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Nanohole volume dependence on the cure schedule in epoxy thermosetting networks: A PALS study

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Abstract

A systematic study on the dependence of the volumes at nanoscale in epoxy systems cured with two selected aminic hardeners at different pre-cure temperatures is presented. Nanohole volumes were measured by positron annihilation lifetime spectroscopy. Additional information regarding the structure of the thermosets was obtained using dynamic mechanical analysis. Volume results obtained are discussed in terms of the cure schedule applied to the epoxy systems, their characteristic glass transition temperatures and their crosslink density. The pre-cure temperature and the structure of the hardeners govern the packing of the molecular chains of the epoxy network. Using together positron and mechanical experimental techniques allows to conclude that a strong change in the volume and number density of the nanoholes takes place when the pre-cure temperature crosses the glass transition temperature of the systems.

Keywords: Epoxy; Hardener; Cure schedule

1. Introduction

Epoxy resins are widely used in industrial applications ranging from high performance aerospace composites to encapsulants for microelectronics, as a consequence of high thermal resistance, high tensile strength and modulus and good chemical resistance. The most important factors influencing their performance are molecular architecture, ratio between epoxide and hardener, and curing conditions, as described by several authors [1–3]. As a matter of fact, by choosing monomers with an appropriate molecular structure the rigidity of epoxy networks can be controlled, while stoichiometry and curing conditions predominantly affect crosslinking density, free volume but also mechanical properties.

Some investigations about the influence of the chemical structure and curing conditions on the local free volume in epoxy systems were developed by different authors [4–7]. Nevertheless, relatively scarce publications on the relation between the macro- and nanoscale volume variations and chemical structure of thermosetting networks exist [8–10].

The dimensions of the free-volume holes are uniquely determined from positron annihilation lifetime spectroscopy (PALS). In molecular solids and liquids, a fraction of the positrons injected from a radioactive source form positronium (Ps), which can annihilates from the *para*-positronium (*p*-Ps), singlet spin state, or from the *ortho*-positronium (*o*-Ps), triplet spin state, with a relative formation probability of 1:3 [11–13]. Usually, three components appear in the lifetime spectra of amorphous polymers, these are attributed to the annihilation of *p*-Ps, free positrons (not Ps), and *o*-Ps. *p*-Ps decays mainly via self-annihilation with a lifetime in vacuum of about 125 ps. The lifetime of *o*-Ps (142 ns in vacuum) decreases in matter, typically to the low nanosecond range due to the pick-off annihilation process. In such a case, it is possible that the positron of the *o*-Ps state can annihilate with an electron other than its bound partner (and opposite spin). Typically, if *o*-Ps is

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confined to the free-volume holes in amorphous polymers, its lifetime is reduced to the 0.5–5 ns range. Besides, the characteristic lifetime of the pick-off annihilation process is highly sensitive to the size of these free-volume holes, for more details see [14–16]. PALS measurements have demonstrated their usefulness for studying the size of the free-volume holes of polymer glasses as a function of the temperature [17] and also for characterizing the microscopic mechanical state [18–22].

This paper focuses to the study of how changes on the sizes of free-volume affect the properties of epoxy systems at the macro and nanoscales in epoxy systems cured with selected aminic hardeners at different pre-cure temperatures. As after curing, the low reactivity amines (4,4′-methylene bis-(chloro 2,6-diethylaniline), MCDEA and 4,4′-methylene bis-(2,6-diethylaniline), MDEA) chosen in this study conduct to epoxy systems with high thermal properties, they can compete with the more toxic aromatic amines, widely used in many applications.

Post-cure at 200 °C was carried out in order to be sure that the highest glass transition temperature, T_g, was achieved for each epoxy system. In addition to lower reaction rate, the presence of chloride atom in the chemical structure of MCDEA can lead to different nanoscale behaviour, with respect to MDEA-cured system.

A detailed analysis on the effect of the pre-cure temperatures allowed to gain further information regarding the results published.

2. Experimental

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, a 4,4′-methylene bis-(3-chloro 2,6-diethylaniline) (MCDEA) and 4,4′-methylene bis-(2,6-diethylaniline) (MDEA) were used.

For both systems, the stoichiometric amount of diamine was added to the liquid epoxy monomer at 100 °C. The mixture was then vigorously stirred for 10 min, leading to a homogeneous solution. The corresponding blend was poured into two treated glass plates, which were separated by a stainless steel spacer and clamped with several c-clamps. 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 to remove the trapped air. The curing treatment followed consisted of: pre-cure at 130, 150, 170 and 190 °C during a time chosen; then post-cure at 200 °C during 2 h for all systems, and finally the samples were slowly cooled to room temperature (RT) and then separated from the glass. In Table 1, the molecular structures of both aminic hardeners as well as the cure schedule used are shown.

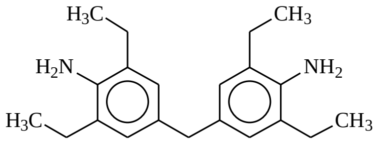
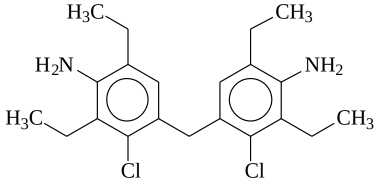
Dynamic mechanical analysis (DMA) was carried out on the thermoset networks with a Perkin–Elmer DMA7 in order to obtain three point bending dynamic mechanical spectra (storage modulus E' and loss factor $\tan \delta$) between 30 and 270 °C, with a heating rate of 5 °C/min and at a frequency of 1 Hz. The samples used were parallelepipeic bars ($2\times15\times3$ mm^3).

PALS measurements were made using a fast-fast timing coincidence system lifetime. A time resolution (FWHM) of 255 ps was obtained using the code RESOLUTION [23]. Positron lifetime spectra were recorded at RT with a counting rate about 100 cps and a total number of $2–3\times10^6$ coincidence counts using a 20 μCi source of ^{22}Na deposited on a Kapton foil (7.5 μm thick). The source was placed between two identical 20 mm square-shaped and 3 mm thick samples obtained from the sheets prepared. The spectra obtained were deconvoluted using the POSITRONFIT code [23], the best fit was obtained with three discrete lifetime components (τ_1, τ_2 and τ_3, respectively). The results obtained are in very good agreement with those resulting from the spectra decomposition by means of the LT program [24] giving three discrete lifetime components.

Following the common interpretation for PALS measurements in polymers, the long-lifetime component (τ_3) is associated with *ortho*-positronium annihilation by pick-off process. From that, the mean size of the holes forming the free volume can be roughly estimated by means of the Tao-Eldrup model [25,26]. In such a model, *o*-Ps in a hole is approximated to a particle in a spherical potential well with radius R_{h0}. It is assumed that an electronic layer forming a thickness δR_h is

Table 1

Cure schedules of the epoxy systems and molecular structures of the two aminic hardeners used

Hardener	Cure schedule[a] T (°C)/t (min)	Chemical structure
MDEA	130/330 150/180 170/120 190/75	
MCDEA	130/330 150/180 170/120 190/75	

[a] Each system has been post-cured at 200 °C for 2 h.

present on the walls of the hole, whose effective radius is consequently reduced to $R_h = R_{h0} - \delta R_h$. As a consequence, the following semi-empirical equation relating R_h (nm) and τ_h (ns) is commonly used:

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

According to Ref. [26], the value 0.166 nm for δR_h was used. As was discussed in detail in a previous paper [27], the values of the radii obtained from Eq. (1) should be interpreted only as a rough estimation, since real holes are irregularly shaped (see also Ref. [16]).

3. Results and discussion

In Fig. 1 mechanic dynamical properties, i.e. the storage modulus E' and loss tangent tan δ, as a function of the temperature are plotted for both aminic hardeners MDEA and MCDEA. In this figure, it is only shown the evolution for the lower and higher pre-cure temperatures used. The behavior of both E' and tan δ versus T is representative of the curves obtained for the intermediate pre-cure temperatures. From each curve, the glass transition temperature T_g and the average molecular weight between crosslinks $\bar{M}_c$ were obtained. The T_g, was determined from the maximum of the peak corresponding to the loss tangent curve. On the other hand, $\bar{M}_c$ values were obtained from the storage modulus evaluated at $T_g + 50$ K using the following equation [28]

$$\bar{M}_c = \frac{\rho RT}{G'} = (2.84)\frac{\rho RT}{E'} \quad (2)$$

where ρ is the density of each system, R is the ideal gas constant [8.314 J/(mol K)], $T = T_g + 50$ K is the temperature in degrees Kelvin and G' is the storage shear modulus. The 2.84 pre-factor was obtained considering that $G' = E'/2(1+\nu)$ with a Poisson ratio equal to 0.42 [29,30].

In Fig. 2, for each thermoset network the dependence of T_g and $\bar{M}_c$ on the difference between the pre-cure (T_{pre}) and the glass transition temperatures (T_{pre}–T_g) is presented. As can be seen, for both thermoset networks the glass transition temperatures are above the pre-cure temperatures 130 and 150 °C. However, in DGEBA/MDEA samples the other two pre-cure temperatures applied (170 and 190 °C) are higher than T_g, while in the DGEBA/MCDEA systems one of the two highest (170 °C) is close to T_g and that of 190 °C is about 20 °C higher than the transition temperature. The dynamic mechanical results for both hardeners show that, within the experimental scatter, both parameters T_g and $\bar{M}_c$ are almost constant in the whole pre-cure temperatures. Nevertheless, there is a downward tendency of T_g upon T_{pre}–T_g, whilst $\bar{M}_c$ slightly increases. This behaviour is possibly related with small variations in networking features induced by the different cure rates linked to each pre-cure temperature used for each system.

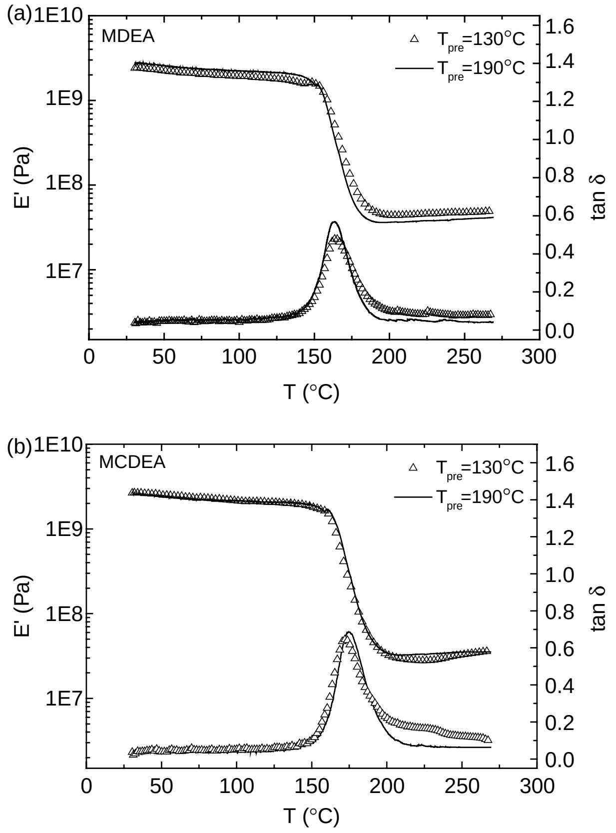


Fig. 1. Dynamic mechanical behavior (storage modulus and tan δ) as a function of temperature. The curves shown correspond to samples pre-cured at 130 and 190 °C with: (a) MDEA and (b) MCDEA.

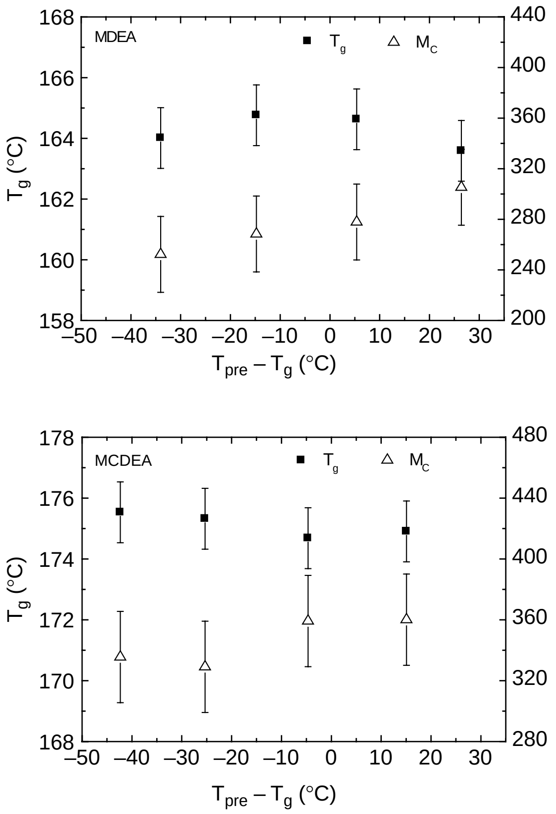


Fig. 2. Dependence of T_g and $\bar{M}_c$ on T_{pre}–T_g, for (a) DGEBA/MDEA and (b) DGEBA/MCDEA thermoset networks.

Taking into account the conversion evolution for both hardeners reported by Eloundou et al. [31] and the pre-cure times employed at each pre-cure temperature, the difference between the two hardeners for pre-cure temperatures lower than T_g could be attributed to the presence of Cl in the MCDEA chemical structure, which leads to a decrease in the reactivity rate and a high difference in the conversion degree obtained at each pre-cure temperature.

In Fig. 3, the evolution of the nanohole volumes v_h obtained for MCDEA and MDEA hardeners is plotted as a function of $T_{pre}–T_g$. Depending on the amine hardener, the results obtained show different behaviors of v_h versus T_{pre}. For MDEA, an almost constant v_h, within the error bars, is seen in the range of T_{pre} lower than T_g. For $T_{pre} \sim T_g$ a decrease of the nanohole volume is observed. Finally, v_h stays at this minimum absolute value reaching a plateau when $T_{pre} \geq T_g$. For MCDEA at pre-cure temperatures near or higher than T_g the behavior of v_h is almost the same to that described for the MDEA hardener. However, in the region in which T_{pre} is lower than T_g (130 and 150 °C) a clear increment of v_h is observed.

At this point, it is worth mentioning that in a previous work we reported v_h data for the system DGEBA/MDEA cured at 140 °C 200 min/200 °C 2 h obtained from the distributed lifetime curve (LT analysis) [10]. Considering the well-known relationship $\langle\tau_h\rangle = \tau_h \exp(\sigma_h^2/2)$ [24,32], which allows to directly link the characteristic parameters of the distributed (τ_h and σ_h) and discrete ($\langle\tau_h\rangle$) long-lifetime component, the value previously obtained (indicated in Fig. 3 as ○) is in good agreement with the ones plotted in this figure. Moreover, as a part of a more general study the system DGEBA/MCDEA was specifically cured at 200 °C for 4 h (200 °C 2 h/200 °C 2 h). Using LT analysis, the value obtained for v_h was 67.6 Å^3 (indicated in Fig. 3 as ▲). This additional experimental data point allowed us to confirm that pre-cure at temperatures above T_g leads to a plateau in the variation of hole volume with the pre-cure temperature.

Micro-scale free volume modifications caused by the pre-cure temperature and measurable by PVT technique could be masked by the experimental scatter, as shown in Fig. 4. Details of the PVT measurements are given in Goyanes et al. [10].

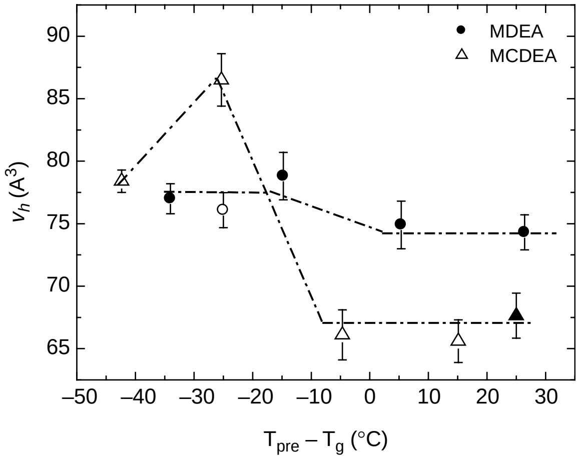


Fig. 3. v_h as a function of the difference between pre-cure and glass transition temperatures for systems cured with both hardeners used. Lines are only eye guides.

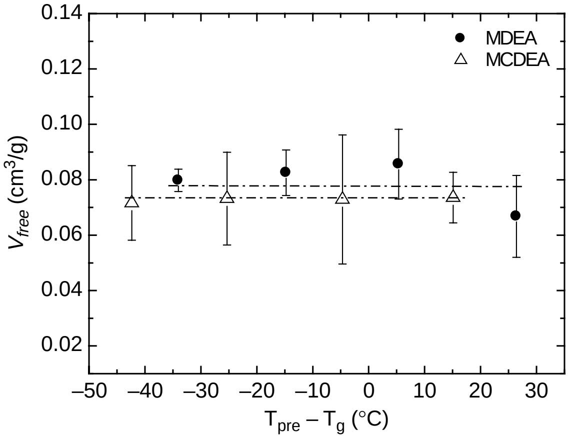


Fig. 4. Free volumes obtained from PVT curves versus pre-cure temperatures for (a) DGEBA/MDEA and (b) DGEBA/MCDEA thermoset networks. Lines are only eye guides.

As deduced from Fig. 3, though we have previously shown [10] that the chemical structure of hardener does affect both specific volume and the average size of subnanometer-size local free volumes, more work has to be done for knowing the relationships between specific volume changes and nanovolume variations. For an epoxy resin cured with the same hardener at different pre-cure temperatures, factors such as microstructural variations due to thermal annealing during post-curing could also have a contribution on the free volume variations at microscale. The different variations of free volume and nanovolume upon $T_{pre}–T_g$, above all for the mixture cured with MCDEA, outline the need for using similar temperature differences when nanovolume variations on thermosetting systems have to be investigated.

Various approaches were used to get the fractional free volumes from positron data. However, care needs to be taken when using different approximations to determine changes in the fractional free volumes (see more details in Refs. [16,27]). Following Dlubek et al. [9], the free volume V_{free} is related to the cavity size v_h by the equation

$$V_{free} = N_h v_h \tag{3}$$

where N_h is the number density of holes per mass unit.

From Fig. 3, the decrease in v_h and the relatively constant values of the free volume mean that pre-cure temperatures above the T_g lead to a significant increase in the number density of holes per mass unit.

In view of the results obtained and to explain the hole size dependence on the pre-cure temperature, some considerations have to be taken into account. Firstly, when pre-cure takes place at temperatures above T_g, the high reaction rate, because of the high temperature, leads to the formation of shorter chains and consequently to a high crosslink density reaching high conversion values. Therefore, through post-curing, there are no significant changes in the three-dimensional network owing to the low mobility of crosslinked chains. This fact leads to a high density number of holes with a significant reduction in the hole sizes confirming the strong decrease observed in v_h when pre-cure temperature is carried out through the T_g. Secondly, when the pre-cure temperature is 130 °C, the conversion reached is low enough to avoid gelation, which leads to the formation of relatively large linear chains. Thus, during post-cure treatment the mobility of those large chains and the reaction rate are high, leading to the formation of small hole sizes but greater than the ones pre-cured above T_g due to the initial chain length. On the other hand, when the pre-cure temperature selected is 150 °C, the hole volume size increase could be attributed to the existence of a higher crosslink density and of a greater number of dangling chains between crosslink points than in the case of the pre-cure at 130 °C.

The behavior of the parameters studied for the system DGEBA/MCDEA described above for the range of pre-cure temperature between 130 and 150 °C was not observed, within the error bars, for the MDEA hardener. This fact could be assigned to a greater reaction rate for this hardener than for MCDEA, thus, taking into account the pre-cure times employed (Table 1) the conversion reached for 150 and 130 °C was very similar for this system [31]. It is worth noting that the hole volume values at pre-cure temperatures above T_g, where both systems should have maximum crosslinking after post-curing, are slightly lower for the MCDEA. This difference could be attributed to the presence of the additional Cl in the structure of MCDEA (Table 1) inside the holes between crosslink points.

4. Conclusions

The experimental results presented in this work show the effect of the pre-cure cycle applied to two epoxy-amine systems on the nanosize holes measured by positron annihilation lifetime spectroscopy. In addition, values of the glass transition temperature and the molecular weight between crosslinks were obtained by dynamic-mechanical analysis. Both techniques were used to improve the knowledge on the thermoset structures. The pre-cure temperature and the structure of the hardeners are responsible for the molecular chains packing of the epoxy network, concluding that a strong change in the volume and number density of the nanoholes takes place around the glass transition temperature for both systems.

The results reported also allow to gain information about the conditions in which the hole volume results, measured by PALS, must be compared to the free volume dependent mechanical properties in different thermoset systems, i.e. the comparison must be done in thermosets pre-cured in the same conditions respect to each system T_g due to the fact that a strong modification in the hole number occurs at pre-cure temperatures close to T_g and therefore, a discontinuity in the proportionality factor between hole volume and free volume is produced.

The different variations of the free volume and the nanovolume upon T_{pre}–T_g, above all for the mixture cured with MCDEA, outline the need for using similar temperature differences when nanovolume variations on thermosetting systems have to be investigated.

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