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Direct relationships between volume variations at macro and nanoscale in epoxy systems. PALS/PVT measurements

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Abstract

The free volume in epoxy systems fully cured with aminic hardeners having different chemical structures was studied by means of positron annihilation lifetimes spectroscopy. The results are compared with those obtained from the analysis of the macroscopic specific volume changes by using pressure–volume–temperature experimental technique. An excellent correlation between the volumes measured at macro and nanoscales was found. From this fact, it can be asserted that the variation of the specific volume is mainly controlled by the variation in the average size of sub-nanometer size local free volumes, which are fixed by the chemical structure of hardener in fully crosslinked epoxy networks. These results give the first evidence of the direct relation existing between macro and nanoscales in thermosetting networks. © 2004 Elsevier Ltd. All rights reserved.

Keywords: Epoxy; Hardener; Chemical structure

1. Introduction

Epoxy resins are being used increasingly in structural applications ranging from high performance aerospace composites to encapsulants for the microelectronics industry, due to their high thermal resistance, high tensile strength and modulus, and good chemical resistance. It is well known that the most important factors influencing their performance are molecular architecture, ratio between epoxide and hardener, and curing conditions [1–4]. As a matter of fact, it is an useful thinking that by choosing monomers with appropriate molecular structure the rigidity of epoxy networks can be controlled, while stoichiometry and curing conditions predominantly affects crosslinking density, free volume but also mechanical properties.

Some researchers [5–8] have investigated on the influence of chemical structure and curing conditions on local free volume in epoxy systems. Despite of some investigations [9,10] have been carried out with thermoplastics to compare macro and nanovariations of volume at our knowledge, there are no works dealing together with both local variations and macroscopic volume changes and with their dependence on the chemical structure of thermosetting networks.

Positron annihilation lifetime spectroscopy (PALS) is an increasingly important analytical technique that can be used as bulk probe of sub-nanometer voids in porous media and free volumes in polymers [11–16]. *Ortho*-positronium (*o*-Ps) lifetime is know to be correlated to the size of free volume holes. More specifically, the long-lived lifetime component obtained from the deconvolution of the lifetime spectra, associated with *o*-Ps annihilation is particularly sensitive to variations in the packing of polymer chains. Therefore, this nuclear technique allows to monitor changes of the local free volume induced by different external agents as temperature, pressure or hardener type used for curing epoxy resins.

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Pressure-volume-temperature (PVT) measurements involve measuring the specific volume of a polymer as a function of pressure and temperature. The PVT relationships, including the thermal expansion coefficient and isothermal compressibility, and the crystallization and melting behaviour of polymers are closely related to their composition and structure. Moreover, PVT data can be described by empirical and theoretical equations of state, such as Tait [17], Simha-Somcynsky [18,19], and so on. Furthermore, as reported in another paper [20], since the density of thermosetting resins depends on the degree of crosslinking the curing can be investigated using the specific volume as a measure for the extent of reaction. Therefore, the combination of PALS (which measure the average volume and the size distribution of the free volume holes) and the PVT experiments (which measure the specific volume), allows to estimate the number of holes.

The goal of this work deals with the understanding of the variables controlling the local free volume generation and macroscopic volume changes, and their relation upon the chemical composition of hardener in fully cured epoxy systems.

In the present work, we have used PALS to analyse the variations in local free volume that occur when epoxy prepolymers are cured with different aminic hardeners. Complementarily, the use of PVT technique has allowed us to measure the changes in the specific volume, relating them to the packing variations of polymer chains of the crosslinked networks. To our knowledge, this is the first time that such relationships are presented for these thermosetting networks. This work is the first one of a series of articles in which we will attempt to deal with the influence of molecular structure of hardener, stoichiometry and curing conditions on the relationships between volume variations at macro and nanoscale in epoxy systems.

2. Experimental

2.1. Materials

The thermoset precursors were a diepoxy monomer based on diglycidyl ether of bisphenol-A (DGEBA, DER 332, Dow Chemicals), having an epoxy equivalent of around 175. As hardener, stoichiometric amounts of different diamines have been used. Both molecular structures of the different aminic hardeners as well as cure schedules used are summarised in Table 1.

The stoichiometric amount of diamine was added to the liquid epoxy monomer at 100 °C, except for 3DCM system (added at 50 °C) and DDS (at 135 °C). The mixture was then vigorously stirred for 10 min, leading to a homogeneous solution. The blend was poured into treated glass test tubes, for further PVT measurements use, and between two treated glass plates which were separated by a stainless steel spacer and clamped with several c-clamps, for further PALS measurements use. The glass was pre-treated with an anti-adhesion agent, and pre-heated to the cure temperature. The samples were placed for 10 min in a vacuum oven at the cure temperature to remove the trapped air. The cure schedules are also shown in Table 1. After post-curings, the samples were slowly cooled to room temperature (RT) and then separated from the glass.

2.2. PVT measurements

The PVT evolution was followed using cylindrical samples in a PVT 100 analyzer (SWO/Haake). The samples were previously removed from the test tubes and placed into the measurement cylinder, sealing it with PTFE sealings The instrument covers a temperature and pressure range from 25 to 400 °C and 200–2500 bar, respectively, with 1 bar data being extrapolated from pressure data. Isobaric experiments were carried out from 200 to 800 bar with 200 bar steps. Specific volume measurements were recorded from RT until about 260 °C, with a heating rate of 5 °C/min.

2.3. PALS measurements

A fast-fast timing coincidence system was used as lifetime spectrometer for the PALS measurements. A time resolution (FWHM) of 255 ps was obtained using the code RESOLUTION [21]. Positron lifetime spectra were recorded at RT with a counting rate about 100 cps and a total number of $2-3 \times 10^6$ coincidence counts using a 20 µCi source of ²²Na deposited on a Kapton foil (7.5 µm thick). The source was placed between two identical square-shaped samples of 3 mm thick and 20 mm side obtained from the same sheets used for PVT analysis.

According to the common interpretation for PALS measurements in polymers [22], PALS spectra were deconvoluted into three lifetime components using the LT program [23], with an adequate source correction. From the analysis, two discrete lifetimes and a continuous one corresponding to the long-lived component were obtained. This longest lifetime gives the o-Ps lifetime component represented by the continuous distribution $\xi(1/\tau_3)$. Positron lifetime spectra were also analysed using the POSITRONFIT program [21] giving three discrete lifetime components (τ_1 , τ_2 and τ_3 , respectively). The results obtained showed a very good agreement with those obtained from the decomposition of the PALS spectra using the LT program. As mentioned above, in the last series of decompositions a discrete lifetime component for the *o*-Ps component (τ_3) was considered.

The mean size of the holes forming the free volume can be roughly estimated by means of a simple quantum mechanical model [24–26]. *o*-Ps in a hole is approximated to a particle in a spherical potential well with radius R_0 . It is assumed that an electronic layer forming a thickness δR is present on the walls of the hole, whose effective radius

 Table 1

 Cure schedules of the epoxy resin and molecular structures of the different aminic hardeners

Hardener	Cure schedule	Molecular structure
DDS	135 °C 6 h/200 °C 1 h	H ₂ N 0 0 0
DDM	110 °C 90 min/200 °C 2 h	H ₂ N NH ₂
3DCM	50 °C 4 h/190 °C 4 h	H ₂ N CH ₃ CH ₃ NH ₂
DETDA80	140 °C 200 min/200 °C 2 h	$H_{3}C$ $H_{3}C$ $H_{2}C$ $H_{3}C$ $H_{2}C$ $H_{3}C$ CH_{3} C
MDEA	140 °C 200 min/200 °C 2 h	H ₃ C H ₂ N H ₃ C H ₃ C CH ₃ CH ₃
MMIPA	140 °C 260 min/200 °C 2 h	H_3C CH_3 H_3C CH_3 H_2N H_3C CH_3 H_3C CH_3
MDIPA	140 °C 260 min/200 °C 2 h	H_3C CH_3 H_3C CH_3 H_2N NH_2 H_3C CH_3 H_3C CH_3

is consequently reduced to $R = R_0 - \delta R$. As a consequence, the following semi-empirical equation relating R (nm) and τ_3 (ns) is usually used:

$$\tau_3 = 0.5 \left[1 - \frac{R}{R + \delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \delta R}\right) \right]^{-1} \tag{1}$$

According with the literature [22], the value 0.166 nm for δR was used.

The continuous distribution of inverse lifetime $\xi(1/\tau_3)$ can be obtained by analysing the PALS spectra and is related to the radius distribution f(R) by means of [24,25]:

$$f(R) = 2\delta R \left[\cos \frac{2\pi R}{R + \delta R} - 1 \right] \frac{\xi(1/\tau_3)}{(R + \delta R)^2}$$
(2)

Then, it is easy to obtain the free volume distribution [25], $g(v_h)$, as $g(v_h)=f(R)/4\pi R^2$. Thus, the centroid of the log-

normal free volume distributions $g(v_h)$ and the dispersion $\sigma(v_h)$ can also be obtained. On the other hand, the fraction of positrons annihilating in cavities with volumes between v_h and $v_h + dv_h$ is $g(v_h)dv_h$ [24,25].

3. Results and discussion

From PALS measurements, the size distribution of the free volumes inside the epoxy samples cured with the different hardeners (see details in Table 1) is shown in Fig. 1. As can be observed, for all samples the distributions only have one peak which is extended from about 20 Å³ till 200 Å³. The cavity size v_h and the distribution width, $\sigma(v_h)$, were obtained from these data (see Table 2).

It is worth to note that the value of v_h increases as hardener chemical structure grows in complexity (see



Fig. 1. Free-volume distribution $g(v_h)$ for the different samples studied.

Table 1) and that such a complexity could hinder good packaging of the molecular structures. These results are in good agreement with other literature reports [5,6,25–28], where is mentioned that changes in the topology of the molecular network (considered as the spatial configuration or geometric characteristic of the molecular segments in the network) are associated to modifications in the free volume content. It should be also noticed that the v_h values for DDS and DDM are comparable and reflect the close similarity in

Table 2 The cavity size, distribution width and specific volume for the different analyzed aminic hardeners

their molecular structures. Jefrey and Pethrick [5] have studied the free volume for DGEBA/DDM and DGEBA/ DDS systems by PALS, reporting similar values to those presented in this work. These authors explained the small decrement in the value of v_h for the DDS respect to the DDM as due to strong intermolecular interactions generated for the polar sulphone group leading to a more closely packed structure with a smaller free volume.

Table 2 also shows an increase in the $\sigma(v_h)$ values with the increase in chemical structure complexity of the aminic hardeners. An explanation for this behavior can be intended considering that the number of bonds of the hardener is related with the number of configurations that it can take and, this last one with the dispersion in the topology of the molecular network. That means, that an increase in the number of bonds of the hardener will be reflected in an increase in the $\sigma(v_h)$ value. The trends above described can be visualized in Fig. 2, where v_h and $\sigma(v_h)$ values are plotted as a function of hardener complexity in arbitrary units.

From PVT measurements on chemically identical samples to those employed in PALS studies, the curves of specific volume V as a function of temperature T in the range between 25 and 270 °C and for different pressure values were obtained. As an example, the curves V vs. T obtained to a pressure of 1 bar (atmospheric pressure) are shown in Fig. 3. From these curves, the specific volume values at

•		•		
Hardener	$v_{\rm h}({\rm \AA}^3)$	$\sigma(v_{\rm h})$ (Å ³)	$V_{1\text{bar}}$ (cm ³ /g)	V _{800bar} (cm ³ /g)
DDS	47.5±1.3	27.9 ± 0.6	0.8242	0.8041
DDM	54.3 ± 1.4	26.2 ± 0.5	0.8649	0.8448
3DCM	59.7 ± 1.0	30.4 ± 0.4	0.9133	0.8821
DETDA80	62.4 ± 1.1	32.4 ± 0.4	0.8872	0.8621
MDEA	63.4 ± 1.4	33.0 ± 0.6	0.9190	0.8814
MMIPA	71.7 ± 1.0	32.2 ± 0.4	0.9296	0.8918
MDIPA	78.3 ± 1.0	39.5 ± 0.4	0.9576	0.9166



Fig. 2. The centroid of the cavity size distribution and the distribution width $\sigma(v_h)$ as a function of the hardener complexity.



Fig. 3. Temperature dependence of the specific volume at atmospheric pressure for all systems DGEBA-aminic hardeners analyzed.

room temperature and at a given pressure can be obtained. In Table 2, the V values for two extreme pressures (1 and 800 bar) and for the different hardeners used have also been included. To compare PVT and PALS behaviors, these data and the v_h values of Fig. 2 are plotted together in Fig. 4. An excellent similarity can be observed, thus reflecting the closeness between macroscopic behavior and molecular packing of polymeric chains in the thermoset network.

Schmidt and Maurer [29] have reported for PMMA an excellent correlation between the free volume derived from PVT measurements and the size of free volume cavities measured by PALS. In a recent work on PVC with 10 and 30 wt% of di-n-butyl phthalate as plasticizer, Dlubek et al. [10] showed that an estimate of the number of holes per mass unit can be obtained if the specific volume is related with v_h as

$$V = V_{\rm occ} + V_{\rm fo} + N_{\rm h} v_{\rm h} \tag{3}$$

where V_{occ} is the specific occupied volume, N_{h} is the number density of holes per mass unit, and V_{fo} takes into account a possible deviation of the average hole volume estimated from the *o*-Ps lifetime τ_3 . In this work, it has been assumed that $V_{\rm fo} \ll V_{\rm occ}$

It is well-known the relationship between V_{occ} and the scaling volume V^* [31–33]:

$$V_{\rm occ} = 0.95V * \tag{4}$$

To obtain V^* we have used the Simha–Somcynsky equation of state for polymers [30–32] at atmospheric pressure, which can be approximated by the following universal scaling relationship for $T > T_g$:

$$\ln\frac{V}{V^*} = A + B\left(\frac{T}{T^*}\right)^{3/2} \tag{5}$$

where A = -0.1033 and B = 23.835 are universal constants; V^* and T^* are scaling parameters, dependent on the specific structure of polymer. V^* was obtained by fitting the specific volume data above the glass transition temperature T_g , given in Fig. 3.

In Fig. 5, the solid lines represent a linear fitting of the experimental V-T data by using Eq. (5). As a result, a very good fit was obtained. Furthermore, the scaling parameter T^* can be obtained from the slope of the straight lines:

$$T* = \left(\frac{B}{\text{slope}}\right)^{2/3} \tag{6}$$

and V^* from the ordinate:

$$V* = \exp(\operatorname{ordinate} - A) \tag{7}$$

In Table 3, the values of T^* , V^* , V_{occ} and $V_{free(1bar)} = V_{1bar} - V_{occ}$ are shown.

In Fig. 6, the experimental values of $V_{\text{free(1bar)}}$ are plotted against v_{h} for the systems investigated. Given that all epoxyamine systems were fully cured the number density of holes per mass unit should be the same for all of them. As it can be seen, a linear relationship seems to exist between both parameters. The solid line represents the fit of the data by using Eq. (3). From the fitting results, within the error bars,





Fig. 5. Fitting of the experimental V-T data using Eq. (5).



 $N_{\rm h} = (1.3 \pm 0.2) \times 10^{21} {\rm g}^{-1}$

For comparative purposes, it should be mentioned that there are several works in the literature where the number density of holes is calculated for different thermoplastic systems [10,34,35]. In these works, values of $N_{\rm h}$ between $0.3 \times 10^{21} \text{ g}^{-1}$ and $0.8 \times 10^{21} \text{ g}^{-1}$ were reported. On the other hand, similar available information in thermoset polymers is very scarce. Yang et al. [36] reported that in DGEBA–DDM the value of $N_{\rm h}$ should be higher than 10^{20} g^{-1} but they did not give a specific value for the number density of holes.

When analyzing the obtained value of N_h , it is worth to note that in these fully cured epoxy-amine systems the number density of holes approximately duplicates that obtained for thermoplastics. Following the study of Dlubek et al. [37], who showed that for poly(diethylene glycol bis(allyl carbonate)) crosslinked at different extents N_h was a function of the concentration of the comonomer, the higher N_h observed with respect to that existing in thermoplastics should be a consequence of the different crosslinking extent of both types of systems.

The results presented in this work give new experimental evidence of the relationship among the specific volume and the free-volume cavity size measured by PALS as was reported by Schmidt and Maurer [9,29] and, more recently, by Dlubek et al. [10]. Besides, this work clearly shows that



Fig. 6. Correlation between the free volume obtained from PVT and the cavity size obtained from PALS.

the specific volume and the size of the free volume cavity in epoxy-amine systems is a function of the chemical structure complexity of the aminic hardeners.

4. Conclusions

An investigation on the correlation between volumes measured at macro and nanoscales has been carried out in epoxy systems fully cured with aminic hardeners having different chemical structures. The results give the first evidence of the direct relation existing between macro and nanoscales in thermosetting networks. The variation in the local free volume cavity sizes has been investigated using PALS. Macroscopic specific volume changes have been analyzed by PVT measurements. The average size of the holes forming the free volume was estimated to be between 47.5 and 78.3 $Å^3$ depending on the chemical structure of the hardener. An excellent correlation between both volume scales was found, which supports the view that molecular structure of hardener is the responsible for packing of molecular chains constitutive of the epoxy network. It is worth to note that for the epoxy networks investigated, all of them fully cured with diaminic hardeners, the number density of holes was the same within the experimental error. These observations outline by the first time the fact that the

Table 3

Scaling parameters, occupied volume and free volume obtained from the PVT measurements

Hardener	Ordinate	Slope	V^* (cm ³ /g)	$T^{*}(\mathbf{K})$	$V_{\rm occ}~({\rm cm}^3/{\rm g})$	$V_{\rm free(1bar)} ({\rm cm}^3/{\rm g})$		
DDS	-0.324	2.06×10^{-5}	0.802	11,042	0.762	0.062		
DDM	-0.272	2.03×10^{-5}	0.845	11,134	0.803	0.062		
3DCM	-0.223	2.04×10^{-5}	0.887	11,098	0.843	0.071		
DETDA80	-0.256	2.13×10^{-5}	0.858	10,800	0.815	0.072		
MDEA	-0.221	2.12×10^{-5}	0.889	10,804	0.845	0.075		
MMIPA	-0.225	2.18×10^{-5}	0.886	10,626	0.842	0.088		
MDIPA	-0.208	2.31×10^{-5}	0.901	10,231	0.856	0.102		

variation of the specific volume is completely controlled by the variation of the average size of subnanometer-size local free volumes, which are fixed by the chemical structure of hardener in fully crosslinked epoxy networks.

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