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Positron annihilation study of free volume in cross-linked amorphous polyurethanes through the glass transition temperature

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The dependence of free volume on temperature has been monitored in some cross-linked polyurethanes, with different chain lengths, by using positron annihilation lifetime spectroscopy (PALS). The spectra were analysed in terms of continuous distributions in order to obtain the distribution of the longest component, τ_3. The relative number and the mean size of free volume holes have been evaluated as a function of temperature: for $T < T_g$ both the number and the volume of the holes increase; for $T > T_g$ the number of the holes reaches a plateau while the hole volume increases significantly. The amplitude of the plateau widens with the cross-linking and the hydrogen bond interactions. At the end of the plateau the number of the holes increases more than the hole volume: the analysis of hole distribution indicates that the dispersion decreases with increasing temperature. The dispersion of the size of the nanovoids around their average values at the various temperatures has been estimated by a suitable computer code that uses a continuous sum of the decay curves with a log-normal distribution. For each sample a glass transition temperature has been estimated and compared with that obtained by d.s.c. The influence of cross-linking on the free volume is discussed. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: polyurethanes; positron annihilation; free volume)

INTRODUCTION

Polyurethanes (PUs) are widely used polymeric materials, with many technical applications, such as synthetic hides, sponge materials and hard or soft products. From a fundamental point of view, polyurethanes are characterised by the presence of various chemical groups. Indeed, their chemical composition and the relative concentration of the chemical groups may be varied by altering the nature of the reagents and the molecular weight of the non-isocyanate components. The modification of the chain composition changes the physico-chemical properties of the polymer, such as the glass transition temperature, the concentration of the hard or soft zone, etc., mainly because of the different hydrogen bond density.

Even when PUs appear amorphous from X-ray and d.s.c. analysis, short-range order is still possible. In both linear and cross-linked PUs the hydrogen bond interactions between the urethane groups present in different chains are responsible for the formation of short-range regions that segregate into the so-called 'hard' domains. The long chains between urethane groups, consisting of oligomeric diols or diamine, bind the 'hard' zones, forming 'soft' domains where the interaction forces among the chains are 'soft' and of the van der Waals type, and allow the free movements of the chains above T_g.

The modern explanation of several features of polymeric materials—such as viscoelastic and mechanical properties and even the diffusivity of permeants—is based on the free volume theory[1,2]; the experimental determination of free volume microscopic holes is, therefore, of paramount importance, both for theoretical analysis of the behaviour of polymers and for practical applications such as the development of polymers with controlled properties. Indeed there is no unequivocal definition of the free volume[3]. This implies that not only it is not easy to define the free volume quantitatively, but it is also difficult to evaluate it experimentally. We will not go into this argument here, but will discuss it in relation to the experimental technique adopted here.

Unfortunately, only very few experimental methods are nowadays available for this task: wide-angle X-ray diffraction, photoisomerization of photochromic probe molecules[4] and positron annihilation[5]. In particular, this last technique is revealing itself to be a promising tool to directly probe the properties of the free volume holes in a non-destructive way. It is therefore useful to recall a few points concerning the spectroscopies based on positron annihilation.

A positron injected into a non-metallic solid from a radioactive source, after a fast slowing-down requiring some picosecond at most[6], becomes thermalized and is strongly attracted by the electrons of the medium. Eventually, annihilation between positron and one of the surrounding electrons takes place: the pair disappears with

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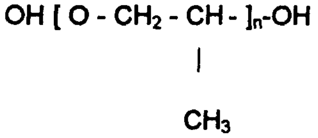
production of two—or, much more rarely, three—photons. However, before this last event, the positron can be involved in a short although complex history: for instance, it can be annihilated into microscopic domains characterised by different electron densities (amorphous and crystalline regions, different kind of defects, etc.). Moreover, it can form, with an electron of the medium, a bound system which is called positronium (Ps). The result is a positron annihilation spectrum with different components, whose study is potentially useful to obtain information on the structure of the host medium. In the case of the lifetime spectroscopy (PALS), the most common positron technique, a timing spectrum is typically formed by three components, corresponding to annihilations from *ortho*-Ps, from free positrons and from *para*-Ps (in order of decreasing lifetime). Concerning the PALS technique, it is important to point out that two kinds of free volume holes could be considered according to the behaviour of the polymers: hard and rigid for glassy polymers and an intermediate state between the glassy and the melt state (liquid-like) for rubbery polymers. In the case of glassy polymers, the local motions of the atoms oscillating in a cage of their neighbours create some 'free volume' in the empty spaces of random packed materials. Since the amplitude of the atom oscillations increases with temperature this free volume also has to increase with temperature in a manner similar to the thermal expansion of the glassy polymer (bulk expansion coefficient). On the other hand, in rubbery materials chain rotational movements, that involve many monomeric units (in the case of polyurethanes about 15 monomeric units), dominate and the free volume holes are strictly related to these movements. Before discussing any experimental PALS results it is important to relate the lifetime of a positronium trapped in an hole with the frequency of atomic oscillation or of the rotational movements of the chains and with the lifetime of the holes. The period of the swinging of the chains involving 15 monomeric units is of the order of 10^{-12} s [7], that is, 1000 to 100 lower than the lifetime of a positronium. This means that during its mean life a positronium is able to evaluate the mean diameter of the hole. The lifetime of a hole may be estimated to be of the same order of magnitude of polymer relaxation time, that is of the time needed for the chains to change their conformation, disentangle or slide over one another, and so on. For polymers the relaxation time is of the order of magnitude of seconds (sometime of hours), that is at least 10^9 greater than the lifetime of *ortho*-Ps. Therefore, in rubbery polymers due to the chain dynamics holes are formed and destroyed is such a way that their mean number and mean size are constant during the mean life of Ps.

In the present study, PALS data on some amorphous cross-linked polyurethanes are reported, in the temperature interval 100–400 K, which contains the temperature range for the normal use of these polymers (280–370 K). In this interval, a glass transition and, possibly, transitions due to the breaking of the hydrogen bonds between soft and hard zones, may be present. Our data allows one to follow the behaviour of the free volume as a function of the temperature in the investigated materials. To this purpose we used the well-known fact that Ps formation in a polymer takes place in the free volume holes[8], and that the spectral component associated to *ortho*-Ps is particularly sensitive to variations in the number as well as in the size of the holes. Analysis in terms of a continuous distribution of Ps lifetimes allowed us to get insight into the dispersion of the holes size around their average values.

EXPERIMENTAL

Materials

Dow Chemical poly(oxy propylene)glycol (PPG) having the general formula:



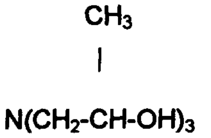
$$\mathrm{OH\,[\,O-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\,]_n\!-OH}$$

and different molecular weights were used.

The mean molecular masses of the used polyols—estimated by titration of the hydroxyl groups of dry polyols with phthalic anhydride in pyridine[9]—were, respectively, 430, 1230, 2180. In the following the diols will be indicated with their nominal MW.

Toluene-diisocyanate: CH_3–$C_6H_3(NCO)_2$ (Bayer) was a 2,4 and 2,6 mixture (80:20).

Triisopropanolamine (TIPA) (Fluka) was used as a trifunctional cross-linking agent:



$$\mathrm{N(CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-OH)_3}$$

Stannous octoate was the catalyst in the cross-linking reaction.

Ethylacetate (EA) RP by Carlo Erba was used as solvent in all the reactions.

Polymer and film preparation

First stage: prepolymer preparation. The NCO-terminated prepolymers were obtained by refluxing under nitrogen an ethylacetate solution of PPG and TDI, in the molar ratio 1:2.1. The reaction was carried out for 5 h at the solution boiling temperature: the addition of two TDI molecules on each PPG chain is assured with the experimental conditions used, even with higher molecular weight polyols. The reaction was followed by evaluating the NCO content according to the ASTM D 2572–70 method[10].

The reaction temperature (around 80°C) avoids the formation of allophanates, biurets, and secondary compounds[11].

Lower molecular weight PPG reacts more quickly due to the higher hydroxyl groups concentration C_{OH} ($C_{OH} = 2W/VM$, where V is the solution volume and W and M are the weight and the molecular weight of the polyol). The choice of the reacting mixture molar ratio m = TDI/polyol = 2.1 has been suggested by the opportunity of terminating all the prepolymer chains with NCO groups. A statistical calculation of the molecule distribution carried out according to Flory[12] shows that for $m = 2$, no OH groups are present at the end of the polymer chain, while NCO-terminated molecules are of the type T, TPT, TPTPT, and TPTPTPT, where T is the TDI and P is the diol. The molar fraction of the TPT units is calculated to be maximum for $m = 2$. Some free unreacted TDI is present in this condition.

The prepolymers prepared with the described procedure are stable up to 8 months in inert atmosphere and absence of water.

Second stage: cross-linking reaction. The following procedure was used: about 10 g prepolymer solution (66% by weight in EA) were diluted to 50% with dry solvent (EA) in a 100-ml beaker. An amount of EA solution of the cross-linking agent (25% TIPA concentration) was added by means of a syringe and under slow stirring, so as to reach an OH/NCO ratio between the hydroxyl groups of the cross-linking agent and the NCO groups of the prepolymer equal to 1.1:1. After elimination of any gas bubbles by gentle heating, the solution was cooled to room temperature and stannous octoate was added in the amount of about five parts per 1000 of the prepolymer solution. As soon as the solution began to cross-link (after about 5 min), it was poured on to a flat glass previously cleaned with EA and dried. The membrane was prepared by spreading the polymer with a Gardner knife and allowing a very slow evaporation of EA. After complete gelation and solvent evaporation, the film was detached from the glass by immersion into water. Films, having a thickness of 20–100 μm, were stored between filter papers. In some cases the samples were obtained by casting the solution into suitable silicone-based moulds. All the PU samples proved amorphous using X-ray analysis.

Experimental set-up

The thermal behaviour of the PUs was studied with a Mettler TA 3000 d.s.c. in the range 223–373 K.

The positron source, a few μCi of ^{22}Na from a carrier-free neutral solution, was evaporated between two identical Kapton foils (1.08 mg/cm^2 each); they were then glued together and inserted into the specimen in the usual sandwich configuration. The thickness of each sample was sufficient to stop all the injected positrons. The measurements were performed at various temperatures, which were different for the various samples; a liquid nitrogen cryostat (DN 1714 Oxford Instruments) ensured stability of the temperature within 0.3 K. The specimen was introduced into a copper sample holder, constituting the 'tail' of the cryostat; after accurate degassing, each sample was immersed in a gaseous He atmosphere. The lifetime spectrometer consisted of a standard fast–fast coincidence apparatus; the γ-rays corresponding to the birth of the positron ('start') and to the annihilation event ('stop') were revealed by two cylindrical NE111 plastic scintillators, whose dimensions (1″ × 1.5″ and 0.5″ × 1.5″, for the start and the stop channels, respectively) ensured a good compromise between resolution and efficiency of the spectrometer. The scintillators were coupled to Philips XP2020 photomultipliers. The resolution resulted to be about 235 ps; it was obtained through the deconvolution of time annihilation spectra of ^{207}Bi. Each spectrum consisted of about 10^6 counts; at least three measurements were carried out for each investigated temperature. The lifetime spectra were analysed through the Lifetime (LT) program by Kansy[13].

RESULTS AND DISCUSSION

ortho-Positronium (o-Ps) lifetime and transition in polymers

A PALS spectrum can be analysed into discrete components; however, within this framework it is possible to draw conclusions only on the mean size of the holes[14,15]. On the other hand, information on the distribution of the holes around their mean size would be extremely important in order to increase the knowledge of the free volume and the microphysical structure of polymers[16,17]. The hole distribution may be obtained by analysing the time annihilation spectrum $S(t)$ in terms of a continuous distribution of the lifetimes:

$$S(t) = R(t) * N \int_o^\infty \lambda\alpha(\lambda)\exp(-\lambda t)\,d\lambda + b \qquad (1)$$

where b is the background, N is the total number of counts and R represents the resolution function (the symbol * stands for convolution). The inversion of equation (1)—in order to obtain the decay probability density $\lambda\alpha(\lambda)$—is a difficult mathematical task[18]. A computer code (CONTIN) for the numerical solution of the above integral equation was first developed by Provencher[19] and modified by Gregory and Zhu[20] to adapt it to positron annihilation spectra. A different approach based on a non-linear Bayesian method has been recently proposed[21–23]. The corresponding computer program MELT, which uses the maximum entropy principle, has been successfully applied to the analysis of positron lifetime spectra in various materials[24].

In the present investigation, we used the LT program[13]; it allows a positron spectrum to be analysed in terms of discrete components, as well as in terms of a continuous sum of the decay curves given with a log-normal distribution. Furthermore, the program is able to carry out a 'mixed' analysis, in the sense that some components can be requested to be discrete whilst others can be treated as continuous ones. We chose this last possibility, by assuming that the two shortest lifetimes are discrete; the longest one, on the contrary, is allowed to display a distribution of lifetimes. The physical justification for the adopted procedure is related to the fact that the shorter components should not give large distributions, owing to their origin, whilst the longest one should reflect the hole distribution.

The distribution of *o*-Ps lifetimes was obtained by the following procedure. For each polymer, all the spectra corresponding to the same temperature were first analysed into three discrete components by means of the LT program, in order to obtain the zero channel time t_0; in this case, the LT program supplies identical results to the Positronfit program[25]. Next, the spectra were summed, by taking into account shifts of t_0. In such a way a single spectrum with better statistics for each T was obtained, and possible drifts of the experimental apparatus were compensated, at least in a first approximation. The resulting spectrum was analysed by the LT program by letting the longest component to be continuous.

According to the common interpretation we attribute the distributed lifetime of the longest component to *o*-Ps decay. The lifetimes τ_1 and τ_2 are associated to annihilation of positrons not forming bound states, but localised into regions characterised by different electron densities. τ_1 should be considered as a weighted mean of two different components, since it contains annihilations from *para*-Ps.

The trend of τ_3, centroid of the lifetime distribution of the longest component, *versus* the temperature, is shown in *Figure 1* for the various PUs; a monotonic increase is observed, which is very similar for the various samples. Three temperature regions can be distinguished: the 'low' and 'high' temperature regions ($T < 200$ K and $T > 320$ K, respectively) where there is a moderate variation of τ_3 with T, and the 'intermediate' region where a sharp increase of the rate of variation of τ_3 with T is evidenced. The change in the τ_3 variation between 'low' and 'intermediate' temperatures is associated with some morphological transition since *o*-Ps lifetime is sensitive to the electron density surrounding Ps and, therefore, to the size of the free volume holes.

For low T the molecular movement of the polymer chains

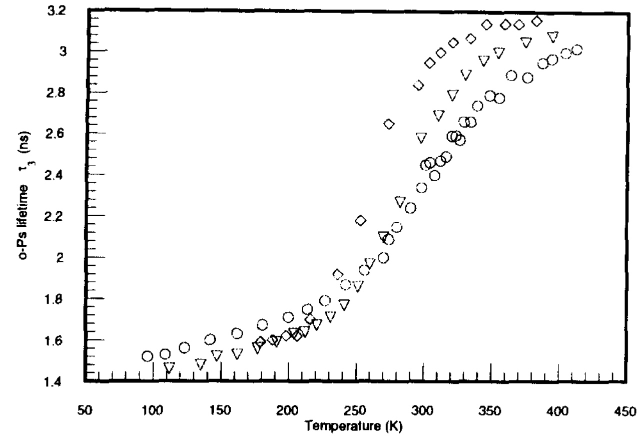


Figure 1 *o*-Ps lifetime (ns) for the different investigated PU as a function of temperature (K): ○, molecular weight 400; ▽, molecular weight 1200; ◇, molecular weight 2000

Table 1 Glass transition temperature: T_g' from PALS; T_g'' from d.s.c.

Polymer	T_g' (K)	T_g'' (K)
PU 400	260	300
PU 1200	240	250
PU 2000	220	226

in the 'soft' domains is 'frozen in' (glassy state) by the van der Waals forces among the chains, only small fluctuations are allowed and the free space around the chains is small: any increase of T produces small effects on the thermal motion of the polymer chains and, consequently, only a small increase of the free volume, that is, of the size of the free volume holes. Therefore small variations of τ_3 *versus* the temperature must be expected, according to the reported data.

On the other hand, by increasing the temperature the thermal movements of the chains also increase, and at a certain value of T the fluctuation energy becomes of the same order of the interaction energy. At this condition the amplitude of the fluctuations may increase followed by an increase of the free volume around the chains. The temperature at which this phenomenon occurs is called glass transition temperature T_g, since this temperature marks the 'glassy state' and the 'rubbery state' transition of the soft fraction of the PUs.

For $T > T_g$ the soft polymer fraction is in a rubbery state, the increased mobility of the chains and the average size of the holes both increase with temperature. Therefore *o*-Ps lifetime also shows an increased variation with the temperature.

The glass transition temperature is 'classically' determined by following the polymer-specific volume V *versus* temperature and drawing the intersection of the straight lines which are tangential to the $V(T)$ *versus* T curve around the T_g. According to Williams, Landel and Ferry (W.L.F)[1] the free volume is a constant below T_g, but increases linearly with $(T - T_g)$ above T_g. The data of *Figure 1* which show $\tau_3(T)$ above T_g agree with the prevision of W.L.F., but they do not correspond to the W.L.F. assumption of constant V_f below T_g: this assumption, however, seems not to be true, as shown by many experiments, especially by physical ageing[26].

The polymer glass transition temperature T_g' has been estimated, according to the general procedure, through the intersect of the two straight lines interpolating the experimental values of τ_3 *versus* temperature, in the low and intermediate temperature regions[27]. The data of T_g' are collected in *Table 1* for the different PUs. In the same Table the T_g'' values obtained from samples of the same batch by differential scanning calorimetry (d.s.c.) are also shown; these last values of T_g are systematically higher than those obtained from positron spectroscopy. We outline that the T_g is not a thermodynamic property but a kinetic one. It is well known that high heating rates[28], as used in d.s.c., determine higher T_g values than at low heating rates. In this connection we note that more time is available for the transition from the glassy to rubbery state in the case of positron annihilation in polymers than in the case of d.s.c., owing to the different experimental running times required by the two techniques (that for positron spectroscopy is much longer[8]).

Therefore, a systematic difference in the determination of T_g can be expected; in particular, the glass transition temperature T_g' as determined by PALS should be lower than T_g'', the glass transition temperature determined by d.s.c.. Moreover T_g'' is related to the heat capacity of the polymer, that is to a change from small scale to large scale movements of polymer chain segments consisting of 5–10 monomeric units, whilst T_g' is related to a change, at the molecular scale, in the amplitude of the movements of very short polymer segments which are involved in the thermal process of the hole formation. This last process could begin at temperatures even lower than those involved in the ordinary T_g determination. In other words, PALS analysis could be more sensitive, showing the initial movements of the short chain segments which need very low energy. This last statement could explain why the T_g' values of some PUs are close to T_g'' while in other cases they are remarkably different. *Table 1* shows T_g' and T_g'': the difference $\Delta T_g = T_g'' - T_g'$ is high in the case of PU 400 probably due to a stronger interaction between urethane groups existing in higher concentration, which may reduce the mobility of soft segments.

According to the previous argument the difference $\Delta T_g = T_g'' - T_g'$ should be related to the chain interactions or the cross-linking density, in the sense that the higher the chain interaction, the higher should be the ΔT_g. The data in *Table 1* confirm this fact, which was already observed in some epoxy resins[29].

In the region of 'high' temperatures (*Figure 1*) a decrease in the rate of variation of τ_3 with temperature, $d\tau_3/dT$, is evident. A possible explanation is related to the presence of the cross-linking: it can be reasonably guessed that cross-linking somehow constrains the movements of the polymer segments, by preventing the hole volume to increase at the same rate as in the absence of cross-links. It seems possible that the hole volume of the polymer is constrained by cross-links at $T > T_g$. A similar behaviour was already shown in an amine-cured epoxy polymer[30].

Figure 2 shows the mechanical dynamical behaviour of PU 400 cross-linked with TIPA. The real part G' of the shear modulus changes from 10^9 to 10^6 MPa in the temperature range 270–320 K. This lowering of G', accompanied by the G'' maximum, corresponds to the glass transition of the polymer. It must be observed that G' reaches the limit value (rubber plateau) beyond the glass transition. This proves that the chains are cross-linked: no interchain slipping can therefore happen and the chains cannot become disentangled. So the free volume should not increase but for the thermal polymer expansion.

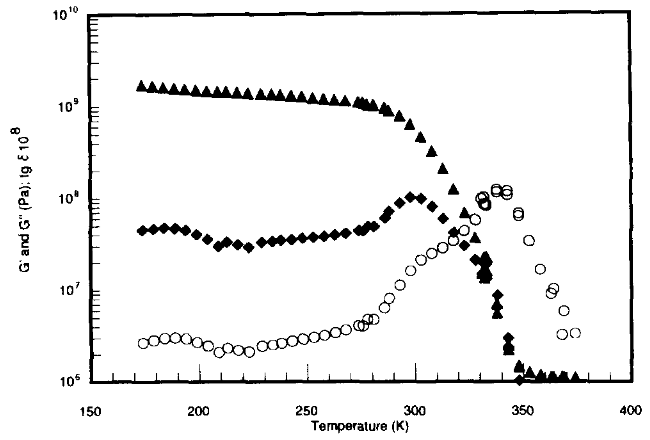


Figure 2 Real (G' (△)) and imaginary (G'' (◆)) part of the complex shear modulus *versus* temperature for PU 400. Input frequency, 1 Hz. ○ show the values of $t_g\ \delta \times 10^8$

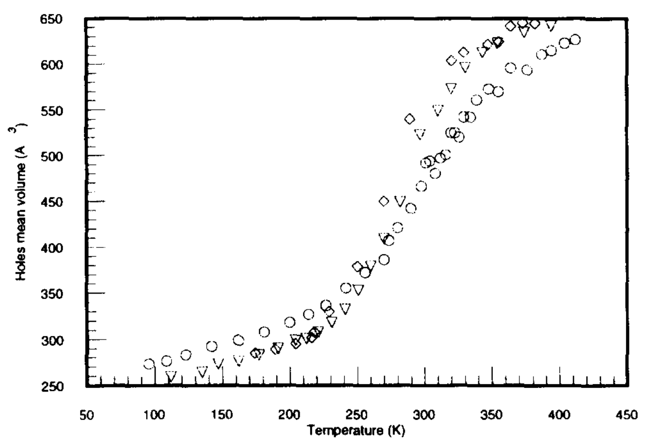


Figure 3 Dependence on the temperature (K) of the average volume of the holes (Å^3) in PU membranes with molecular weight PU 400, PU 1200 and PU 2000. The symbols have the same meaning as in *Figure 1*

The mean size of the holes forming the free volume can be roughly estimated by means of a simple quantum mechanical model [14,15]: *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 is consequently $R = R_0 - \delta R$. The following equation relating R (Å) and τ_3 (ns) is obtained[14]:

$$\tau_3^{-1} = 2[1 - R/R_0 + 0.159 \sin(2\pi R/R_0)] \quad (2)$$

If the value 1.66 Å for δR- obtained by fitting positron annihilation data in porous materials of known hole size—is accepted from the literature[31], the semi-empirical equation (2) allows one to find the average volume of the hole $V_h = 4\pi R^3/3$, in spherical approximation. The dependence of V_h on the temperature reflects the behaviour of the centroid τ_3; *Figure 3* shows V_h for the investigated polymers PU 400, PU 1200, PU 2000 which are characterised, respectively, by molecular masses between the cross-links of 907, 1706 and 2657 Da: this shows that the number of cross-links per unit volume (c.d.) is decreasing regularly from PU 400 to PU 1200 and PU 2000. It is easy to see that the hole volume below T_g' is nearly similar for the low cross-linked polymers and it is slightly higher in the case of PU 400; also, the slopes dV_h/dT are similar. The highly cross-linked PU 400 cooled from room temperature to $T < T_g$ cannot reach easily the minimum free volume due to the greater molecular constraints. The polymers which have lower c.d., such as PU 1200 and PU 2000, on the contrary, more easily reach the minimum free volume. Above T_g, the V_h of the different PUs is higher the lower the c.d. is. The slope dV_h/d_T increases slowly for all the polymers at the highest T.

From the lifetime distribution it is possible to obtain the hole volume distribution functions, which are shown in *Figures 4–6* for the investigated structures at some selected

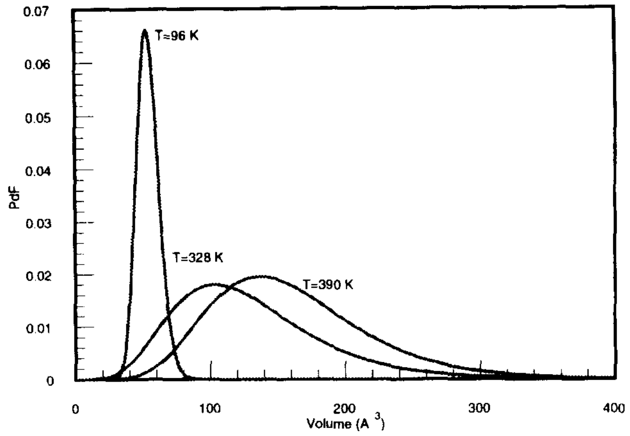


Figure 4 Probability density function of hole volumes for PU 400 at some selected temperatures

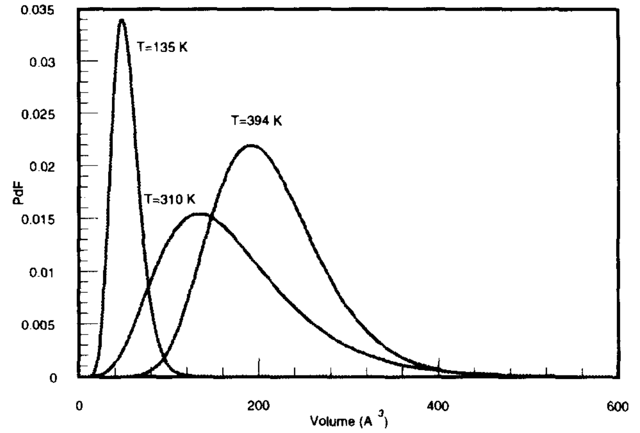


Figure 5 Probability density function of hole volumes for PU 1200 at some selected temperatures

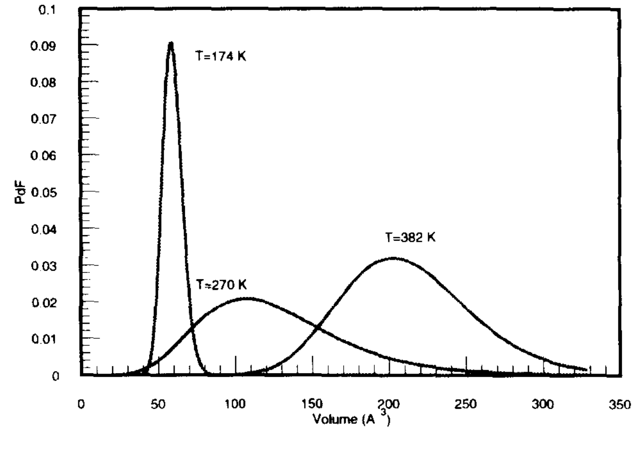


Figure 6 Probability density function of hole volumes for PU 2000 at some selected temperatures

temperatures. The hole volume distribution shows an increased dispersion, Δ_3, of the values going from $T < T_g$ to $T > T_g$ reflecting the higher freedom of movements of the macromolecular segments, which means an average increase in the size of the holes but also an increase of the dispersion in their volume around the mean value. Indeed, it is reasonable to suppose that the various molecular motions require different expenditures of energy, and consequently are achieved in different amounts, at fixed temperature.

Owing to the hindrance of the enlargement of the free volume holes at high temperature, such as by cross-links, the larger holes will stabilise themselves whilst the volume of the smaller holes will grow with temperature. This fact implies an increase of the mean volume of the holes, and therefore of τ_3, that must be correlated to a decrease in the hole dispersion, owing to the decrease of the number of small volume holes, while the volume of large holes remains constant. All this is supported by the decrease of Δ_3, as shown in *Figures 4–6*. In agreement with the previous analysis the variation of the hole distribution with temperature should strongly depend on the presence and nature of chain interaction.

o-Ps intensity and hole densities.

The analysis of a time annihilation spectrum supplies, for each component, its relative intensity. The intensity of the longest component, I_3, is generally correlated to the density of holes N_h which can be considered as a kind of trapping centres for Ps. Such a correlation has a firm experimental basis. For instance, a PALS study on PEEK (poly aryl-ether-ketone) indicates that I_3 is directly proportional to the whole-sample average concentration of free volume holes, that is, the percentage of amorphous material present[32]. PALS studies in poly(vinyl acetate) also suggest that I_3 is proportional to the number of the holes per unit volume[33]. Although the exact functional dependence of the hole density N_h on I_3 is not known, we can follow the usual assumption of a linear dependence between N_h and I_3, which is consistent with the results of recent experiments[34,35]. In *Figure 7* the intensity I_3 is shown as a function of the temperature, for all the investigated polymers. Three temperature regions corresponding to the change in the I_3 trend can be distinguished: in the low temperature region the intensity I_3 increases with T; such an increase appears linear, from the lowest investigated temperatures. Near T_g and above it, I_3 remains constant, for a region roughly corresponding to the 'rise' of τ_3; at 'high' T, I_3 starts to increase again.

The interpretation of this experimental data, according to the above-mentioned assumption, is that the density of holes increases linearly with the temperature when the polymer is in the glass-like state; it becomes constant in the temperature interval (T_g,$T_g + \Delta T$); then, it starts to increase at the highest temperatures. It is difficult to properly explain the increase of I_3 beyond the plateau. However it may be suggested that the hydrogen bonds of the hard domains, present in an amorphous matrix, could be destroyed by heating the polymer above T_g[36]: in this event the polymer segments reach further mobility and hole formation is favoured. The d.s.c. of PU 400, when performed at high heating rates (0.33 K/s), shows a small thermal effect at around 340 K that could be attributed to hydrogen bond breaking. The values of ΔT for the plateau depend on the polymer and the following values can be measured: $\Delta T_{PU400} \approx 100$ K; $\Delta T_{PU1200} \approx 75$ K; $\Delta T_{PU2000} \approx 50$ K: it is quite easy to remark that the temperature interval where the I_3 is constant increases with the density of cross-linking. The trend in I_3 values adds information to the previous discussion on the hole volume behaviour throughout the glass transition temperature: the transition from the glassy state to a rubber-like state not only implies a strong increase of the amplitude of the motion at molecular scale but also an end to the increase in the number of holes. In the case of the PU studied, the thermal energy given to the system in the neighbourhood of T_g will be distributed mainly to increase the volume of the holes, not their number.

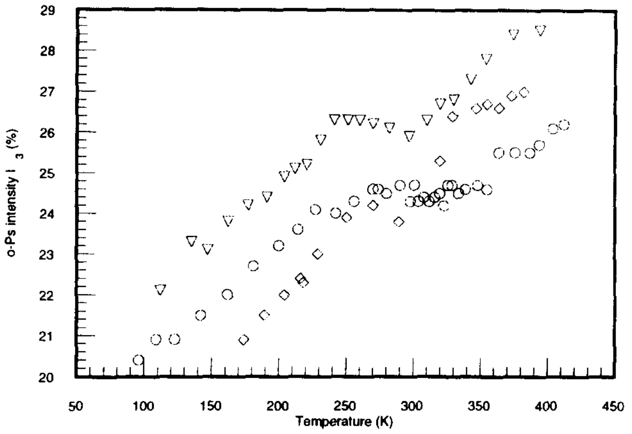


Figure 7 *o*-Ps intensity (%) for the investigated PU against the temperature (K). The symbols have the same meaning as in *Figure 1*

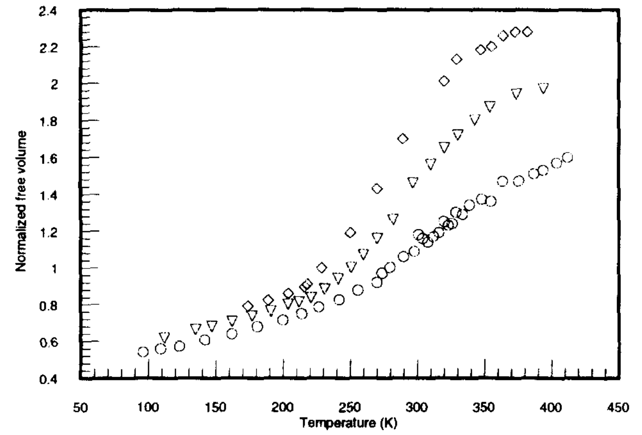


Figure 8 Normalised fractional free volume ($f(T)/f(T_g)$) in the different PU networks as a function of temperature (K). Symbols have the same meaning as in *Figure 1*

Free volume fraction and thermal expansion coefficient.

From the reported data, the fractional free volume $f(T)$ trend at the different temperatures can be evaluated: indeed, the free volume V_f is assumed to be proportional both to the density of holes and to the average volume of each hole:

$$f(T) = \frac{V_f}{V_t} = \frac{N_h V_h}{V_t} = \frac{C I_3(T) V_h(T)}{V_t} \qquad (3)$$

The values of $f(T)/f(T_g)$ *versus* T are reported in *Figure 8* for the different polymers; we can observe a sigmoid behaviour, with markedly different slopes above, below and in the central region of the glass transition. The functional dependence of $f(T)$ on T is partially in agreement with W.L.F. free volume theory, which predict that going beyond the T_g region, the free volume changes from a constant value (2.5% of the specific volume) at $T \leq T_g$ to higher values which increase linearly with $\Delta = T - T_g$ and the dilatation coefficient of the free volume, $\alpha_f = (1/V_f)(dV_f/dT)$, is about twice the dilatation coefficient of the glassy phase. The W.L.F. equation is based on the above model and is accepted above T_g. Below T_g[26] the free volume is assumed not to be constant but to change slowly as a function of T and of the duration of the experiment.

The total volume V_t of a polymer may be expressed as the sum of the occupied volume V_o and the free volume V_f. The thermal expansion coefficient α_V is defined as:

$$\alpha_V = \frac{1}{V_t}\frac{dV_t}{dT} = \frac{d\ln(V_t)}{dT} = \frac{d\ln(V_o + V_f)}{dT}$$

$$= \frac{d\ln[V_o(1 + V_f/V_o)]}{dT}$$

$$\alpha_V = \alpha_o + \frac{d}{dT}\left(\frac{V_f}{V_o}\right) \tag{4}$$

where $\alpha_o = (1/V_o)(dV_o/dT)$ is the thermal expansion coefficient of the occupied volume (or van der Waals volume); in the last passage it is supposed $V_f < V_o$.

By developing the derivative one gets:

$$\alpha_V = \alpha_o\,\frac{1-2f}{1-f} + \alpha_f\,\frac{f}{1-f} \tag{5}$$

which, by taking only linear terms in f, assumes the following expression:

$$\alpha_V = \alpha_o(1-f) + f\alpha_f \tag{6}$$

The first term at the second member is the contribution to the volumetric expansion coefficient due to the volume occupied by the atoms while the second one is the contribution due to free volume.

According to the equation (3) and the definition of α_f one gets:

$$\alpha_f = \left[\frac{d\ln I_3}{dT} + \frac{d\ln V_h}{dT}\right] = \beta_I + \alpha_h \tag{7}$$

The contributions to the free volume expansion coefficient are due to the variation of the number of holes (β_I) and of the hole volume (α_h) and are reported in *Table 2*. The behaviour of α_h and β_I is different for the various temperature ranges. At $T < T_g$, $\alpha_h > \beta_I$; on the other hand, in the intermediate temperature range, α_h increases whilst β_I is zero; indeed, according to the previous discussion, the glass transition region is characterised by the increase of the hole volume, the number of holes remaining constant. At higher temperatures, the hole volume contribution α_h decreases to values less than those found in the glassy state, conversely β_I assumes the values found at low temperature range.

Table 2 Thermal coefficient (K^{-1}) for the holes α_h and for the number of holes β_I evaluated in different temperature ranges

	Low temperature		Middle temperature		High temperature	
	α_h	β_I	α_h	β_I	α_h	β_I
PU 400	4.0	1.1	7.4	—	3.0	1.1
PU 1200	2.8	1.2	10.4	—	0.7	1.3
PU 2000	2.9	1.3	13.0	—	0.7	1.5

All the values have been multiplied by 10^3

Table 3 Contribution to the thermal expansion coefficient α_V of the free volume $\alpha_f \times 10^4$ evaluated in different temperature ranges for the PUs studied

	Low temperature	Middle temperature	High temperature
PU 400	1.3	1.8	1.0
PU 1200	1.0	2.6	0.5
PU 2000	1.1	3.2	0.6

According to the W.L.F. theory at $T = T_g$ the free volume fraction is equal for all solids: $f(T_g) = 0.025$. By assuming that this value holds also near around the T_g value, one gets the values of the contribution of the free volume expansion coefficients, $f\alpha_f$ (*Table 3*), to the volume expansion coefficient. The values reported in *Table 3* are in the range of the volume expansion coefficient for polymers.

CONCLUSION

The variation of the total free volume in a polymer with temperature is determined by the variations of the number of free volume holes and of the hole volume. It is thus possible to define a coefficient of thermal expansion of the free volume α_f as a sum of two contributions: the first one β_I due to the increase of the number of holes, and the second one α_h to the increase of the hole volume.

Both the thermal expansion coefficient β_I and α_h are constant in some temperature range, a change in their value occurring when a glass-like transition takes place in the polymer. Alternately stated, when a glass-like transition occurs in the polymer a variation in the values of the thermal expansion coefficient related to the number of holes and/or to the hole volume can be expected. Obviously with a macroscopic experimental technique, such as d.s.c. or dilatation measurements, only the global phenomenon is observed and no detailed information can be obtained on the transition phenomena at molecular level. The study of transitions on a microscopic scale, with a technique such as PALS that uses an atomic probe, seems to be suitable to give more fundamental information on what occurs at a molecular scale.

For the polyurethanes under investigation it is possible to say that at $T < T_g$, by increasing the temperature, the thermal energy is distributed either to increase the volume of the holes (*Figure 1*) (external work), or to overcome the van der Waals forces and create new holes (internal work). From the analysis of the lifetime distribution of the longest component it is possible to obtain the hole volume distribution function, the values of which are narrowly distributed around the centroid. As the temperature approaches T_g, the thermal energy shifts to external work, and at $T > T_g$ all the thermal energy is used to increase the volume of the holes, not their number, the hole volumes increase significantly and their values are smoothly distributed around the centroid of the distribution function. By further increasing the temperature, the constraint due to the cross-linking becomes active and curbs the further increase of hole volume. The thermal energy shifts from external work to an internal one, and the number of holes starts to increase again. A new glass-like transition also occurs as revealed by d.s.c. analysis under proper conditions.

The analysis of the distribution function of the hole volume at high temperature (*Figures 4–6*) reveals that the values are less dispersed around the centroid: this suggests that the increase of the mean value of the volume is mainly due to the increase of smaller hole volumes rather than an effective increase of the volume.

We would like to add the following critical remark. Since

o-Ps lifetime $\tau_3 > 0.5$ ns, PALS is able to detect only hole diameters > 0.34 nm; therefore, this technique cannot be expected to reveal contributions to the volume expansion induced by fast chain vibrations. This means that, at sufficiently high temperature, the segmental motions in a polymer probably become so fast that Ps can easily be excluded from part of the free volume sites. Such polymer expansion, which is not detected by Ps, could require a critical reflection on the general validity of equation (3), as well as, in our particular case, of the given explanation in term of 'saturation' of τ_3 at high temperature induced by the presence of cross-linking. To this purpose, work is in progress in our laboratories for the synthesis of linear PU membranes and their characterisation by PALS.

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