cabanelas, J. C., Prolongo, S. G., Serrano, B., Bravo, J. & Baselga, J. (2003). Water absorption in polyaminosiloxane-epoxy thermosetting polymers. *Journal of Materials Processing Technology*, 143-144, pp. 311-315.

Water absorption in polyaminosiloxane-epoxy thermosetting polymers

J.C. Cabanelas, S.G. Prolongo, B. Serrano, J. Bravo, J. Baselga*

Inst. Tec. de Quimica y Mat. Alvaro Alonso Barba, Avda de la Universidad 30, Leganes, University Carlos III de Madrid, Madrid 28911, Spain

Abstract

Water absorption is a common problem in epoxy-based composites, especially in interfacial regions. In contrast to epoxy resins, silicones are hydrophobic materials. Modificatio of epoxy thermosets with silicones should improve physical properties because of decrease in water diffusion. Bisphenol-A diglycidyl ether (DGEBA) was cured with a synthesised aminopropyl perfunctionalised siloxane. Water absorption was analysed by different techniques, including near infrared (FTIR) water absorbance at 5200 cm^{-1} and gravimetry. Fick's law diffusion coefficient were calculated. Swelling equilibrium of the resin was also analysed. Absorbed water catalyses the curing reaction strongly, allowing to reach high conversions.

Keywords
Diffusion; Epoxy resin; Siloxane

1. Introduction

Water uptake in epoxy systems is a challenging issue due to the irreversible changes that water operates on the polymer properties. It is believed and there are enough experimen-tal evidences that entrance of water induces: (a) swelling of the system and build-up of residual stresses at and near the interfaces [1], (b) rupture of adhesive bonding between the system and a given substrate [2], (c) aperture of oxirane re-maining groups [3], (d) modificatio of the local stress state and creation of microcrazes through environmental stress cracking [4].

There is no universal model to cover all types of water diffusion [1]. Several mechanisms for the water entrance have been proposed: (a) diffusion governed by Fick's law through the free volume of the polymer [5], (b) case II diffusion mechanism by which osmotic swelling is limited by polymer creep [6], (c) swelling induced by a favourable polymer–solvent parameter, (d) osmotic phenomena due to the presence of micropores, channels and other defects in the polymer [7].

It is also frequently found in the literature that the water diffusion coefficien in different epoxy systems is around 10^{-8} to 10^{-10} cm^2 s^{-1} [1,2,8], even for rubber modifie compositions [8]. Similar values are obtained for other glassy polymer systems [2]. Diffusion coefficien measures the initial rate of water absorption and, in principle, it

should be dependent on the chemical nature of the polymer system and on the cross-linking degree for cross-linked systems such as epoxy's. But, as it will be shown in this paper, similar diffusion coefficient are found even for not fully cured systems.

In an effort for designing water resistant epoxy systems, it is necessary to know which material parameters are really involved and control the process of water absorption. In this paper, we study the water absorption properties of a new epoxy formulation based in the use as hardener of a reactive derivative of a hydrophobic polymer, such as polysiloxane. It will be shown that when common bisphenol-A diglycidyl ether (DGEBA) resins are cured in the presence of poly(3-aminopropylmethylsiloxane) (PAMS), equilibrium properties are greatly enhanced. In addition, due to the special characteristics and morphology of this epoxy system [9], a different behaviour against postcuring temperature is found.
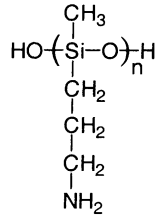
2. Experimental

2.1. Synthesis of PAMS

The polymer was synthesised according to the method reported in Ref. [9]. The structure of the polymer is presented in Scheme 1.

M_n of the synthesised polymer was 1600 g/mol as determined by vapour pressure osmometry, which corresponds to an amine equivalent weight of 58.5 g/eq. NH$_2$; it contained a cyclics weight fraction of 15%.

* Corresponding author. Tel.: +34-1-624-94-67; fax: +34-1-624-94-30.
E-mail address: jbaselga@ing.uc3m.es (J. Baselga).

$$
\begin{array}{c}
\mathrm{CH_3} \\
| \\
\mathrm{HO}\!-\!\!\overbrace{\mathrm{Si}\!-\!\mathrm{O}}^{}\!\!-\!\mathrm{H} \\
\quad\quad n \\
| \\
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} \\
| \\
\mathrm{CH_2} \\
| \\
\mathrm{NH_2}
\end{array}
$$

Scheme 1. Structure of PAMS.

2.2. Materials

DGEBA was supplied by Gairesa (Spain). Before mixing, DGEBA and PAMS were vacuum degassed for 2 h approximately. Stoichiometric mixtures of DGEBA and PAMS were prepared gravimetrically. Once mixed, the mixture was vigorously stirred and vacuum degassed again for 3 min, and injected into a glass mould for curing. The glass walls of the mould were covered with a fin layer of a grease demoulding agent. Samples were cured at 120 °C for 1 h and postcured 1 h at 130 and 150 °C. A second set of samples were cured 2 h at 60 °C and postcured 1 h at 80, 100 and 120 °C. After curing, the samples were demould and cut into pieces of dimensions 1 cm × 4 cm × 0.057 cm.

2.3. Methods

Water absorption was measured gravimetrically at 50 °C. Samples were immersed in distilled water and its weight was measured as a function of immersion time over a 2 weeks period. Prior immersion cured samples were cleaned with CH_2Cl_2. Water content was measured also by near infrared spectroscopy (Perkin Elmer GX2000). Spectrometric conditions were 10 scans from 7000 to 4000 cm^{-1}. The water band ($A_{w,t}$) appears in the range 5360–5020 cm^{-1} [10] and was in-tegrated using the standard routines of the control software. To correct for the effect of volume variations due to swelling, a reference band (4623 cm^{-1}) corresponding to aromatic CH tension vibrations of the resin (A_{ref}) was selected. It has been proved that there exists a linear relationship between inte-grated NIR band and gravimetric amount of water; therefore A_w can be converted into water content, w_t, according to the equation:

$$
w_t = 0.096 + 0.587\frac{A_{w,t} - A_{w,0}}{A_{ref}} \tag{1}
$$

where $A_{w,0}$ is the integrated absorbance at immersion time $t = 0$. Epoxy conversion was measured also by FT-NIR. The epoxy band was integrated in the range 4588–4507 cm^{-1}, and it was also referred to the reference band.

Glass transition temperatures were measured by differential scanning calorimetry (DSC, Perkin Elmer DSC-7) at 10 K min^{-1}, using the standard routines.

3. Results and discussion

3.1. Water uptake and diffusion coefficient

Gravimetric results are presented in Fig. 1 were the fractional amount of water is plotted against $t^{1/2}$. In Fig. 2, the water content measured by FT-NIR for the different samples is also presented.

From the initial linear portion of the curves, water diffusion coefficient can be calculated according to the following equation:

$$
\frac{\Delta w_t}{\Delta w_T} = \frac{w_t - w_0}{w_\infty - w_0} = \frac{4}{e}\sqrt{\frac{Dt}{\pi}} \tag{2}
$$

where w_t, w_0 and w_∞ are the weights of the samples at immersion time t, $t = 0$ and at the saturation equilibrium, e is the thickness of the sample, and D the water diffusion coefficient In Table 1, D and the equilibrium water content are presented. No great differences are observed in function of curing degree.

3.2. Volume change during water uptake

From FT-NIR spectra at different immersion times it is possible to obtain information on the volume change following water uptake. According to the Lambert–Beer law, absorbance at a certain wavenumber, A, were absorption takes place is proportional to the number of absorbing species per unit section. Therefore, $A^{-3/2}$ should be proportional to the volume in which the absorbing species are distributed. If we select some wavenumber specifi of the IR spectrum of the neat resin, sufficientl far away from absorption of water molecules, we can measure the fractional volume change using the following expression:

$$
\left[\frac{A_0}{A_t}\right]^{3/2} - 1 = \frac{\Delta V}{V_0} \tag{3}
$$

were A_0 and A_t are the integrated absorbances of the reference band at 4623 cm^{-1} at immersion times $t = 0$ and t, $\Delta V/V_0$ the fractional volume change following water uptake. In Fig. 3, the fractional volume change is plotted against immersion time.

Table 1
Water diffusion coefficient calculated with Eq. (2) and weight fraction of water at the saturation equilibrium

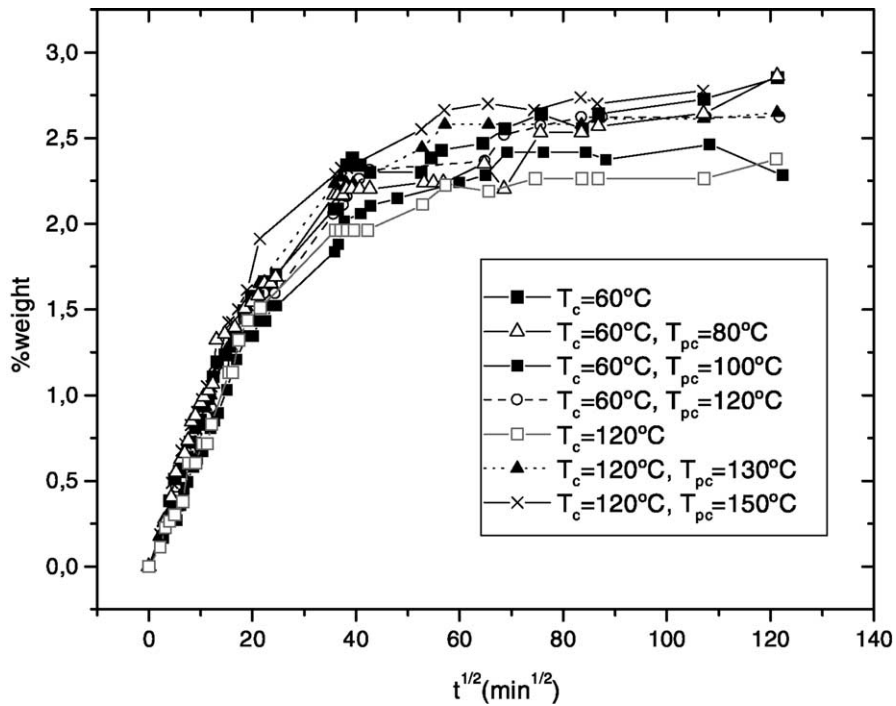| Sample	$(\Delta w_T/w_\infty) \times 100$	$D \ (\times 10^{-8}\ \mathrm{cm^2\,s^{-1}})$
60	2.85	7.54
60–80	2.86	8.75
60–100	2.28	7.40
60–120	2.62	8.11
120	2.38	6.86
120–130	2.65	8.28
120–150	2.78	10.1

Fig. 1. Fractional weight gain against $t^{1/2}$.

3.3. Catalytic effects of absorbed water on curing during water uptake process

The normalised epoxy band was analysed in order to study the effect of water swelling on the extent of curing. In Fig. 4 epoxy conversion against time is represented for samples immersed in water. A relevant increase in conversion is observed especially for the low temperature cured samples, but all the samples present the same behaviour.

It should be noticed that although a plateau is attained for water absorption, epoxide conversion continues to increase even at very long immersion time. The decrease in
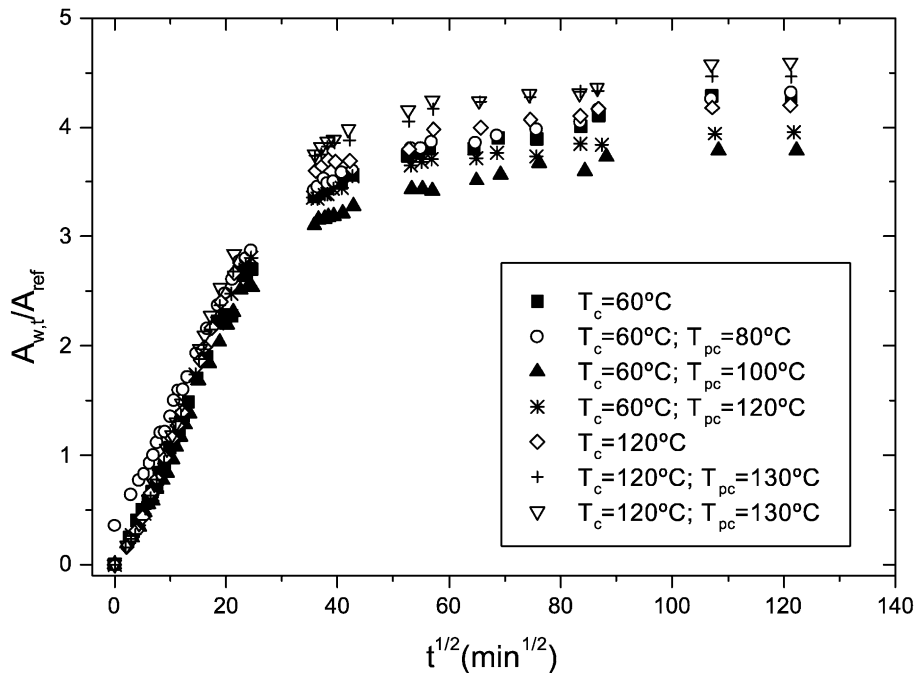

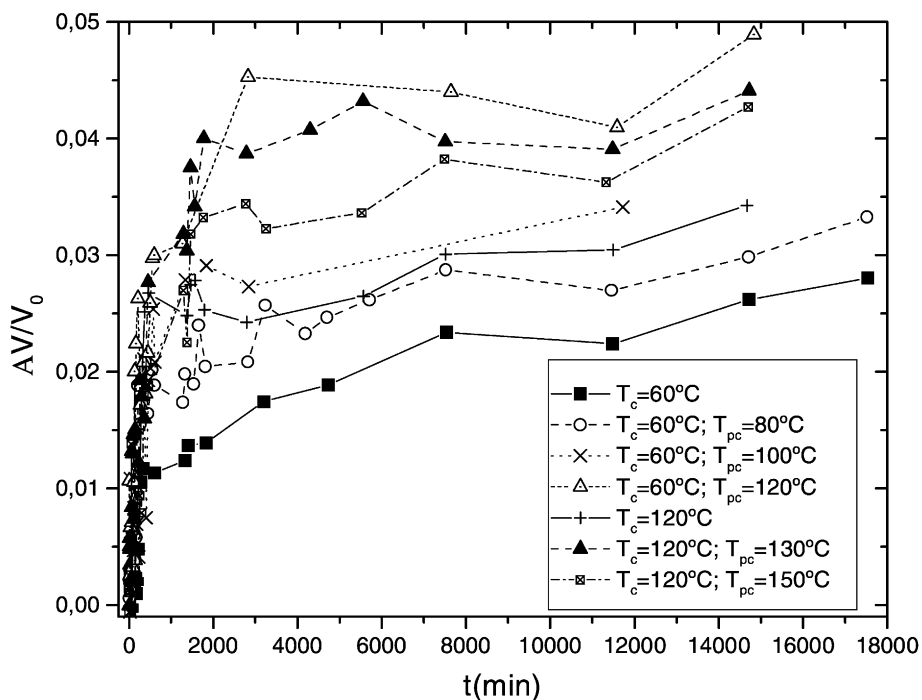Fig. 2. Fractional water content as measured by FT-NIR and Eq. (1).

Fig. 3. Fractional volume change against immersion time.

the epoxy band is accompanied by a simultaneous decrease in the secondary amine NIR band (centred at $6510 \, \mathrm{cm}^{-1}$). Therefore, epoxide ring opening by water without reaction can be rejected. Samples postcured at 60 and $80 \, ^\circ\mathrm{C}$ show

the highest change in conversion. This increase can be due to different reasons: (a) water acts as a plasticiser agent; as a consequence T_g decreases and reaction becomes possible. (b) A temperature effect. The bath of water is thermostated
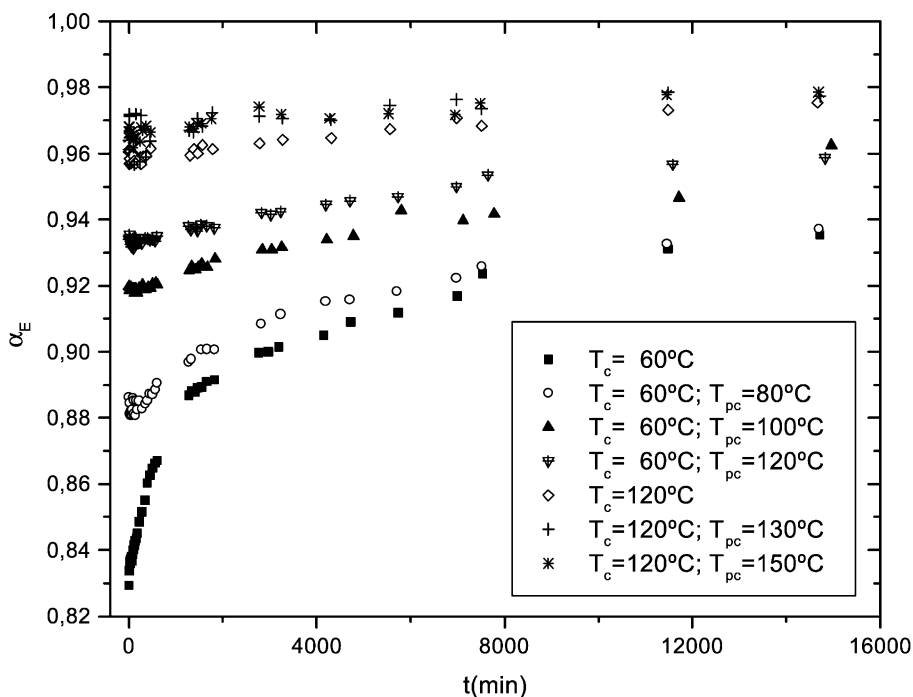

Fig. 4. Time variation for epoxy conversion (α_E).
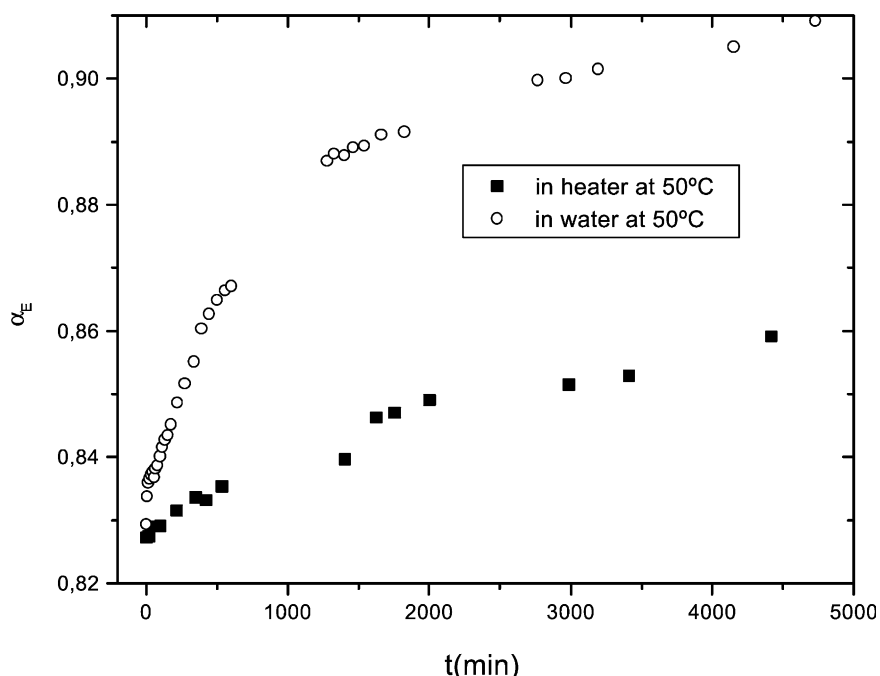
Fig. 5. Time variation of epoxy conversion (α_E) during postcuring at $50\,^{\circ}$C in the presence and absence of water.

Table 2
The T_g of samples before water immersion and after achieving equilibrium water content

T_c (°C)	T_{pc} (°C)	T_g (°C) before water	T_g (°C) after water
60	–	76.3	76.4
60	80	89.9	87.8
60	100	112.3	93.0
60	120	135.4	91.7
120	–	134.5	93.9
120	130	143.7	90.6

at $50\,^{\circ}$C, relatively near the T_g of the samples less cured, and reaction may progress at very long times. To evaluate the water catalysis effect in the postcuring reaction, a sample cured at $60\,^{\circ}$C for 2 h was synthesised and the change of the epoxy conversion with time was studied at $50\,^{\circ}$C in the absence of water. The results obtained are plotted in Fig. 5.

These results show an important catalytic effect of water in the epoxy system. To study of the origin this effect is caused by plastification T_g of the systems were measured. In Table 2 the change of glass transition temperatures in the samples before water immersion and after attaining

saturation is shown. The T_g of the system at the saturation condition is about 88–$93\,^{\circ}$C irrespective of the T_g value attained prior to immersion. It seems that the reduction in T_g due to plastificatio is compensated by an increase on the cross-linking degree.

By extrapolation of results, epoxide conversion of samples postcured at low temperatures will raise till 98% at very long immersion times.

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