PII: S0032-3861(97)00267-X

Polymer Vol. 39 No. 2, pp. 339-345, 1998
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0032-3861/97/$17.00+0.00

Effects of crosslink density on the volumetric properties of high T_g polycyanurate networks. Consequences on moisture absorption

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(Received 23 December 1994; revised 23 May 1996)

Polycyanurate networks, based on the dicyanate of bisphenol A monomer, were synthesized with different extents of reaction ranging from 80% to 100%. The effects of conversion, as measured by d.s.c., on the volumetric properties in the glassy state were investigated. The variations in density, packing density and coefficient of volume expansion were evaluated and then compared with the free-volume holes deduced from positron annihilation spectroscopy lifetime and to moisture absorption. Amongst the various reasons that could explain the large density variation, steric hindrance is the dominant factor: the bulky triazine crosslinks are responsible for the increase in free-volume holes which occurs as the conversion increases and controls the water uptake. © 1997 Elsevier Science Ltd.

(Keywords: cyanate; polycyanurate; volumetric properties)

INTRODUCTION

Cyanate compounds were first successfully synthesized in the early 1960s. The method involved reaction of a phenol and a cyanogen halide in the presence of a base in which an excess of phenoxide was avoided at all stages of conversion[1]. Currently, various cyanate ester monomers and their prepolymers are commmercially available, but the most commonly in use is based on the dicyanate of bisphenol A (DCBA) (*Figure 1*). When heated, the cyanate's functionality (–O–C≡N) undergoes an exothermic cyclotrimerization reaction to form a triazine ring connecting unit (*Figure 1*). This is a step-growth network building process, the reacting system passes through a pregel state characterized by a broad distribution of oligomers to reach gelation at a critical conversion. Finally, a thermoset polycyanurate network is formed. The resulting network has many interesting properties, such as high glass transition temperature (250–300°C), high toughness, low moisture absorption, good thermal stability, low dielectric constant and strong adhesion to metals[2]. This combination of properties is unusual in 250°C T_g resins and commends its use in high performance, technological applications, i.e aerospace and electronic industries.

However, being a thermoset material, the properties described above are directly linked to the value of the crosslink density which could be varied by adding a monofunctional cyanate[3] or by changing the curing cycle. This last case is more representative of industrial processes: owing to the high final T_g of a polycyanurate, high temperatures of curing are needed to reach full conversion of the cyanate functionality. If this condition is not met, the reaction becomes diffusion-controlled as soon as the glass transition temperature of the growing network reaches the curing temperature. As a consequence, only partially cured networks are obtained. We aim at establishing the relationships between crosslink density and properties. We have focused on volumetric, mechanical and viscoelastic behaviour in the glassy state. These two last tasks will be reported in future papers. One interesting question concerns the effect of the residual cyanate groups on the volumetric properties. Only very limited studies have been reported on polycyanurate networks[4,5] and they do not explain the mechanisms responsible for the variation of the density and their consequences on moisture absorption and mechanical behaviour. However, numerous results can be found on epoxy networks. Depending on the variable taken to change the crosslink density, opposite trends have been observed. In the specific case where the extent of cure increased, the room temperature density decreased[6–9]. It is often assumed that these variations are mainly due to the poorer packing of molecules imposed by crosslinks. The bulky crosslinks of polycyanurate networks may increase this phenomenon. As molecular packing and physical properties are linked, it is expected that the study of volumetric properties can lead to a clearer understanding of the relationship between both parameters.

EXPERIMENTAL

Network synthesis

Polycyanurate networks were all based on the DCBA (Ciba–Geigy, Arocy B10) cured either with a catalyst (2 phr of nonylphenol and 200 ppm of copper from copper acetylacetonate) or without a catalyst. Curing cycles are reported in *Figure 2*. They were chosen in order to obtain cyanate conversions, *x*, ranging from 80% to 100%. The samples were then allowed to cool slowly down to room

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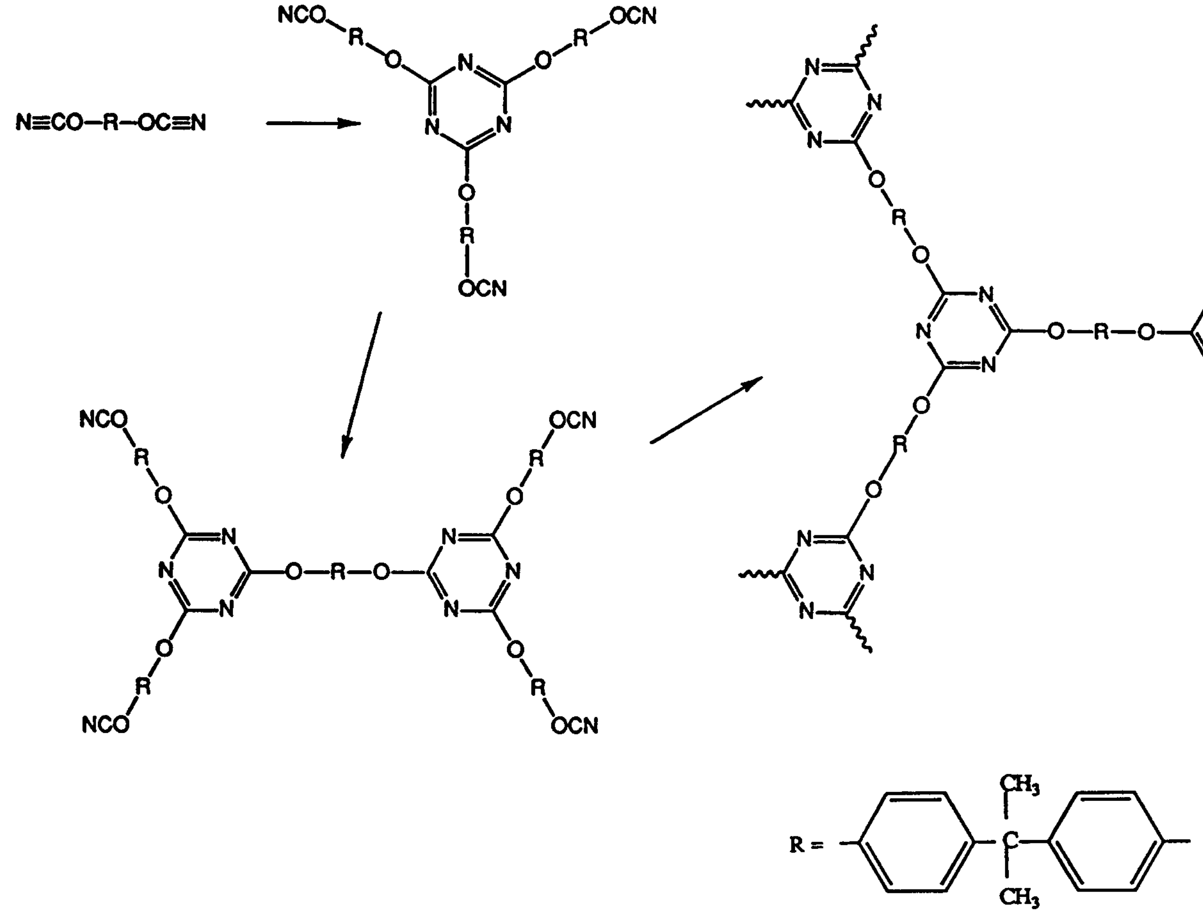


Figure 1 Monomer structure and network formation

temperature. Kinetics studies on the same system have already been reported[10]. A one-to-one relationship between conversion and glass transition temperature was found for both uncatalysed and catalysed systems, independent of cure temperature, meaning that the same network is produced. T_g was therefore used as the most sensitive parameter to measure conversion.

Techniques

Glass transition temperature. T_g was obtained using a Mettler TA3OOO instrument, running at 10°C min^{-1} under argon.

Density. The densities (average value over three measurements) of the cured networks were determined using the Archimedes's method, at room temperature.

Coefficient of volume thermal expansion. The linear thermal expansion coefficient in the glassy state (α_g) was evaluated using a Mettler TA3000 TMA4O apparatus. Since α_g is very small and assuming that the sample is isotropic, the coefficient of volume thermal expansion α_{gv} is given by: $\alpha_{gv} = 3\alpha_g$.

Positron annihilation lifetime spectroscopy. Positron annihilation lifetime spectroscopy (PALS) is a non-destructive molecular probe used to measure the free-volume hole properties in polymeric materials[11–13]. In polymers, positrons combine with electrons to form positronium atoms, Ps. The orthopositronium survives up to a few nanoseconds in the free-volume holes a few ångströms in size. The lifetime of o.Ps, τ_3, is related to the hole size in which it is thermalized and the corresponding intensity I_3 contains information about the free-volume concentration. The following semi-empirical equation was used to correlate τ_3 and the hole radius R, expressed in nanoseconds and ångströms, respectively:

$$\tau_3 = \frac{1}{2}\left\{1 - \frac{R}{R+\Delta R} + \frac{1}{2\pi}.\sin\left(\frac{2\pi R}{R+\Delta R}\right)\right\}^{-1} \tag{1}$$

where ΔR is the electron layer thickness (ΔR = 1.66 Å). Positron annihilation measurements were performed using a conventional fast–slow method on the least crosslinked, uncatalysed network ($x = 0.85$). After drying at 130°C, intensity I_3 and lifetime data were measured at both −196°C and 20°C. Then the sample was successively post-cured *in situ* in the apparatus in order to minimize scattering in the data due to sample geometry. At each step, I_3 and τ_3 were recorded and the increase in x was independently simulated by d.s.c. Finally, the variations in I_3 and τ_3 as functions of cyanate conversion were obtained.

Moisture absorption. The specimens were dried at 30°C under vacuum until a constant weight was obtained prior to immersion in distilled water at 80°C. Water uptake was recorded by weighing the sample after different times of exposure. The percentage gain at any time was determined by

$$M(\%) = \frac{W - W_d}{W_d} \times 100 \tag{2}$$

where W_d and W denote weight of dry material and weight of moist material.

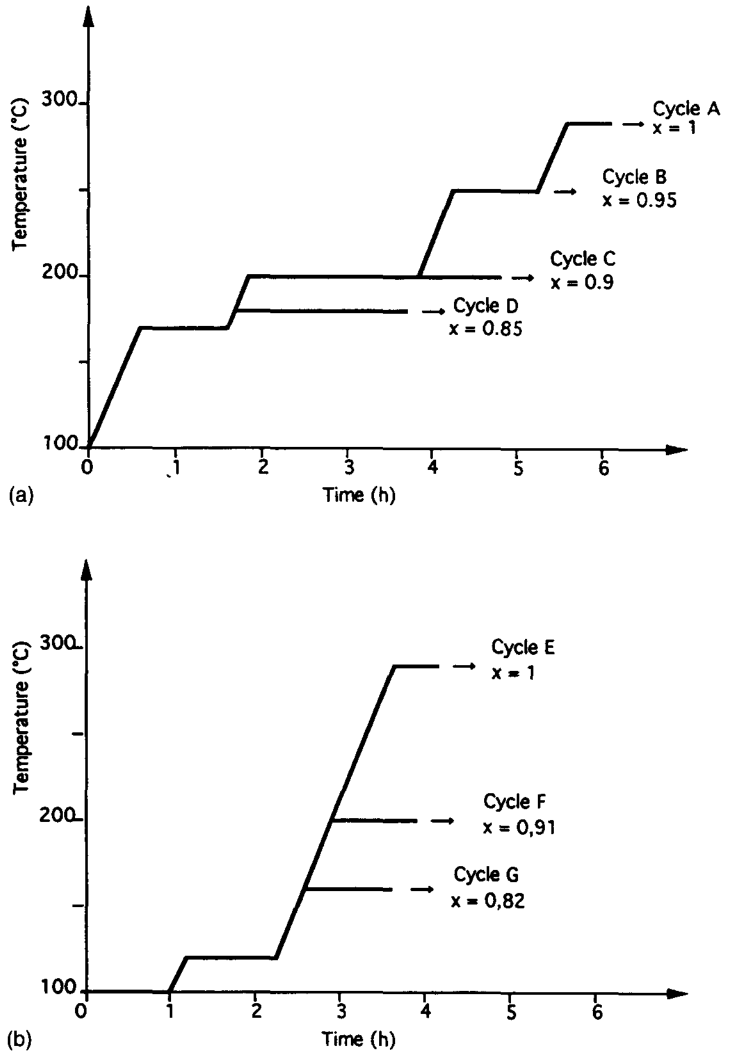


Figure 2 Curing cycle: (a) uncatalysed networks; (b) catalysed networks

Infrared spectroscopy. *FTi.r.* measurements were made using a Nicolet MX-I spectrometer with KBr pellets containing the finely ground material. Structural changes could be evidenced by following the absorption bands of $-C{\equiv}N$ at 2270–2240 cm^{-1}, and the triazine ring at 1366 cm^{-1} and 1566 cm^{-1}.

RESULTS AND DISCUSSION

Sample characteristics

The crosslink density, X, is defined by the number of moles of triazine ring per kilogram of product in which each of the three arms goes to infinity. If one of these conditions is not obeyed, the triazine ring acts as a chain extender, if two of these conditions are not observed the triazine ring becomes included in a free chain end. X was calculated *versus* conversion by following the method developed by Georjon *et al.*[14]. The values of T_g, cyanate conversion x, calculated crosslink density X, and thermal expansion coefficients α_{gv} are shown in *Table 1* for the two series of networks. As expected, the first three variables follow the same variations. However, a small variation in conversion ($\Delta x = 18\%$) results in a considerable increase in both crosslink density and T_g, as mentioned previously[10,14]. The thermal expansion coefficients in the glassy state show a slight decrease as the crosslink density is increased.

Density

The density data, ρ, as a function of conversion are presented in *Figure 3* and *Table 1*. Samples with the highest conversion have the lowest density. If this result is not striking by itself, the large-scale of variation in ρ is worth noting (about five times as great as the variation in epoxy networks). Catalysed networks show a slightly lower density than uncatalysed networks. The extrapolated density at 0 K or at T_g can be calculated using the value of the thermal expansion coefficient. The result is that the variation in ρ with the conversion is the same whatever the temperature between 0 K and T_g.

The different factors influencing the density values are:

- The atomic composition: but obviously it is the same for all the polycyanurates under study.
- Hydrogen bonding: from the observation that an amine excess leads to a density increase in epoxy–aromatic amine networks, hydrogen bonding was suspected to be one of the parameters responsible for the variation in ρ[15]. The triazine ring may be envisaged as a hydrogen bond acceptor but since there is no donor site in polycyanurate, hydrogen bonded interactions can be excluded.
- Structural relaxations occur as the polymer ages because the free volume decreases slowly towards its equilibrium value and a decrease in specific volume is observed. As the different cyanate networks were cured just above their

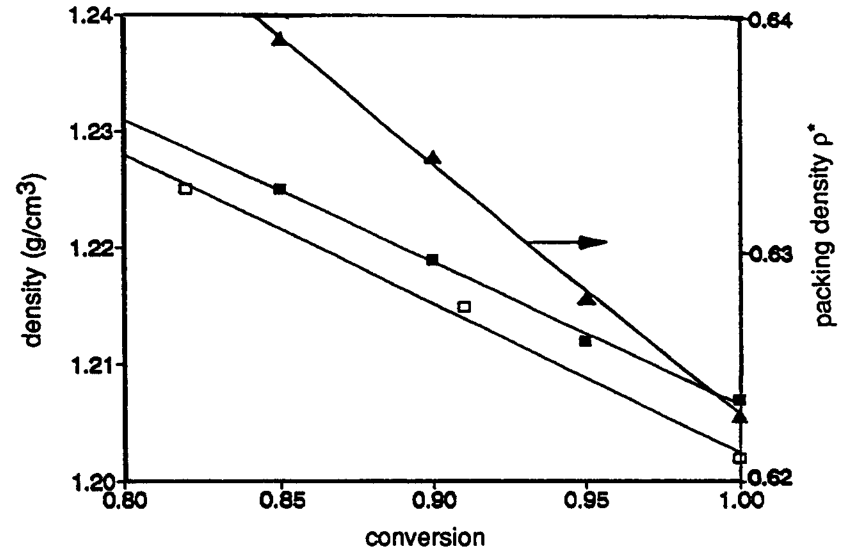


Figure 3 Density values as a function of conversion (at room temperature): ■, uncatalysed networks; □, catalyzed networks; ▲, packing density of uncatalysed networks

Table 1 Main characteristics of polycyanurate networks

Curing cycle	A	B	C	D	E	F	G
T_g (C)	290	265	212	168	275	202	149
x (d.s.c.)	1	0.96	0.91	0.85	1	0.91	0.82
X (mol/kg)	2.39	1.94	1.52	1.14	2.34	1.57	0.91
ρ_{exp} (25°C)	1.207	1.212	1.219	1.225	1.202	1.215	1.225
ρ_{cal} (25°C)	-	-	-	-	1.200	1.211	1.221
α_{gv} (10^{-4} K^{-1})	1.55	1.67	1.68	1.78	1.58	1.65	1.75

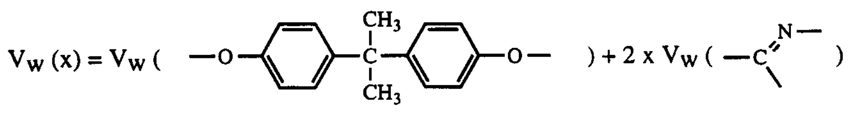
Curing cycle, see *Figure 2*; T_g, glass transition temperature (d.s.c.); x, conversion of cyanate group; X, theoretical crosslink density; ρ_{exp}, density measured at 25°C; ρ_{cal}, theoretical density of catalysed networks; α_{gv}, thermal expansion coefficient in the glassy state

final T_g and quenched in the same way, the density tends towards its maximun value for a given conversion and it cannot be influenced by physical ageing.

- Change of Van der Waals volume during polymerization. Van der Waals volume and density are related each other through the packing density:

$$\rho^* = \frac{V_w}{V_m} = \rho.\frac{V_w}{M} \tag{3}$$

where M is the molar mass of the monomer unit and V_m is the molar volume. From this equation, the decrease in ρ could be explained either by an increase in V_w or a decrease in packing density ρ^*. The Van der Waals volume of a partially cured polycyanurate can be calculated by the following relation:



$$V_W(x) = V_W(\text{—O—C}_6\text{H}_4\text{—C(CH}_3)_2\text{—C}_6\text{H}_4\text{—O—}) + 2\,x\,V_W(\text{—C}\overset{\text{N—}}{\diagup}\diagdown) + 2\,(1\text{-}x)\,V_W(\text{—C}\equiv\text{N}) \tag{4}$$

The individual group values of V_w given by Bondi[16] or the Sybyl software from Tripos have been used. The Van der Waals volume is equal to 123.71 cm^3/mol for a bisphenol unit (without H), 14.7 cm^3/mol and 9.94 cm^3/mol for a –C≡N group and for a –C=N– group (in a triazine ring), respectively. Therefore, the variation in V_w at 293 K as a function of x will be given by:

$$V_w(x) = 123.71 + 9.94 \times 2 \times x + 14.7 \times 2 \times (1 - x) \tag{5}$$

$$V_w(x) = 153.11 - 9.52x. \tag{6}$$

The formation of a triazine ring from three cyanate functions leads to a decrease in V_w as generally observed in the case of cycle formation[16]. It should be noticed that the opposite change is observed during the formation of epoxy networks in which the epoxy cycle is opened to form a hydroxy–ether unit[6,17]. The data on packing density are presented in *Figure 3*. They show that the more highly crosslinked samples have the lower packing densities.

- Finally, the main parameter which can explain the density variation is the packing effect. The bulky crosslinks do not provide a suitable environment for the close packing of chains. Consequently, more 'free volume' may be trapped in the network as the conversion (or crosslink density) increases. The problem of quantifying the free volume and defining it in terms of measurable quantities can be done using different approaches but often leads to a lack of consistency. The next section will present an approach based on positron annihilation spectroscopy.

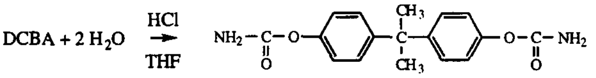
Catalysed networks show lower densities than uncatalysed networks. The low density of nonylphenol, 0.937 g cm^{-3}, contributes to the decrease in ρ. However, with the hypothesis that a catalysed network is a blend of uncatalysed network and nonylphenol, and their respective volumes are additive, the theoretical density, ρ_{cal}, of catalysed networks can be calculated (*Table 1*). The decrease in ρ_{exp} as x is increased appears lower than it should be if we compare the values of ρ_{exp} to ρ_{cal} evaluated using an additive blend law. This result may be explained by the fact that the long aliphatic chains of nonylphenol partially fill the empty volumes.

Positron annililation lifetime spectroscopy

All PALS spectra were resolved into three lifetime components. The orthopositronium intensity I_3 is constant ($I_3 = 21.5\%$) whatever the conversion or the temperature of measurements. It means that the number of individual volumes, reflected in I_3, is the same. As shown in *Figure 4* and *Table 2*, τ_3 increases as the conversion and the temperature increase. Average void dimensions can be calculated using equation (1). Variations in the equivalent sphere cavity radius are from 0.29 to 0.33 nm at room temperature, the highest radius being obtained for the fully cured network. It reflects the lower ability of the chains to achieve good packing. Indeed the mean free-volume radii of polycyanurate are higher than those observed in epoxy/amine networks. For a given conversion, τ_3 and R are lower at 77 K than at room temperature. As we did not observe a large variation in the thermal expansion coefficient in the glassy state, it is, therefore, expected that similar variations in τ_3 and R are obtained as a function of conversion. The use of a single value to describe the void size is not strictly correct, because holes are distributed in size. However, we did not extract the lifetime distribution from our data as suggested in the literature[18]. The values of the free volume fraction f can be expressed as a product of free volume V_f (as deduced from τ_3) and I_3 as $f = V_f.A.I_3$, where A is a constant. Generally, I_3 values are not the same as f. They could be enhanced by a factor of 1 to 10 depending on the type of polymer[12]. The value of A is unknown for polycyanurate, so f cannot be calculated. We can only conclude that the free volume fraction increases with the conversion because a constant value was found for I_3.

Moisture absorption

Figures 5 and 6 show the percentage moisture absorption M of both uncatalysed and catalysed polycyanurate networks, as a function of $t^{1/2}/e$. The initial linear relationship between M and $t^{1/2}$ is clearly observed in each case. However, for a long time there is evidence of continuing absorption, showing that equilibrium has not been reached. For higher conversions, i.e more complete cure, the amounts of absorption increased. This behaviour is slightly less pronounced for the catalysed networks. It can also be noticed that the larger deviation from an equilibrium absorption value is observed for the less crosslinked networks. It is known that water can react with a cyanate group[19,20] to form carbamate after the rearrangement of an iminocarbonic acid intermediate.



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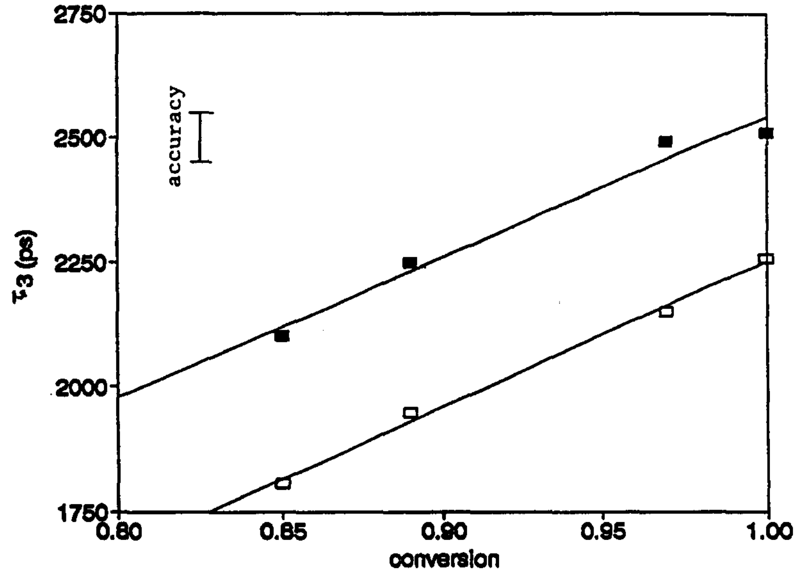

Figure 4 τ_3 variations as a function of conversion in uncatalysed networks: ■, 293 K; □, 77 K

Table 2 Characteristics obtained by positron annihilation lifetime spectroscopy

x	0.85 (without drying)	0.85 (after drying)	0.89	0.97	1
τ_3 (ps) 273 K	2052	2101	2249	2491	2509
τ_3 (ps) 77 K	1796	1806	1947	2149	2257
R (nm) 293 K	0.290	0.295	0.307	0.327	0.328
R (nm) 77 K	0.266	0.267	0.281	0.299	0.308

x, conversion of cyanate group; τ_3, lifetime of o.Ps; R, hole radius.

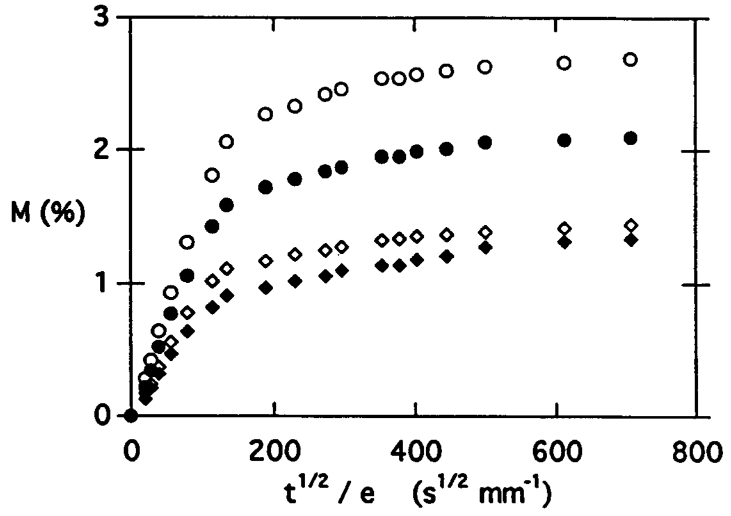

Figure 5 Plots of M *versus* $t^{1/2}/e$ for uncatalysed networks (e, sample thickness in mm): ◆, $x = 0.85$; ◇, $x = 0.90$; ●, $x = 0.95$; ○, $x = 1$

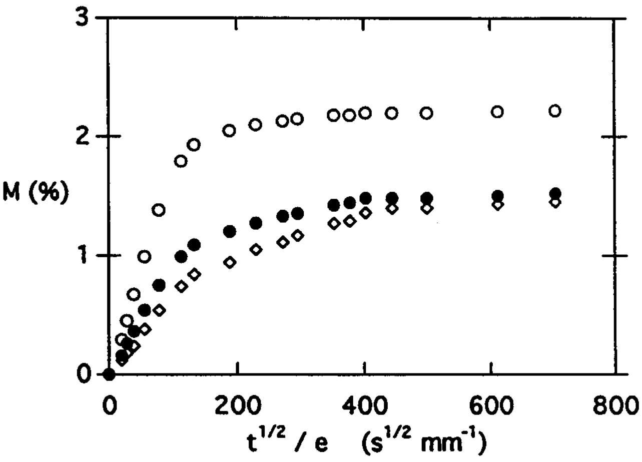

Figure 6 Plots of M *versus* $t^{1/2}/e$ for catalysed networks (e, sample thickness in mm): ◇, $x = 0.82$; ●, $x = 0.90$; ○, $x = 1$

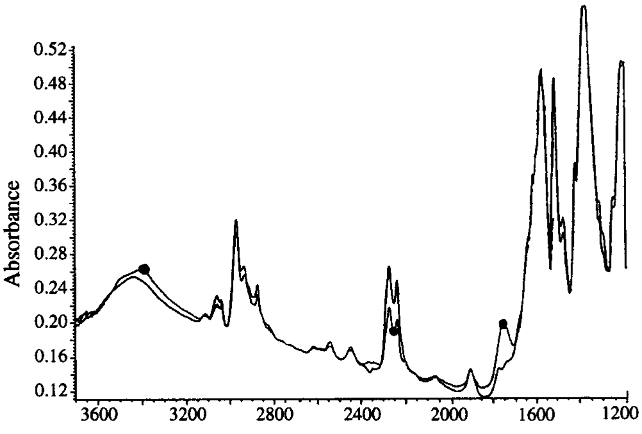

Figure 7 Infrared spectra of dry partially cured network as compared to an aged sample (•)

The i.r. spectra of the partially cured network, $x = 0.85$, before and after hygrothermal ageing at 80°C are plotted in *Figure 7*. There is a clear decrease in the absorbance of the cyanate group at 2240–2270 cm^{-1} but without any increase in the peak corresponding to the triazine ring (1366 and 1566 cm^{-1}). However, a –C=O peak appears at 1750 cm^{-1} as well as a –NH shoulder at 3400 cm^{-1}. These chemical modifications are explained by the formation of carbamate. The same behaviour is observed with a partially cured catalysed network but not with a fully cured network. The rate of formation of carbamate is low whatever the type of polycyanurate network: it is not in evidence after 2 days of immersion in water, although the sample has absorbed 75% of its total mass of water.

This reaction may have several consequences on the final structure of the network when an aged sample is post-cured. If a partially cured saturated sample is post-cured, carbamate might undergo thermal decomposition[20] and produce structural defects.

Hygrothermal ageing has two sources: one results from chemical interactions between the penetrating water and the hydrophilic groups of the polymer, the other is due to appropriate size holes. In the first case a swelling of the sample is noticed, whereas no changes in dimension are evidenced in the second case. In our case, both explanations seem, a priori, correct. On the one hand, Snow[21] has shown that hydrogen bonding with triazine is stronger than with a cyanate group. Therefore, the increase in water absorption with an increase in conversion is expected. On the other hand, we have found that the free volume fraction increases with the conversion, which also explains the behaviour of the water absorption. In order to find out which of the two hypotheses is true, the variation in the volume of a sample, Δv, has been measured twice: a day after (end of the linear part of the curve) and a month after. *Figure 8* shows the results of these measurements plotted as a function of the volume of water absorbed, V_{H_2O}. After 24 h of hygrothermal ageing, no change in the macroscopic volume of a network is observed, whatever the conversion is, meaning that water molecules are only inside the free holes of the material. At this stage, water uptake is directly linked to the free-volume fraction, which increases with the conversion. After 1 month of exposure in water, the volume of all the samples has increased. Such an increase is explained by chemical interactions between water and triazine rings by hydrogen bonding. These interactions explain the deviation from the Fickian behaviour that we noticed previously. However, chemical interactions are a second-order parameter as compared with the volumetric approach. The opposite point of view is generally used to explain water absorption in epoxy networks: in that case hydrogen bonding is the main

Table 3 Effects of moisture absorption on the glass transition temperature

x(%)	100	95	90	85	C*100	C*91	C*82
T_{gdry} (°C)	293	265	212	168	275	202	149
ω_{H_2O}%	2.62	2.06	1.43	1.32	2.17	1.44	1.39
T_{gwet} (°C)	252	221	188	159	235	178	146
T_{gFox} (°C)	248	233	194	155	240	185	136

x, conversion of cyanate group; T_{gdry}, glass transition temperature of dry networks; w_{H_2O}, wt% of absorbed water; T_{gwet}, glass transition temperature of wet networks; T_{gFox}, glass transition temperature calculated using the Fox law; C*, catalysed networks

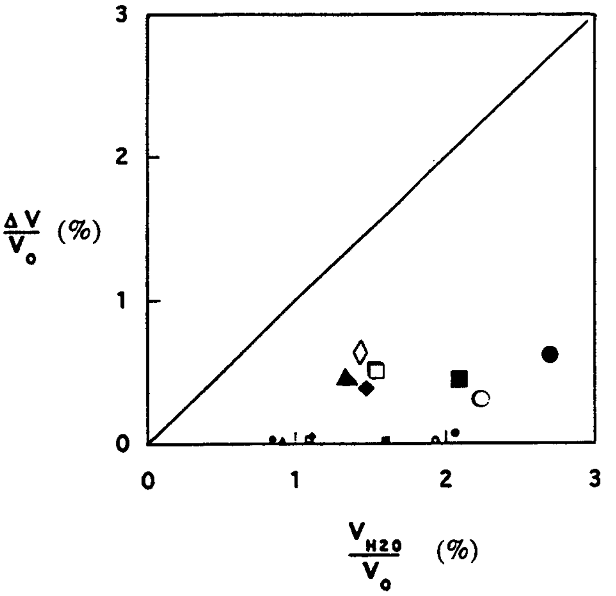

Figure 8 Variation in $\frac{\Delta V}{V_0}$ as a function of $\frac{V_{H_2O}}{V_0}$: small symbols, 1 day of immersion in water; large symbols, 1 month of immersion in water; ▲, $x = 0.85$; ◆, $x = 0.90$; ■, $x = 0.95$; ●, $x = 1$; ◇, $x = 0.82$; □, $x = 0.90$; ○, $x = 1$

parameter. The small variation in the sample volume due to the hygrothermal ageing is of a great interest from a technological point of view, because it means that there is no change in dimension as the sample undergoes water desorption.

The effect of moisture absorption is clearly evidenced in the value of the glass transition temperature measured after 1 month of ageing (*Table 3*). As expected, a decrease in T_g is observed: the more highly crosslinked networks exhibit the higher decreases in T_g. The combination of two reasons explain this fact: first, $T_{g(dry)}$ is higher, second, water absorption is higher. The value of T_{gwet} can be calculated using Fox's law:

$$\frac{1}{T_{gwet}} = \frac{w_{H_2O}}{T_{gH_2O}} + \frac{1 - w_{H_2O}}{T_{g(dry)}}$$

where $T_{gH2O} = -140$°C. The general trend of variation in T_g as a function of conversion is followed, but the fit to experimental values is not very good. The largest deviation is equal to 12°C. The deviations can be explain by the fact that the model does not take into account chemical interactions and chemical structural changes.

CONCLUSIONS

In this study, the effects of conversion (i.e. crosslink density) on the room temperature volumetric properties of polycyanurate networks have been investigated. The DCBA monomer was cured using different curing cycles: as extent of conversion increased, T_g increased, Van der Waals volume, packing density and density all decreased, and water absorption increased. The increase in free-volume holes with conversion has been measured using positron annihilation lifetime spectroscopy and can be explained by the presence of bulky triazine crosslinks which do not provide a suitable environment for close packing. In such networks, the free volume is considered to control the amount of water absorbed and this is accompanied by limited swelling of the network.

ACKNOWLEDGEMENTS

The authors thank the DGA/DRET (Délégation Générale de l'Armement/Direction des Recherches et Techniques) and the Aerospatiale for financial support. The assistance from M. Moser of CENG (Centre d'Etude Nucléaire de Grenoble) for PALS measurements is gratefully acknowledged.

REFERENCES

1. Grigat, E. and Putter, R., *Chem. Ber.*, 1964, **97**, 3012.
2. Shimp, D. A., Christenson, J. R. and Ising, S. J., in *34th SAMPE.* Symposium, Reno, NV, 1989, p. 222.
3. Cozzens, R. F., Waliter, P. and Snow, A. W., *J. Appl. Polym. Sci.*, 1987, **34**, 601.
4. Armistead, J. P. and Snow, A. W., *Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1992, **66**, 457.
5. Armistead, J. P. and Snow, A. W., *Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1994, **71**, 819.
6. Gupta, V. B. and Brahatheeswaran, C., *Polymer*, 1991, **32**, 1875.
7. Jordan, C., Galy, J. and Pascault, J. P., *J. Appl. Polym. Sci.*, 1992, **46**, 859.
8. Enns, J. B. and Gillham, J. K., *J. Appl. Polym. Sci.*, 1983, **28**, 2831.
9. Arohime, M. T., Peng, X. and Gillham, J. K., *J. Appl. Polym. Sci.*, 1986, **32**, 3589.
10. Georjon, O., Galy, J. and Pascault, J. P., *J. Appl. Polym. Sci.*, 1993, **49**, 1441.
11. Deng, Q., Sundar, C. S. and Jean, Y. C., *J. Phys. Chem.*, 1992, **96**, 492.
12. Deng, Q. and Jean, Y. C., *Macromolecules*, 1993, **26**, 30.
13. Dai, G. H., Dolvek, J. Y. and Moser, P., *Le vide, les couches minces*, 1992, **260**, 77.
14. Georjon, O., Galy, J., Pascault, J. P. and Williams, R. J. J., *Polym. Bull.*, 1993, **31**, 503.
15. Bellenger, V., Dhaoui, W. and Verdu, J., *J. Appl. Polym. Sci.*, 1988, **35**, 563.
16. Bondi, A., *Physical Properties of Molecular Crystals and Glasses.* Wiley, New York, 1968.
17. Won, Y. G., Galy, J., Pascault, J. P. and Verdu, J., *Polymer*, 1991, **32**, 79.
18. Deng, Q. and Jean, Y. C., *Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1993, **67**, 151.
19. Shimp, D. A. and Ising, S. J., *Am.Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1992, **66**, 504.
20. Mirco, V., Mechin, F. and Pascault, J. P., *Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1994, **71**, 688.
21. Snow, A. W. and Armistead, J. P., *Am. Chem. Soc. Div. Polym. Mat. Sci. Eng.*, 1992, **66**, 508.