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Changes of the hole volume in model epoxy networks

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Positron annihilation lifetime spectroscopy measurements were conducted on a series of epoxy specimens, prepared by systematically varying the network rigidity and crosslink density. The investigations demonstrate that changes in the molecular structure of the constituent monomers change the microscopic parameters of the epoxy networks. An increase of chain rigidity increases the size and the number density of the trapping sites where orthopositronium localizes, which leads to an increase of the hole volume fraction at T_g. It was found that the hole volume fraction at T_g approximates a linear relationship with the packing densities of the epoxies under investigation. The results are interpreted as a decrease of the efficiency of molecular packing with increasing network rigidity. As a result, macroscopic materials properties such as glass transition temperature, density and thermal expansion show considerable variations.

(Keywords: epoxy networks; p.a.l.s. measurements; microscopic parameters)

INTRODUCTION

Epoxy resins are used in a wide range of applications because their properties, e.g. thermal stability, mechanical response, density, adhesion, electrical resistance and others, can be varied considerably. It is well known[1,2] that the most important factors influencing their performance are the molecular architecture, the ratio of the epoxide and the curing agent(s), and the curing conditions; and in the case of composite materials it is necessary to account for the properties of the additional phases. By choosing monomers with appropriate molecular structure it is possible to control the rigidity of the epoxy networks, while the stoichiometry and the curing conditions will predominantly affect the crosslink density.

The roles of molecular architecture and the network parameters have been studied extensively[1–4], but there are still unanswered questions, because it is difficult to evaluate separately the effect of the rigidity of the network, on the one hand, and the influence of the crosslink density, on the other. Furthermore the molecular architecture itself might affect the crosslinking kinetics. Recent investigations demonstrate that some degree of partitioning is possible by using specially 'designed' epoxies with systematic variation of the network rigidity while keeping the crosslink density constant and vice versa[5,6]. The results from dynamic mechanical testing, over wide ranges of frequencies and temperatures, show that the rigidity and the crosslink density change considerably the thermal and viscoelastic properties of the materials[5,6]. The goal of the present work is to expand the scope of the studies and obtain microscopic information with regard to the molecular arrangements in these networks. To achieve this goal, macroscopic measurements of the densities, thermal expansion and calorimetry are combined with microscopic results obtained from positron annihilation lifetime spectroscopy (p.a.l.s.).

In the last two decades the p.a.l.s. method has become a more and more powerful tool for studying the molecular structure of polymeric materials in general[7,8], and epoxy resins in particular[9,10]. The method utilizes the interactions between the positrons (emitted, usually, from a radioactive material) and the electrons from the host material. It is established[7,8,11] that upon entering the polymer the positron can form bound states (positronium) with electrons from the medium. Depending on the spin configuration the positronium can be in a singlet (para-) or triplet (ortho-) state. It has been found that the lifetimes and relative intensities of the positron itself and the parapositronium (p-Ps) are not directly related to the materials characteristics, while the lifetime (τ_3) and relative intensity (I_3) of the orthopositronium (o-Ps) are influenced by the structure of the host material. The lifetimes of the p-Ps and e^+ (0.125 ns and 0.5–0.6 ns respectively) are much shorter than the intrinsic (vacuum) lifetime of o-Ps ($\sim$ 142 ns). In polymeric solids the o-Ps localizes in regions with lower electron densities or 'holes', picks off another electron

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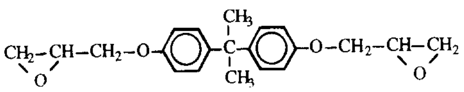
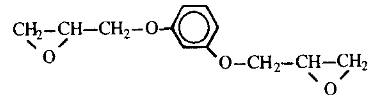
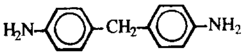
Table 1 Epoxide structures and glass transition temperatures

Constituent[a]	Structure	Epoxy	T_g (°C)
Backbone			
DGEBA		E1a DGEBA-DDM	181
		E2a DGERO-DDM	135
		E1b DGEBA-HMDA	119
DGERO		E2b DGERO-HMDA	78
		E1c DGEBA-HMDA-HA	68
		E2c DGERO-HMDA-HA	42
Amine			
DDM			
HMDA	$H_2N{-}(CH_2)_6{-}NH_2$		

[a] DGEBA, diglycidyl ether of bisphenol A; DGERO, diglycidyl ether of resorcinol; DDM, 4,4′-diaminodiphenylmethane; HMDA, hexamethylenediamine; HA, hexylamine

from the surroundings and annihilates. As a result of the 'pick-off' annihilation, the lifetimes decrease considerably, and for most amorphous polymers are in the range 1.5–3 ns. The values of τ_3 can be correlated with the radius of the 'holes' where o-Ps is entrapped via a semiempirical relationship, while I_3 is generally considered proportional to the number density of microvoids in the material[12].

EXPERIMENTAL

Materials

The epoxies used in the present research are based on the diglycidyl ether of bisphenol A (DGEBA) or diglycidyl ether of resorcinol (DGERO), purchased from Bakelit Co. and Lancaster Inc., respectively. From the epoxide structures shown in *Table 1*, it is apparent that a polymer chain composed of DGERO repeat units will be more flexible than a DGEBA counterpart. Primary diamines (DDM and HMDA—*Table 1*) in stoichiometric proportions were used as curing agents to produce densely crosslinked networks. Similarly to the epoxide chains the two curing agents have different flexibilities, with the DDM being the most rigid. The crosslink densities were modified by using stoichiometric mixtures of primary diamines and homologous primary monoamines (HMDA-HA) without significant changes of the chain flexibilities. Details on the synthesis and the curing regimes are supported in refs 5 and 6. Thus by varying the molecular characteristics one can obtain a representative set of epoxy networks with systematic variation of the 'main' and 'side' chain rigidities and crosslink densities. Note that, while some recent evidence from n.m.r. suggests that not all the secondary amines are reacted[26], our goal of systematically varying the network parameters has been achieved, as evidenced by the systematic changes in the glass transition temperatures. This conclusion is supported, also, by the p.a.l.s. measurements reported in the present paper.

Macroscopic measurements

The thermal expansion of the specimens was measured by using a TA Instruments thermomechanical analyser (t.m.a.) in a temperature interval from −80 to +225°C. This temperature range covers the glass transition regions of all six epoxy networks (*Table 1*). Before the measurements the specimens were heated above the glass transition, in order to erase the previous thermal histories, and then cooled rapidly to −80°C. The data were recorded after equilibration at each temperature step.

The glass transition temperatures were determined by using a Perkin Elmer DSC instrument at a heating rate of $20^\circ C\,min^{-1}$. The d.s.c. response was measured also by a TA 2200 instrument equipped with a modulator 2920, which allows a periodic modulation ($\pm 1^\circ C\,min^{-1}$) of the heating rate ($5^\circ C\,min^{-1}$). The signal from the oscillating heating rate can be separated into reversible and irreversible (due to structural relaxation) components of the heat capacity. The densities of the materials at 23°C were obtained by using a gradient density column, filled with dichloromethane (density $1.325\,g\,cm^{-3}$) and 1,2-dichloropropane (density $1.155\,g\,cm^{-3}$). The error of the density measurements was less than $5 \times 10^{-4}\,g\,cm^{-3}$. The amount of liquid medium absorbed by the epoxy was negligible as determined from weight-gain measurements.

Positron annihilation lifetime spectroscopy measurements

The p.a.l.s. spectra from the epoxies were collected in the temperature interval 22–200°C. The temperature change was provided by a small heating tape wrapped around the specimens; the temperature was maintained stable to ±0.5°C by a temperature controller. All measurements were done in air. Before the data collection the specimens were 'refreshed' similarly to the specimens used for volumetric measurements. A $25\,\mu Ci$ ^{22}Na sample deposited on an aluminium vessel was used as a positron source. As a result the intensity of the o-Ps component is approximately half of that determined with the source sandwiched between two samples.

Table 2 Properties of epoxies

Epoxy	Density ($g cm^{-3}$)	τ_3 (ns)	R (Å)	I_3 (%)	F_h (%)	V_h (rel. un.)	Linear α ($\times 10^{-5}$) $T_{exp} > T_g$	$T_{exp} < T_g$
E1a	1.195	2.20	3.03	13.44	5.5	17.0	16.7	6.4
E2a	1.269	1.74	2.60	12.36	3.9	9.0	17.3	5.8
E1b	1.163	2.06	2.91	12.51	4.8	13.0	17.92	7.43
E2b	1.237	1.58	2.43	10.21	3.0	6.3	20.48	5.46
E1c	1.141	1.97	2.83	12.27	4.3	12.5	20.10	6.7
E2c	1.183	1.86	2.72	11.01	3.9	8.8	22.25	6.42

The positron lifetime spectra were obtained by a conventional fast-timing coincidence method. The data were collected and stored in a Micro VAX (Digital model 3100) based multichannel analyser. The three lifetimes and relative intensities, together with the time resolution, were determined by a FORTRAN program PFPOSFIT[13]. The full width at half-maximum of the time resolution prompt curve was 300 ps as determined by a ^{60}Co source. The first (τ_1) and second (τ_2) components, which can be associated with p-Ps and bulk positron annihilation respectively, were found to be unaffected by the temperature change, and thus will not be considered further. The long-lived third (τ_3) component, which is associated with the annihilation of o-Ps trapped in the 'holes', was sensitive to the structural changes induced by the temperature increase. A collection time of 2 h per spectrum was sufficient to ensure statistical error in determining τ_3 and I_3 to no more than $\Delta(\tau_3) = \pm 0.008$ ns and $\Delta(I_3) = \pm 0.1\%$ respectively.

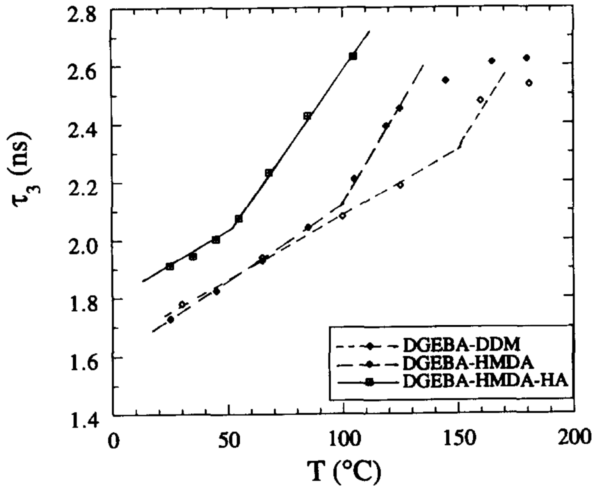


Figure 1 Temperature changes of the o-Ps lifetimes of the DGEBA-based epoxies

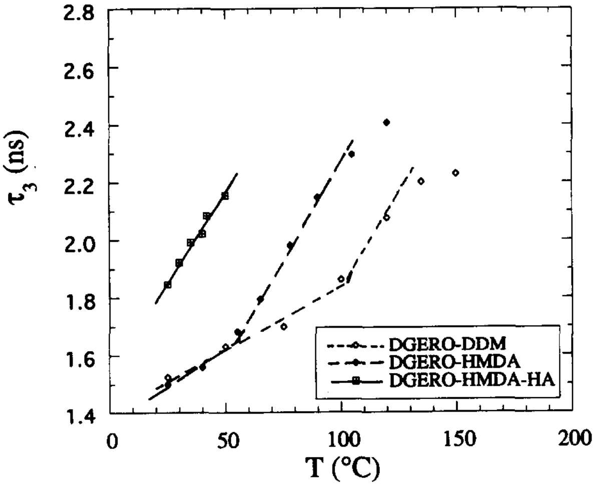


Figure 2 Temperature changes of the o-Ps lifetimes of the DGERO-based epoxies

RESULTS

In accordance with previous observations[5,6], a comparison of the glass transition temperatures of the pairs E1a–E2a, E1a–E1b and E2a–E2b (*Table 1*) demonstrates that T_g is affected by the chain rigidity, with a more rigid network exhibiting a higher glass transition temperature. The same effect is obtained when the crosslink density increases without changing the network rigidity (pairs E1b–E1c and E2b–E2c in *Table 1*). The volumetric measurements indicated that a change of the molecular parameters affects also the thermal expansivity of the epoxies (*Table 2*)—the thermal expansion coefficient of the high-temperature (rubbery) phase decreases with increasing network rigidity and/or crosslink density.

Figures 1 and *2* summarize the changes of τ_3 with increasing temperature. With the exception of E2c it is evident that the curves from all specimens exhibit changes of slope, which is characteristic for a material undergoing glass transition[10,14,15].

A simple spherical hole model was used to relate τ_3 with the radius (R) of the hole where the o-Ps localizes[16,17]. If one assumes that inside the hole it decays at its vacuum rate ($\lambda_{o\text{-}Ps} = 1/142\,\text{ns}^{-1}$), and o-Ps only penetrates a small distance (ΔR) into the wall of the hole, where it annihilates at the spin-averaged rate ($\lambda_{spin} = 1/(4 \times 0.125) + 3/(4 \times 142)\,\text{ns}^{-1}$) as it is surrounded by an electron cloud, the average o-Ps annihilation rate of such a localized o-Ps can be given by:

$$\tau^{-1} = \lambda_{spin} G + \lambda_{o\text{-}Ps}(1 - G) \qquad (1)$$

where

$$G = 1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R + \Delta R}\right)$$

is the quantum-mechanical probability that o-Ps is in the electron cloud, R is the radius of the hole and $\Delta R = 1.612$ Å.

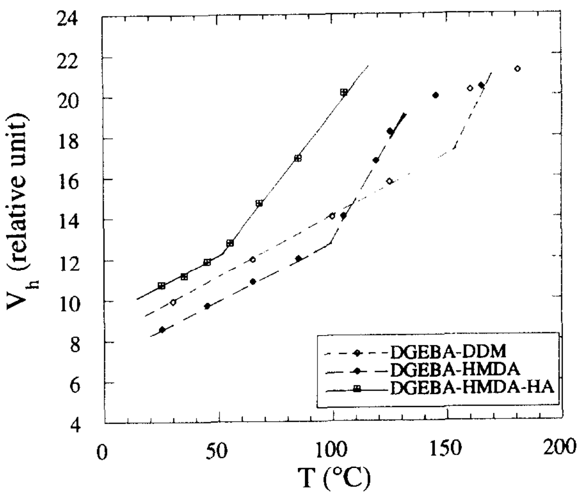


Figure 3 Temperature changes of the open volume (relative units) in DGEBA-based epoxies

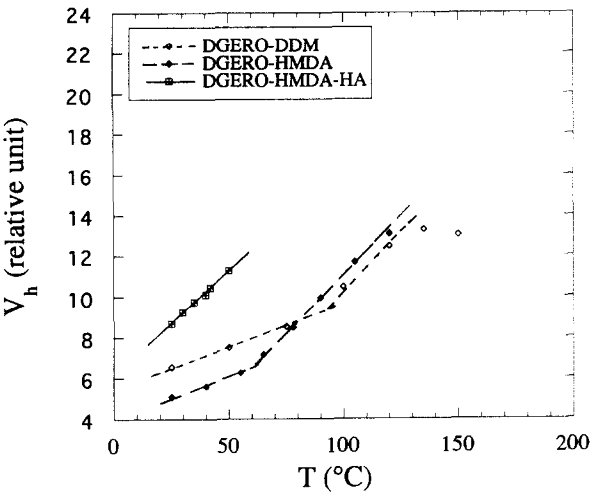


Figure 4 Temperature changes of the open volume (relative units) in DGERO-based epoxies

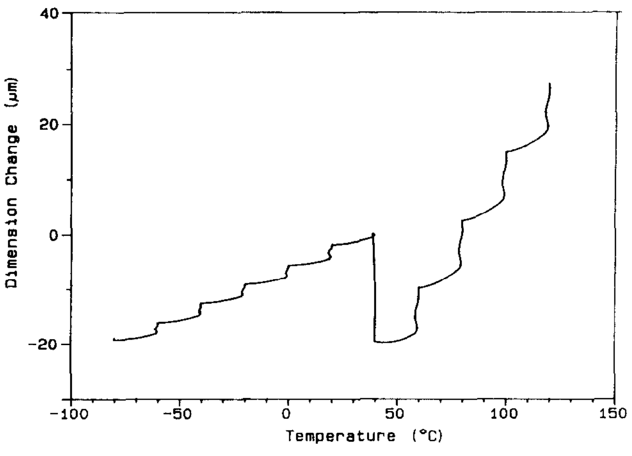


Figure 5 Trace of the dimensional change of specimen E2c as a function of temperature. The d.s.c. glass transition temperature of this sample is ~ 42°C

The relative intensity of the o-Ps component (I_3) is commonly assumed to be proportional to the number density of the holes; thus the total hole volume V_h is proportional to the product of the average volume of a single hole $v_h = 4\pi R^3/3$ (R is obtained from equation (1)) and I_3:

$$V_h = C v_h I_3 \tag{2}$$

where the normalization constant C remains to be determined.

The changes of τ_3 in *Figures 1* and *2* correspond to changes of the average hole radius from ~ 2.3 Å (v_h ~ 50 Å^3) to ~ 3.4 Å (v_h ~ 160 Å^3). The intensities (I_3) of all specimens were effectively constant in the temperature range under investigation. This is probably the most substantial difference between the p.a.l.s. responses of thermoplastics and relatively highly cross-linked thermosets. We surmise that in thermoplastics extra open volume is generated from the thermal motion of the chain segments, thus resulting in an increase in I_3. In thermosets no long-range segmental motion is possible even above T_g; thus the number of o-Ps trapping sites is constant, resulting in constant I_3. This is an interesting observation because it implies that the T_g phenomenon does not need to be related to long-range segmental motions and can be a localized dynamic phenomenon.

Since the I_3 values were nearly constant, the products of v_h and I_3, e.g. the hole volumes V_h in relative units, follow the temperature changes of τ_3 (*Figures 3* and *4*; $\Delta V_h = \pm 0.03$). The glass transition temperature derived from the p.a.l.s. measurements (*Figures 3* and *4*) are consistently lower by 10–20°C when compared to the d.s.c. glass transitions. The sources of these discrepancies are most probably the different timescales of the d.s.c. and p.a.l.s. experiments, coupled with the kinetic nature of the glass transition process. The 'fresh' epoxy samples are in a highly non-equilibrium state after quenching to room temperature, and the material will undergo structural (volume) relaxation towards a lower-energy molecular configuration. The structural relaxation, also known as physical ageing, is much faster in the vicinity of the glass transition[18], and depending on the specifics of the particular experiment the amount of relaxation will vary significantly. A calorimetric measurement usually takes less than 1/2 hour, while to obtain tolerable statistical errors the respective p.a.l.s. experiments require 1–2 hours per spectrum (per data point in *Figures 3* and *4*). It is evident that the ageing process will be much more significant during the p.a.l.s. experiments. The above-discussed effects were also directly observed in the course of the volumetric measurements. In *Figure 5* is shown a t.m.a. trace of the change of the sample thickness for the specimen E2c. The shape of the trace, which is characteristic for all specimens, exhibits pronounced volume shrinkage in the vicinity of the glass transition. Another confirmation of this phenomenon can be obtained from the calorimetric measurements with oscillating heating rate. The results for the epoxy E2c, shown in *Figure 6*, indicate the presence of an irreversible (relaxational) component. (An extensive discussion on the kinetic nature of T_g can be found also in ref. 18.) Differences between the glass transition temperatures determined by calorimetry and p.a.l.s. have repeatedly been reported for a wide range of polymeric materials[7].

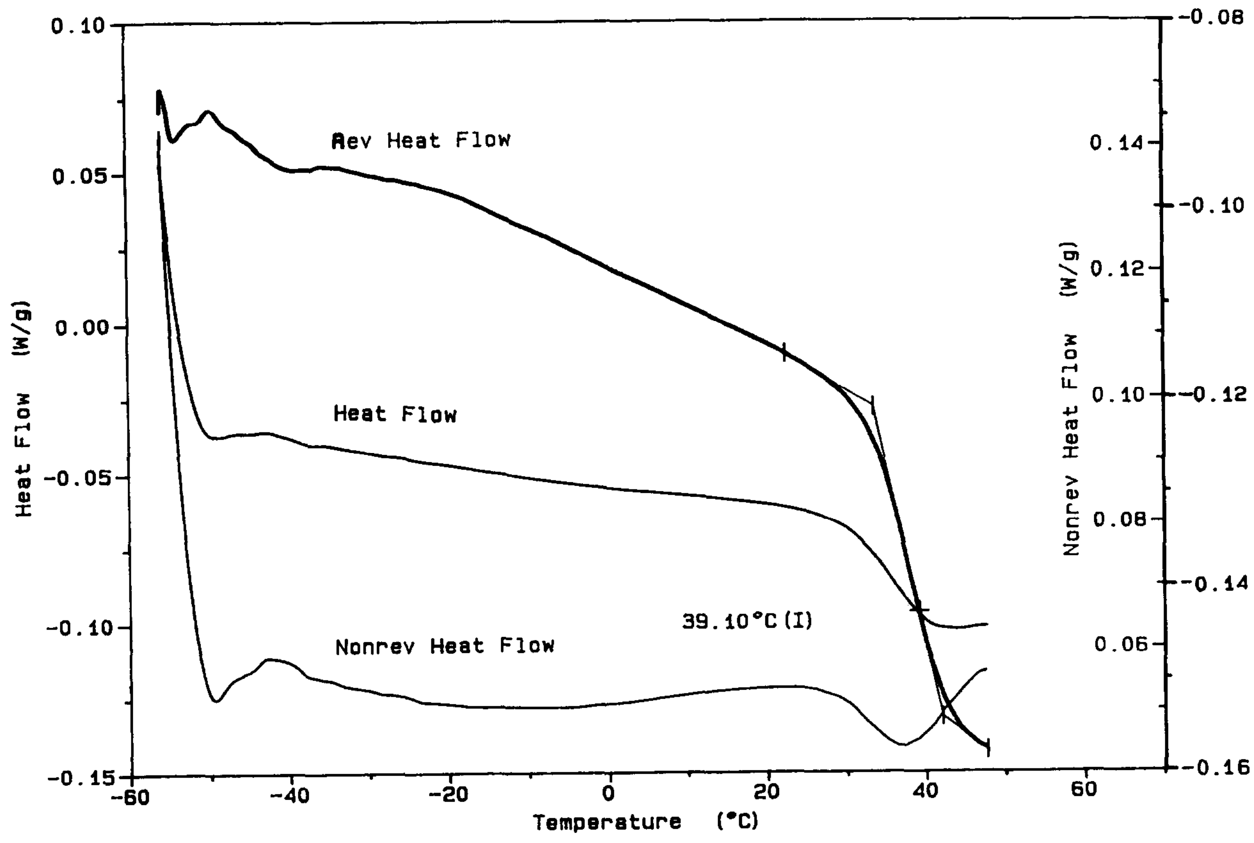


Figure 6 Reversible and non-reversible components of the heat flow obtained during calorimetric measurements with oscillating heating rate—specimen E2c

The p.a.l.s. results for the epoxies with high T_g, e.g. E1a, E2a and E1b, demonstrate that τ_3 (V_h) levels off at temperatures 20–30°C above the glass transition. This effect has been observed for a variety of epoxy resins and other non-crystallizable polymers[7,19]. It is usually interpreted as a transition from 'rigid-wall' cavities to 'soft-wall' cavities with increasing temperature[20]. The softening of the material at temperatures above $T_r > T_g$, in combination with the kinetic energy of the ortho-positronium, leads to formation of bubbles around the o-Ps. As a result the simple model used to substantiate equation (1) is not valid at these temperatures.

DISCUSSION

The fact that I_3 of all specimens is not sensitive to temperature changes is an indication that the number of 'elementary' voids where the o-Ps can localize is fixed during the curing procedure. Subsequent heating or cooling changes the size of the individual holes, but in contrast to thermoplastics[14,15] or low-crosslink-density thermosets[7] there is no thermal generation or annihilation of o-Ps trapping sites. If we compare the average radii (computed from the τ_3 values at the glass transition) of the micro-holes of the pairs E1a–E2a, E1a–E1b and E2a–E2b (*Table 2*) it is evident that R is affected by the chain rigidity; an increase of the rigidity of the epoxy network results in larger holes. A consistent interpretation of these results suggests that it is more difficult to achieve dense packing of rigid polymer chains in comparison to flexible ones. However, variations in the crosslink density, which also should influence the chain packing, did not cause a systematic change in the hole sizes (pairs E1b–E1c and E2b–E2c in *Table 2*).

As indicated in the 'Results' section, the volumetric measurements show a systematic change of the macroscopic expansivities of the rubbery phase (*Table 2*); namely, higher chain rigidity and/or crosslink density decrease the coefficient of thermal expansion. The microscopic expansivities, i.e. the coefficients of thermal expansion of the hole volume defined as:

$$\alpha_h = \frac{1}{V_h}\frac{\partial V_h}{\partial T} \qquad (3)$$

did not show systematic variation with the network rigidity or crosslink density (note that the derivation of α_h does not require conversion of V_h into absolute units). Their values were in the range $(1-1.5) \times 10^{-2}$°C^{-1}, which is more than an order of magnitude larger than the values of the macroscopic counterparts.

To obtain a better understanding of the effects of the epoxy network parameters on the microstructural state of the material, it is useful to compare the total hole volumes of different samples. A direct comparison of the hole volumes by using the data in *Figures 3* and *4* implies that the materials constant C in equation (2) is the same for all epoxies. Physically this is equivalent to assuming that the differences in o-Ps intensities from the various epoxies result only from the different concentration holes in the materials. In other words additional processes affecting the probability of positronium formation, such as spur formation and o-Ps diffusivity[21], do not change from sample to sample. While this may turn out to be a correct assumption the experimental evidence to support this assumption is lacking at the present time. One way to circumvent this problem is to normalize the hole volume into absolute units. In a previous work[22] we demonstrated that such a normalization can be achieved by using the thermal expansion or mechanical deformation of the polymers. The normalization procedure is based on the assumption that the change in the total volume (ΔV) is contributed by the change in the total hole volume (ΔV_h) where o-Ps localizes and the change in the bulk volume (ΔV_b), which cannot be detected by p.a.l.s., i.e. $\Delta V = \Delta V_h + \Delta V_b$. The hole volume fraction $F_h \equiv V_h/V$ can then be written as:

$$F_h = \frac{\Delta V/V - \Delta V_b/V_b}{\Delta V_h/V_h - \Delta V_b/V_b} \tag{4}$$

If we further assume $\Delta V \simeq \Delta V_h$, i.e. $\Delta V_b \ll \Delta V_h$ (this assumption will lead to an upper limit of F_h), in the case of thermal expansion, equation (4) is expressed as[22]:

$$F_h = V_h \frac{\alpha_v \Delta T}{\Delta V_h} \tag{5}$$

where V_h and ΔV_h are in relative units, and α_v are the thermal expansion coefficients of the respective materials. The hole volume fractions at T_g for each specimen, obtained via equation (5), are listed in *Table 2*. We would like to point out that F_h derived from p.a.l.s. measurements may be related to the frequently used 'free' volume[7,9,12,14,15], but it is not necessarily the same quantity. A fundamental problem of using the 'free' volume concept lies in the lack of precise definition of the term 'free volume' (more details and discussions on this subject can be found in ref. 22).

F_h values at T_g (range 3–6%) are close to the values of the 'free' volume fraction obtained on a similar set of epoxies by using viscoelastic measurements[5], but somewhat lower than the open volume fractions at T_g in linear thermoplastics[22,23]. While the hole volume fraction values are in the range expected for this class of materials, it is helpful to obtain additional confirmation. To achieve this goal we propose to use the discontinuity of the thermal expansion coefficients at the glass transition temperature. Taking into account that the volumetric expansion (obtained from macroscopic measurements) is characterized by $(\partial V/\partial T) = (\partial V_h/\partial T) + (\partial V_b/\partial T)$ and assuming that in the vicinity of T_g we have $(\partial V_b/\partial T)_1 \sim (\partial V_b/\partial T)_2$, where the subscripts 1 and 2 stand for $T < T_g$ and $T > T_g$ respectively, the change of α_v is written as:

$$\Delta\alpha_v = (\alpha_v)_2 - (\alpha_v)_1 = \frac{1}{V(T_g)}\left[\left(\frac{\partial V_h}{\partial T}\right)_2 - \left(\frac{\partial V_h}{\partial T}\right)_1\right] \tag{6}$$

The T_g jump of the hole volume expansion coefficient (measured by p.a.l.s.) is:

$$\Delta\alpha_h = (\alpha_h)_2 - (\alpha_h)_1 = \frac{1}{V_h(T_g)}\left[\left(\frac{\partial V_h}{\partial T}\right)_2 - \left(\frac{\partial V_h}{\partial T}\right)_1\right] \tag{7}$$

By dividing equations (6) and (7) the hole volume fraction at T_g is written as:

$$F_h(T_g) = \frac{\Delta\alpha_v}{\Delta\alpha_h} \tag{8}$$

To obtain equation (5) it was assumed that the bulk expansivity is negligible in the temperature interval under consideration, while to derive equation (8) we required only the jump of the bulk expansivity at T_g to be negligible. The values of F_h for the specimens E1b and E2b (with T_g values in the middle of the temperature range used in our work) derived by using equation (8) are reasonably close to the values obtained from equation (5)—4.9 vs. 3.9% and 3.1 vs. 3.3% for the two respective specimens. To our understanding this is a clear indication that both assumptions, namely $\Delta V_b \ll \Delta V_h$ and $(\partial V_b \partial T)_1 \approx (\partial V_b/\partial T)_2$, are compatible with the physical processes underlying the thermal expansion. Thus the F_h values obtained in the present work are realistic measures of the open volume in our epoxies. Taking into account the fact that the volume of an individual hole is of the order of 100 Å^3 one can compute (by using the values of F_h in *Table 2*) that the number density of o-Ps trapping sites is higher than $10^{20}\,\mathrm{cm}^{-3}$. This large number of elementary voids in non-crystalline polymers makes the p.a.l.s. method a very sensitive tool to probe their microstructure.

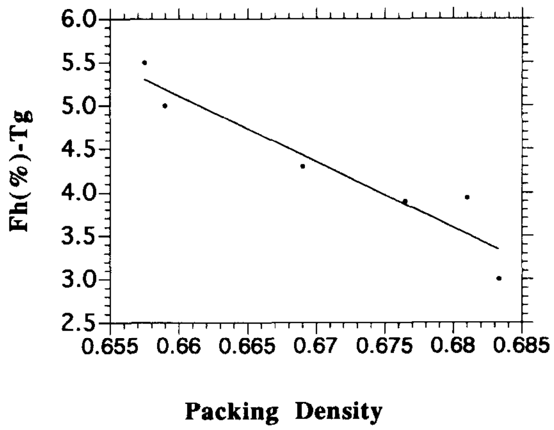


Figure 7 Open volume fractions at T_g for the epoxy specimens (from E1a to E2c) as a function of the packing densities at T_g (see text for details)

Owing to the physical processes involved in the formation and localization of the orthopositronium, it is reasonable to accept the notion that the o-Ps probes the 'empty' space within the polymer. On this basis it seems reasonable to expect that the whole volume fraction will depend on the quality of packing of the molecular segments. To support this point of view we plot in *Figure 7* the hole volume fractions (at T_g) as a function of the packing densities for the different epoxies. The packing densities were computed according to the group contribution procedure of Bondi[24] and represent the ratio of the measured densities vs. the van der Waals densities:

$$\rho^* = \rho_{\mathrm{exp}}/\rho_{\mathrm{Bondi}} = \rho\left(\sum V_i\right)_{\mathrm{Bondi}}\Big/\sum M_i \tag{9}$$

where ρ^* is the packing density, ρ_{exp} is the measured density, ρ_{Bondi} are the computed densities, V_i are the van der Waals volumes and M_i the molecular weights of the different building units (more details on the packing density computation are given in ref. 25). The nearly linear decrease of the p.a.l.s. open volume can be accepted as indication that packing of polymer chains is the main factor determining the amount of trapping sites within the epoxy resins. The increase of the rigidity of the network leads to less efficient packing and increase of the open volume fraction. It is interesting to point out that the conventional concept of free volume would predict the same amount of free volume for all epoxies. The fact that this notion is contradicted by the present results indicates that the free volume concept is not particularly useful in explaining the physical behaviour of thermosets. We point out further that the present results are consistent with compressibility measurements carried out by one of us (AFY), which shows that highest crosslink density epoxies are the most compressible[27].

CONCLUSIONS

The results from our investigation demonstrate that changes in the molecular structure of the constituent change the microscopic parameters of the epoxy networks. An increase of the chain rigidity increases the size (τ_3) and the number density (I_3) of the trapping sites where o-Ps localizes, which leads to an increase of the hole volume fraction at T_g. Specimen E1a (DGEBA/DDM), which is composed of rigid epoxide chains and rigid crosslinks, exhibits the greatest overall hole size. Conversely specimen E2b (DGERO/HMDA; flexible epoxide and flexible crosslinker) has the lowest F_h. It was found that the hole volume fraction at T_g approximates a linear relationship with the packing densities of the epoxies under investigation. The results are interpreted as a decrease of the effectiveness of molecular packing with increasing network rigidity. As a result the macroscopic material's properties such as glass transition temperature, density and thermal expansion show considerable variations.

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