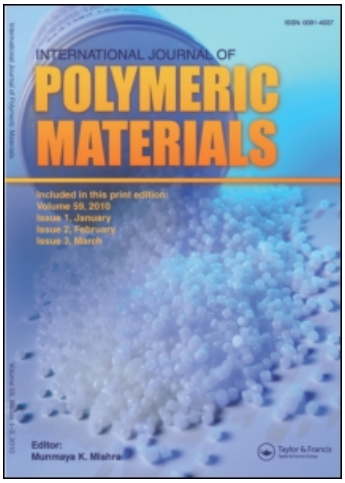

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Structure-Properties Relationships for Bisphenol A Polycyanurate Network Modified with Polyoxytetramethylene Glycol

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Structure-Properties Relationships for Bisphenol A Polycyanurate Network Modified with Polyoxytetramethylene Glycol

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A series of polycyanurate networks (PCNs), based on the dicyanate of bisphenol A monomer (DCBA), were synthesized in the presence of different contents of hydroxyl-terminated polyoxytetramethylene glycol (PTMG). The chemical structure, T_g behaviour, modulus-composition relations and mechanical properties of the modified PCNs were investigated by Fourier transform infrared (FTIR) spectroscopy, dynamic mechanical thermal analysis (DMTA) and mechanical testing. The oligomer modifier influences the structure of the final networks insofar as it is partly incorporates and partly dissolves in the polycyanurate matrix, and, thus, decreases the final T_g of these modified thermosets. All modified polycyanurate networks exhibit a single, broad glass transition that shifted to lower temperature as the modifier content was increased.

Keywords: Modified polycyanurates; Oligomer modifier; Incorporation degree; Glass transition behaviour; Solubility parameter

1. INTRODUCTION

Brittle thermosets are best toughened by the introduction of a rubbery or thermoplastic second phase [1]. The main factors which determine

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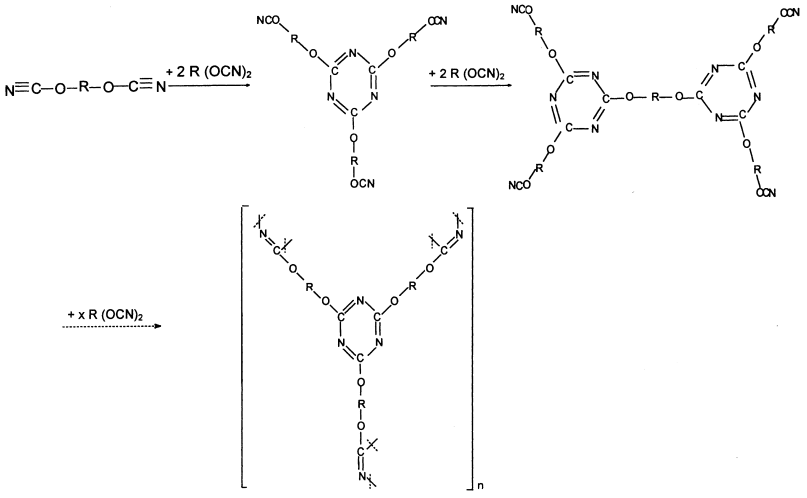
toughening effects are the final polymer blend morphology [2] and the adhesion between the two phases [3]. For initially compatible reactive systems, the latter depends not only on the chemical and physical properties of both the additive and the monomer, but also strongly on the polymerization reaction [4]. The phase separation and morphology formation are very intricate phenomena: their study remains limited up to now, and for thermosetting systems is mainly focused on rubber-toughened polyepoxy matrices [5].

A lot of interest has been devoted to new thermostable polymer matrices over the past few years. Among them, polycyanurates appear to be especially attractive thanks to their excellent dielectric properties, good dimensional stability and their high adhesion to metals up to high temperatures (typically above 250°C) [6]. Polycyanurates are synthesized by polycyclotrimerization of dicyanates.

However, the polycyanurate networks often display a somewhat poor degree of toughness. Rubbers or thermoplastics have been used to improve their mechanical properties [7–19].

Most commercial oligomeric additives bear reactive chain ends. Their ability to react with the matrix is often of great interest since



SCHEME 1 Polycyclotrimerization of dicyanate ester resins.

the effect is to improve the adhesion between phases in the case of a biphasic material, and in any case they ensure a chemical linkage between the modifier and the network. Most rubber or thermoplastic additives used have had amino-, epoxy-, phenoxy- or carboxy-end groups. Recently, the results of a study of a polycyanurate modified with polyurethane have been published [20–29], where the authors [20, 22, 28, 29] have assumed the ability of urethane groups to react with cyanate groups of the developing polycyanurate network.

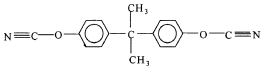
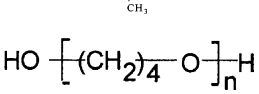
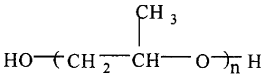
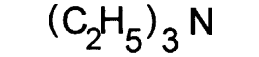
It is a purpose of this paper to study the formation of polycyanurate networks modified by hydroxyl-terminated polyoxytetramethylene glycol, and then investigate the glass transition behaviour, modulus-composition relations and mechanical properties.

2. EXPERIMENTAL

2.1. Materials and Samples Preparation

The cyanate ester monomer used in this work was the dicyanate ester of bisphenol A (DCBA, $>98\%$ purity). Triethylamine (99%) was used as the DCBA cure catalyst (3 mol.% per DCBA). The DCBA and triethylamine were used as received. The polyoxytetramethylene glycol (PTMG) was dried at 80°C under vacuum for 6 h. The cyanate ester, catalyst and polyether were mixed first together, degassed at 80°C for 0.5 h and then were poured into a PTFE-coated mould. All initial mixtures were homogeneous. The curing cycle consisted of two stages: 5 h at 150°C and 3 h at 180°C. The DCBA content was taken in excess for all compositions and the samples with DCBA/PTMG component ratios from 10/1 to 5/1, mol/mol (from 74/26 to 58/42 wt.%) were synthesised. It was impossible to prepare film samples with DCBA/PTMG component ratios smaller than 5/1. To compare the influence of the modifier structure on the polycyanurate network, polyoxypropylene glycol (PPG) was also used as the network modifier at fixed component molar ratio: DCBA/PPG = 7/1 mol/mol. The PPG was dried in the same way as PTMG. The materials used in this study are summarized in Table I.

TABLE I Chemical structures and characteristics of the monomers and additives

Component	*Chemical structure*	*Molar mass, M,* $(g \cdot mol^{-1})$
Dicyanate ester of bisphenol A (DCBA)		278
Polyoxytetramethylene glycol (PTMG)		1000
Polyoxypropylene glycol (PPG)		1050
Triethylamine		101

2.2. Techniques

2.2.1. FTIR Spectroscopy

FTIR analysis was carried out using a Unicam Mattson 3000 FTIR spectrophotometer in the mid-infrared range from 4000 cm^{-1} to 600 cm^{-1}. The degree of OCN-conversion was calculated using the height of the 2272 cm^{-1} band, which is associated with stretching vibration of cyanate group. The CH_3 peak height at 2968 cm^{-1} was used as the internal standard.

2.2.2. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were performed with a Rheometric Scientific Dynamic Mechanical Thermal Analyzer (MK II). The samples were measured in the bending mode at a fixed frequency of 10 Hz from -120 to 300°C using a heating ramp of 4°C/min. The strain was x 4.

2.2.3. Gel Fraction

The gel fractions of the network samples were determined by Soxhlet extraction in boiling acetone for 16 h (no more extract was released after 16 h of refluxing). The solution was filtered and the insoluble fraction was dried to constant weight in vacuo at 70°C. The

experimental values of gel fraction ($w_{g\ exp}$) were defined as the weight fraction of the insoluble part of PCN/PTMG composition. The theoretical value of gel fraction ($w_{g\ theor}$) was calculated using the equation obtained by Monte Carlo simulation [30] and with assumption that the unreacted PTMG must be extracted completely.

$$w_{g\ theor} = (1 - w_{PTMG}) \times (2\alpha - 1)/\alpha^2 \quad (1)$$

α is the OCN-conversion and w_{PTMG} is the weight fraction of PTMG in the initial compositions.

2.2.4. Density

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

2.2.5. Tensile Strength

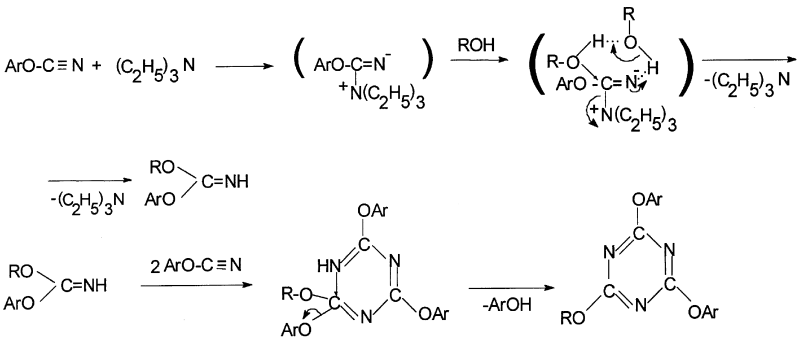
The strength characteristics at room temperature were measured using a FU-1000 test machine at a crosshead speed of 70 mm/min and the specimen dimensions were $40 \times 5 \times 1$ mm.

3. RESULTS AND DISCUSSION

3.1. FTIR Spectroscopy

According to Martin *et al*. [31] aromatic cyanates react with alcohol in the presence of triethylamine with the formation of iminocarbonate and further interaction of one molecule of the latter with two molecules of the cyanate forming six-membered cyanurate rings and elimination of a phenol:

As it can be seen from Scheme 2, the formation of a main product, the mixed cyanurate rings should result. When difunctional monomers are used, the differences are that the polycyanurate network is formed and that the structure R can be incorporated into a polymer chain between network junctions. Figure 1 shows the typical FTIR absorption spectra of (a) neat PCN and (b) the modified 5/1 (58/42 wt.%) PCN/PTMG composition. In both spectra one can see



SCHEME 2 Reaction of cyclotrimerization of aromatic cyanate in the presence of alcohol and triethylamine (as catalyst).

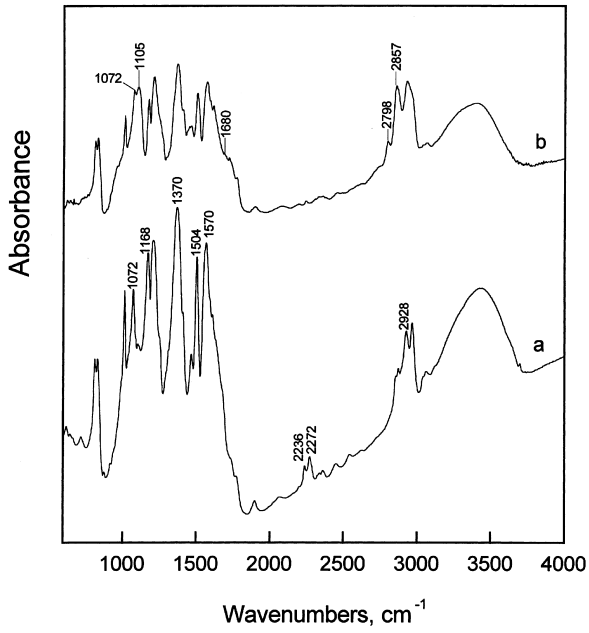


FIGURE 1 FTIR spectra for the PCN homonetwork and a PCN/PTMG composition. (a) Pure PCN and (b) 58 : 42 PCN/PTMG (wt.%).

strong absorption bands at 1370 and 1570 cm^{-1} arising from vibrations of the cyanurate rings (triazine band and phenyl-oxygen-triazine stretching band, respectively). The weak absorption bands at

$2236-2272\,cm^{-1}$ result from the stretching vibration of residual cyanate groups are only found in the FTIR spectra of pure PCN (See Fig. 1a). The OCN-groups conversion calculated for pure PCN was 95%. However, no cyanate group absorption bands at 2236–2272 cm^{-1} were found in the FTIR spectra of all the PCN/PTMG blends. That shows a practically full conversion of OCN-groups in these blends.

3.2. Gel Fraction

In Table II, the compositions and their gel fractions, $W_{g\ exp}$, as well as the calculated incorporated PTMG content (incorporation degree) in the gel fraction and PTMG conversion at incorporation are shown. The theoretical calculation of the gel fraction of the pure PCN (Eq. (1)) with 95% OCN-conversion gave the value of gel fraction to be 99.4%. As was noted above, no OCN-groups were found in the cured PCN/PTMG compositions. Thus, the theoretical values of gel fraction, $w_{g\,theor}$, of PCN component in PCN/PPG blends were calculated by Eq. (1), where $\alpha = 1$. It has been assumed that DCBA is integrated completely into the PCN. The admission that all the DCBA participates in network building allows us to calculate the quantity of PTMG integrated into the network structure by comparison of the theoretical and the experimental gel fractions.

As can be seen from Table II for cured compositions, the gel fraction decreases from 99.9 to 76.8% with increasing PTMG content (0 to 42%) in the initial composition. From comparison of the theoretical and experimental values of gel fraction, it is concluded that not all the PTMG transfers into the sol fraction. Thus, some part of PTMG is chemically incorporated into the polycyanurate network. The conversion of PTMG at incorporation decreases from 80 to 45% with increasing of PTMG content in initial composition from 26 to 42 wt.%. However, the molar ratio of incorporated PTMG and DCBA in the gel is constant and equals approximately 0,1 mol incorporated PTMG per 1 mol of DCBA. As was noted above, aryl cyanate reacts with alcohols to form cyanurate rings with elimination of phenol (Scheme 2). By a certain reaction time sufficient amounts of the more active phenol will have been formed and this reaction (Scheme 2, with R = Ar) could go much faster than that involving alcohol [32, 33].

TABLE II Gel fraction of cured DCBA/PTMG blends as a function of composition

Initial composition		*Gel fraction*, w_g		*Gel fraction composition*		*PTMG conversion at incorporation*,
DCBA/PTMG (*mol/mol*)	*PTMG content*, w_{PTMG} (*wt.%*)	$w_{g\ exp.}$ (*wt.%*)	w_{theor} (*wt.%*)	*PTMG incorporation degree*, $\Delta w_g^*/w_{g\,exp}$ (*wt.%*)	*Moles PTMG per* 1 *mol of DCBA*, $((\Delta w_g/M_{PEth})/(w_{g\ theor}/M_{DCBA}))$ (*wt.%*)	$\Delta w_g{}^*/W_{PTMG}$ (*wt.%*)
PCN	0	99.9	99.8	–	–	–
10 : 1	26	94.8	74.0	22.0	0.08	80
9 : 1	29	95.0	71.0	25.3	0.09	83
8 : 1	31	92.0	69.0	25.0	0.09	74
7 : 1	34	90.0	66.0	26.7	0.10	71
6 : 1	38	82.1	62.0	24.5	0.09	53
5 : 1	42	76.8	58.0	24.5	0.09	45
7 : 1 (PPG)	34	91.0	65.7	27.8	0.10	74

* Note: $\Delta w_g = w_{g\,\mathrm{exp}} - w_{g\,theor^*}$.

3.3. Dynamic Mechanical Thermal Analysis

DMTA of polymer blends can be used to characterize indirectly their microstructure, to establish structure-property relationships, and to determine their damping characteristics. It is well known that generally two separate loss factor peaks (tan δ) indicate an immiscible system, whereas one peak indicates a high degree of miscibility [34]. An intermediate degree of miscibility results in a broad transition, arising from a microheterogeneous morphology which can often be used to develop good damping materials [35]. The parameters of interest in this study were the loss factor peak (tan δ) locations and its width at half height. These parameters will help us to assess the miscibility and phase morphology of polymer blends as function of component content.

The loss factor (tan δ) *versus* temperature plots for the homonetwork PCN and the PCN/PTMG series with different compositions are shown in Figure 2 and T_g values are presented in Table III. The PCN homonetwork exhibits one main relaxation, denoted as α, associated with the glass transition (T_g) at 281°C and two typical secondary relaxations, denoted γ (located at -75°C) and β (broad transition with the maximum near 100°C). The γ relaxation is commonly ascribed to the motion of the phenylene groups present in the links between the planar six-membered three-arm cyanurate structures [25]. The β relaxation could be attributed to the motions of chain fragments between the network junctions. As was shown by Bauer *et al.* [36], this transition yields evidence about the presence of irregular network structures. It is noticeable that all of the PCN/PTMG blends show a single broad glass transition (α relaxation) over the range of composition used, with the tan δ peaks of the blends shifting to lower temperature, towards the T_g of the pure PTMG (-85°C [37]), as the PTMG content increases. The one-step mechanism shown in the storage moduli (E') *versus* temperature plots presented in Figure 3 confirms the absence of gross phase separation in these PCN/PTMG blends. This implies that the PCN/PTMG blends have a fairly high degree of miscibility over a wide range of composition. The apparent miscibility noted might be attributed to the possibly incorporated structure of the PTMG into the PCN due to the participation of PTMG molecules in PCN formation through the iminocarbonate

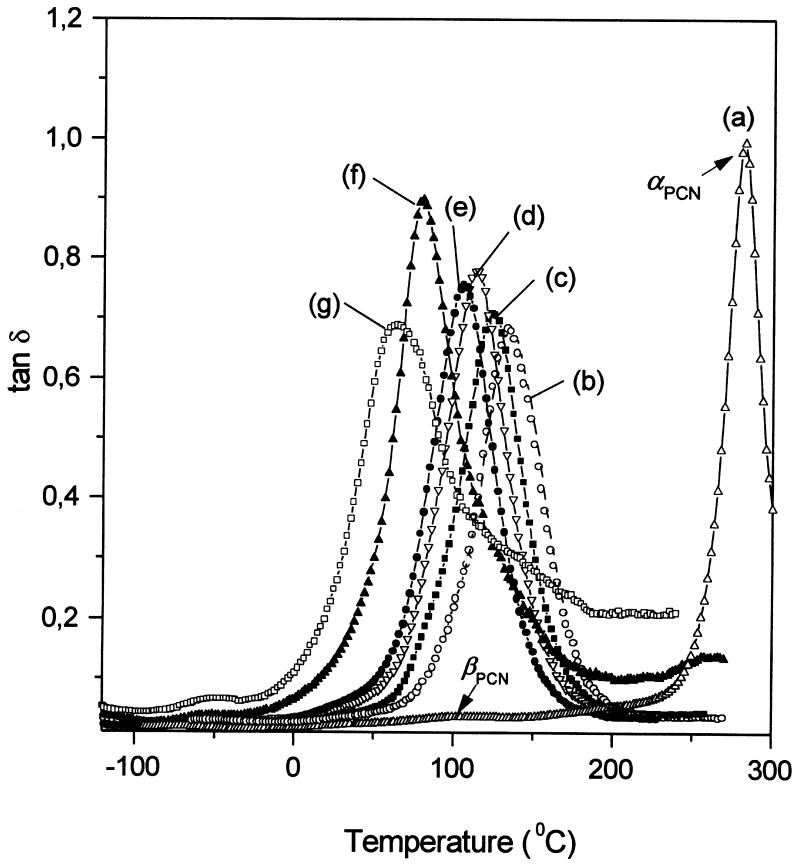


FIGURE 2 Loss factor (tan δ) *versus* temperature for the PCN/PTMG blends. (a) Pure PCN; (b) 74 : 26; (c) 71 : 29; (d) 69 : 31; (e) 66 : 34; (f) 62 : 38 and (g) 58 : 42 PCN/PTMG (wt.%).

TABLE III DMTA (10 Hz) data for PCN/PTMG blends as a function of composition

PCN/PTMG blends		T_g (*tan* δ_{max})	*Tan* δ_{max}
(*mol/mol*)	*PTMG* (*wt.%*)	(°*C*)	(*width at* 1/2 *height*)
PCN	0	281	27
10 : 1	26	134	49
9 : 1	29	123	47
8 : 1	31	115	48
7 : 1	34	105	48
6 : 1	38	80	50
5 : 1	42	65	83

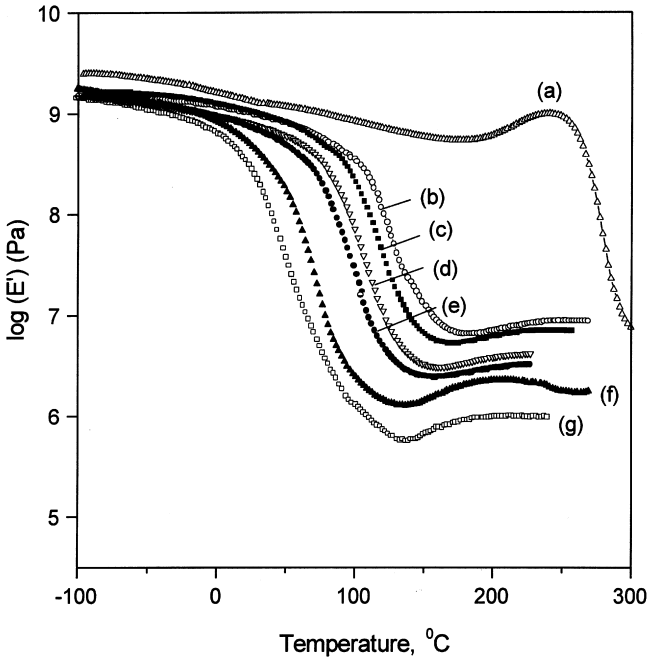


FIGURE 3 Log storage modulus (E') *versus* temperature for the PCN/PTMG blends (a) Pure PCN; (b) 74 : 26; (c) 71 : 29; (d) 69 : 31; (e) 66 : 34; (f) 62 : 38 and (g) 58 : 42 PCN/PTMG (wt.%).

intermediate (Scheme 2). One can assume that the PTMG incorporation will improve the miscibility of the components due to increased affinity of the modified PCN/PTMG network to non-incorporated PTMG (which acts as plasticizer, leading to lower T_g values of the PCN/PTMG blends). The α relaxation of PCN/PTMG compositions overlaps with the secondary β relaxation of PCN network (located at 100°C). The analysis of temperature dependency of the loss modulus (E'') for PCN/PTMG blends presented in Figure 4 shows the existence of low relaxations with maxima near -55°C. This relaxation can be attributed to the shifted PCN γ relaxation or to the non-incorporated PTMG α transition or an overlap of both of them. The above shift to the higher temperatures can be explained by decrease of free volume in the modified PCN network due to the presence of non-incorporated oligomer. One can see that an additional secondary relaxation appears in PCN/PTMG compositions at cryogenic temperatures lower

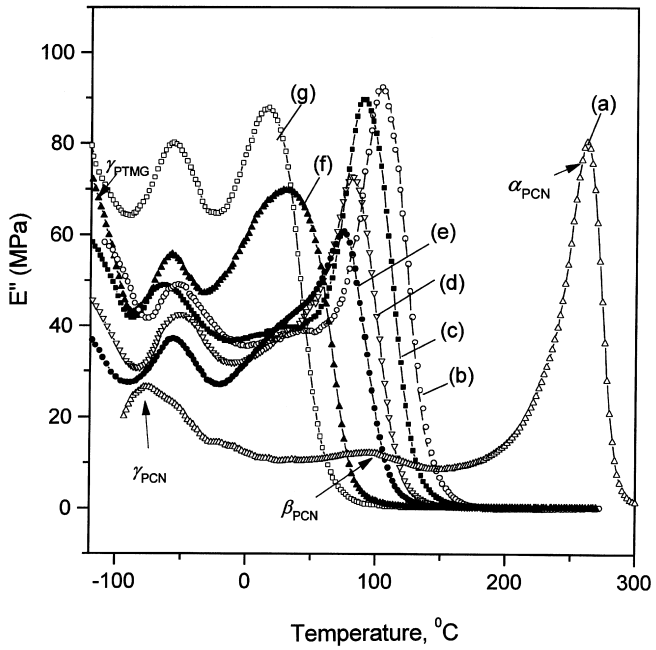


FIGURE 4 Loss modulus (E'') *versus* temperature for the PCN/PTMG blends. (a) Pure PCN; (b) 74 : 26; (c) 71 : 29; (d) 69 : 31; (e) 66 : 34; (f) 62 : 38 and (g) 58 : 42 PCN/PTMG (wt.%).

than $-120°C$. This relaxation could be attributed to the crankshaft motion of the $(—CH_2—)_4$ segments in the PTMG component (γ relaxation) [25].

In multicomponent polymer systems, complete compatibility usually gives a single T_g that depends on the relative weight fractions of the two components and their respective T_g values. The compositional dependence of T_g of the PCN/PTMG blends could be obtained according to the Fox [38] relationship.

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \tag{2}$$

W_1 and W_2 are the weight fractions of the components and T_g, T_{g1} and T_{g2} are the glass transition temperatures of the blend, the neat PCN, and the neat PTMG, respectively. Figure 5 shows the change of Tg with composition, obtained from experimental data (taken at tan δ_{max}) and from the prediction based on the Fox equation. It can be seen that

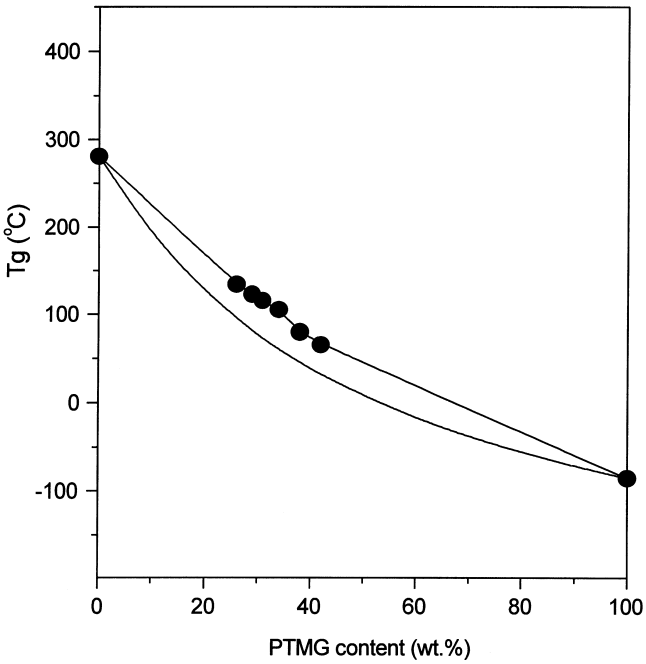


FIGURE 5 Tg values determined by DMTA and calculated from the Fox equation for the PCN/PTMG compositions. (•) Tg determined by DMTA; (—) Tg calculated from Fox's equation.

a slight positive deviation from the Fox equation is observed. Such a deviation indicates that there is some interaction between the PCN and PTMG components in this system [34, 39].

In previous work [40], we have found significant heterogeneity in the phase structure of PPG-modified PCN. It is interesting to compare the viscoelastic properties of PCNs modified with fixed content of PTMG and PPG (equal molar masses). Figure 6 shows the storage modulus, E', and loss factor, $\tan\delta$, *versus* temperature data for the DCBA/polyether = 7/1, mol/mol. One can see that contrary to PCN/PTMG, the PCN/PPG has a two step mechanism in the storage modulus E', *versus* temperature plot (Fig. 6b). Thus PCN/PPG blends are characterized by a higher level of heterogeneity. The same conclusion can be reached from the temperature dependence of E''(Fig. 7b). The shift and convergence of the PCN E'' peaks and PPG components in the mixture are observed, showing the existence of phases of dissimilar

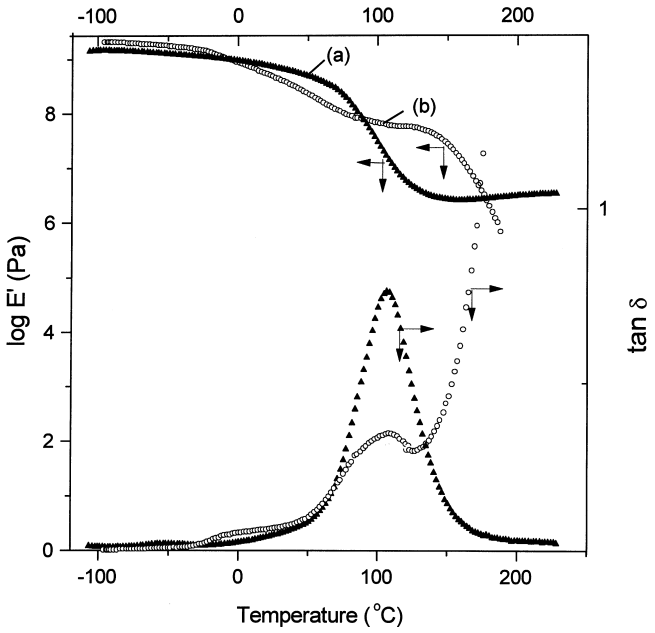


FIGURE 6 Loss factor (tan δ) and log storage modulus (E') *versus* temperature for the PCN/PTMG and PCN/PPG compositions at a fixed component content: PCN/PTMG (PPG) = 7/1 mol/mol. (a) PCN/PTMG and (b) PCN/PPG compositions.

composition, and differing in properties from the pure components, *i.e.*, PCN-rich, the PPG-rich phases and a PCN/PPG mixed phase [40].

3.4. Solubility Parameters

We have tried to explain the above-mentioned difference in terms of solubility parameters of the components. To compare the compatibility of the components of the PCN/PTMG and the PCN/PPG blends the values of the Hildebrand solubility parameter, δ, were calculated by the method of group contributions and cohesive energy (using the Fedors tabular data from [41]).

$$\delta = (\Delta E_{coh}/V)^{0.5} = (\Sigma \Delta e_i / \Sigma \Delta v_i)^{0.5} \tag{3}$$

Δe_i and Δv_i are the additive atomic group contributions for the cohesive energy and molar volume, respectively at a given temperature. In general, if the calculated values of δ for the two components

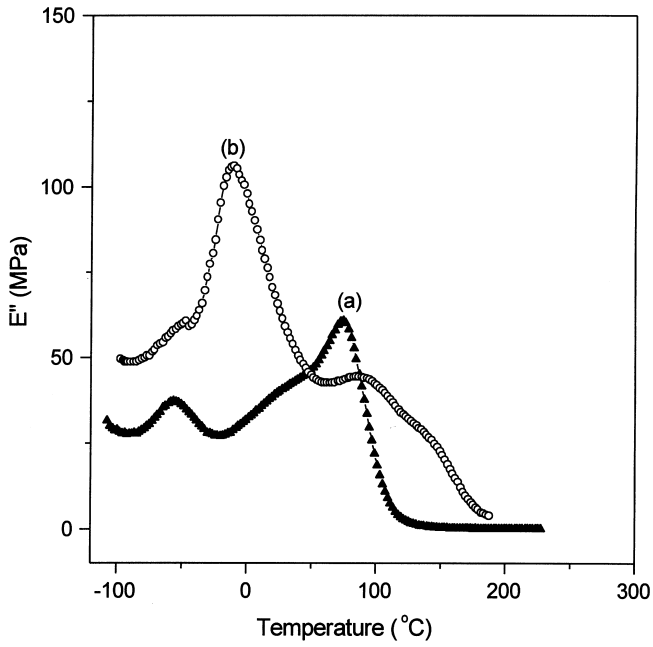


FIGURE 7 Loss modulus (E'') *versus* temperature for the PCN/PTMG and PCN/PPG compositions at a fixed component content: PCN/PTMG (PPG) = 7/1 mol/mol. (a) PCN/PTMG and (b) PCN/PPG compositions.

are similar, this implies that they will be miscible. The calculated solubility parameters for the PCN component was 22.1 $(J/cm^3)^{1/2}$, for the PTMG component was 17.6 $(J/cm^3)^{1/2}$ and for the PPG component was 16.9 $(J/cm^3)^{1/2}$. It is clear that the PTMG should have the higher compatibility with the cyanate. This fact can explain the above glass transition behaviour of PCN/PTMG system. The conversion at incorporation of both PTMG and PPG in DCBA/polyether = 7/1 are nearly the same (71 and 74% in Tab. II, respectively). Thus, one can assume that the higher compatibility in PCN/PTMG blends could be first of all attributed to closer values of δ for PTMG and PCN then to PTMG incorporation or to PTMG dissolved in PCN matrix.

As far as the phase structure of reactive blend depends on the competing curing and phase separation kinetics, the difference in reactivity of primary OH-groups of PTMG and secondary OH-groups of PPG might have been the reason of the distinction found in

TABLE IV Physico-mechanical properties of cured DCBA/PTMG blends as a function of composition

PCN/PTMG blends		*Density*, ρ, (g/cm^3)		*Tensile*	*Elongation*	*Tensile*
(*mol/mol*)	*PTMG* (*wt.%*)	*Exp.*	*Theor.*[a]	*Strength*, σ, (*MPa*)	*at break*, ε, (%)	*Modulus*, *E*, (*MPa*)
PCN	0	1.21	1.21	24.5	6	408
10 : 1	26	1.20	1.16	102.7	42	245
9 : 1	29	1.19	1.15	95.6	44	217
8 : 1	31	1.18	1.14	73.0	54	135
7 : 1	34	1.16	1.14	58.6	58	101
6 : 1	38	1.15	1.13	40.4	66	61
5 : 1	42	1.13	1.12	27.3	80	34

[a] Note: Theor. – the theoretical value of density was calculated using the additive blend law.

morphology of PTMG and PPG too. The kinetic study of process of polycyanurate modification with PTMG and PPG is under current investigation.

3.5. Mechanical Properties

The density (ρ), tensile strength (σ), elongation at break (ε) and tensile modulus (E) for PCN/PPG series are shown in Table IV. The low density of PTMG, $\rho = 1.000\,g/cm^3$, contributes to the decrease in density of modified PCN. However, the decrease in experimental value of density as modifier content is increased appears lower than that predicted by an additive blend law.

The values of tensile strength and tensile modulus pass through maxima with increasing of PTMG content. The maxima are observed for the 26% PTMG. In general, the tensile strength of the modified PCN studied is significantly higher than for the pure PCN. The elongation at break monotonically increases with PTMG content. It is clearly seen that the incorporation of PTMG into PCN significantly improves the network properties, but dissolution of non-incorporated PTMG (at higher contents) in the modified polycyanurate network leads to the opposite effect. From the point of view of technological applications, we see an excellent possibility to obtain composites with the desired properties by changing the oligomer modifier type and content.

4. CONCLUSIONS

A series of polycyanurate networks, based on DCBA, were synthesized in the presence of different contents of oligomer modifier, PTMG. The oligomer modifier influences the structure of the final networks insofar as it partially incorporated in the polycyanurate matrix. The non-incorporated modifier dissolves in polycyanurate matrix, acting as plasticizer.

All of the modified PCN/PTMG compositions exhibit a single, broad glass transition that shifts to lower temperature as the PTMG content increases. DMTA data indicate that PTMG and polycyanurate matrix have a high degree of compatibility. The experimental

composition dependence of T_g of the PCN/PTMG series shows a slight positive deviation from the Fox equation indicating some interaction between this oligomer modifier and the network matrix.

The comparison of T_g behavior of PCN/PTMG and PCN/PPG compositions at the same content has shown that the PCN/PTMG blends are characterized by a higher degree of compatibility. It is interesting to note that PTMG and PPG have shown approximately equal incorporation degree into PCN. On the other hand, calculation has shown closer values of solubility parameter for PCN/PTMG ($\Delta\delta = 22.1 - 17.6 = 4.5\,(\mathrm{J/cm^3})^{1/2}$) then for PCN/PPG ($\Delta\delta = 22.1 - 16.9 = 5.2\,(\mathrm{J/cm^3})^{1/2}$). This seems to be the main reason of high homogeneity in PCN/PTMG. The introduction of PTMG into PCN clearly improves their mechanical properties.

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