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Structure development in aromatic polycyanurate networks modified with hydroxyl-terminated polyethers

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Abstract

A series of polycyanurate networks (PCN), based on the dicyanate of bisphenol A monomer (DCBA), was synthesized in the presence of different contents of hydroxyl-terminated polyethers (PEth), such as polyoxypropylene glycol (PPG) and polyoxytetramethylene glycol (PTMG). We studied the influence of the nature of the oligomeric modifier, initially miscible with DCBA, on the chemical structure, glass transition behaviour, phase morphology and mechanical properties of modified PCN. The possibility of PEth incorporation into the PCN structure through mixed cyanurate ring formation is discussed. A maximum PEth incorporated content of 0.1 mol of PEth per mol of DCBA irrespective of PEth type has been detected. Dynamic mechanical thermal analysis (DMTA) analysis showed the formation of multiphase polymer compositions due to microphase separation of the components occurring during DCBA/PPG curing. The formation of very finely divided morphologies with highly interpenetrated phases, i.e. a PCN-rich phase, a mixed phase of PCN/PPG components and a PPG-rich phase was determined. On the other hand, all PCN/PTMG cured compositions exhibited a single, broad glass transition that shifted to lower temperature as the modifier content was increased and the experimental T_g versus modifier content showed a slight positive deviation from the Fox equation for miscible polymer systems. It can be concluded that the PCN and the PTMG have a higher degree of compatibility than PCN and PPG. The introduction of small additions of modifier (<10 wt%) allow production of the thermosets with high T_g and good strength properties.

Keywords: Polycyanurate network; Polyether; Polyoxypropylene glycol

1. Introduction

Since the late 1970s, cyanate ester resins have been used with glass or aramid fibre in high-speed multilayer circuit boards and this remains their primary application. In this application, the primary performance considerations of a glass transitions temperature (T_g) matching or exceeding molten solder temperatures (220–270°C), low dielectric loss properties (to increase signal speed and facilitate miniaturization) and good peel strength made cyanate esters pre-eminently suitable [1]. Cyanate ester monomers polymerize by a cyclotrimerization reaction to yield cyanurate-linked network polymers (Scheme 1, generalised monomer structure and polycyanurate network formation).

Currently, this polymerization and the physical properties of the resulting polymers have attracted substantial commercial and scientific interest. Polycyanurate matrices resulting from the cure of pure dicyanate monomers have excellent thermal and dielectric properties, but are often very brittle [2]. Several attempts are currently being undertaken in order to improve this particular aspect. There are two basic ways to decrease the high brittleness of high crosslink density polymer networks. Reaction of cyanate group with active hydrogen-containing functional groups to form modified polycyanurates is a developing area. The particularly important examples are the reactions of dicyanates with epoxies to form an oxazolidinone-linked polycyanurates [3–6], with mono- and bis-phenols [3,5–8], diamines [5,7] and with bismaleimides [9–11]. Brittle thermosets are also toughened by the introduction of a rubbery or a thermoplastic dispersed phase [7,12–15]. Generally, at the curing temperature, the initial mixture of monomer(s) and additive is homogeneous. The dispersed phase results from the phase separation induced by the step-growth polymerization of the monomer(s). The studies show that the morphology formed (diameters, number and

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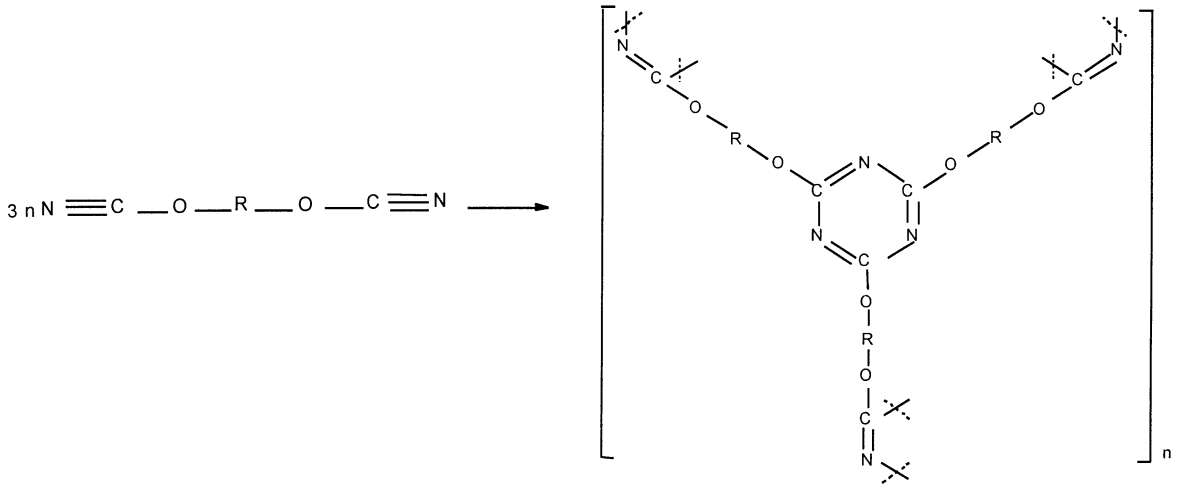


Scheme 1.

volume fraction of the dispersed particles) is determined by the competing effects between the phase separation and polymerization rates [16]. Recently some results have been published [7,14,15], where the researchers had used the combination of the two above-mentioned methods. There are two possibilities to combine these kind of modifications: simultaneous use of reactive co-monomer and inert rubber or thermoplastics to change the chemical structure and phase morphology of polycyanurates [17,18] and use a rubber or a thermoplastic containing reactive chain ends [7,14,15]. In the combined method, the ability of additives to react with the matrix is often of great interest since 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 oligomeric modifier and the network. Polycyanurates with well-defined morphology and improved characteristics have been synthesized [7,14,15].

Recently, results concerning the modification of brittle polycyanurate with flexible polyurethanes has been published [17–24]. Polyurethanes are well known to be synthesized by the reaction between polyether (or polyester), containing hydroxyl groups and diisocyanates. As the dicyanate, is an isomer of diisocyanate, there may be similar chemical reaction between dicyanate and polyether (or polyester) with formation of the so-called iminocarbonate [25], which is isomeric with the polyurethane structure. Such reaction could be used for direct modification of polycyanurates. A few papers only have been published [15,25,26] and there is no clear understanding of the chemistry and how these compounds can be incorporated into the network.

The aim of the present research is to study the formation and structure of polycyanurate networks (PCN) modified with polyethers (PEth) such as polyoxypropylene glycol (PPG) and polyoxytetramethylene glycol (PTMG), their phase morphology, glass transition behaviour and some mechanical properties.

2. Experimental

2.1. Materials and sample preparation

The cyanate ester monomer used in this work was the dicyanate ester of bisphenol A (DCBA, >98% purity). Triethylamine (99% purity) was used as the DCBA cure catalyst of (3 mol% per DCBA). The materials used in this study are summarized in Table 1. The DCBA and triethylamine were used as received. PPG and PTMG were used as the network modifiers. PPG and PTMG were dried at 80°C under vacuum for 6 h. Samples with component ratios of DCBA/PPG from 180/1 to 3/1 mol mol^{-1} (from 98/2 to 45/55 wt%) and DCBA/PTMG component ratios from 10/1 to 5/1 mol mol^{-1} (from 74/26 to 58/42 wt%) were prepared and studied. It was impossible to prepare the film samples with DCBA/PPG ratio smaller than 3/1 mol mol^{-1} and with DCBA/PTMG smaller than 5/1 mol mol^{-1}. The cyanate ester, catalyst and glycol were first mixed together, then degassed at 80°C for 0.5 h and then were poured into a PTFE-coated mould. The curing cycle consisted of two stages: 5 h at 150°C and 3 h at 180°C.

2.2. Techniques

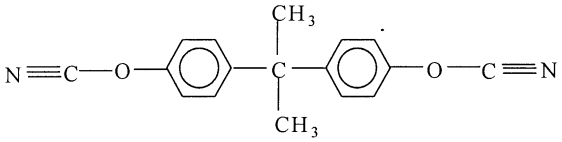
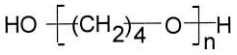
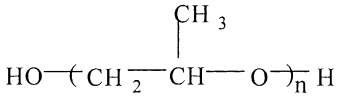
2.2.1. FTIR spectroscopy

FTIR spectroscopy analysis was carried out using a Unicam Mattson 3000 FTIR spectrophotometer in the mid-infrared range from 4000 to 600 cm^{-1}. The degree of OCN-conversion was calculated using the height of the 2272 cm^{-1} band associated with the stretching vibration of the cyanate group. In this work, the CH_3 peak height at 2968 cm^{-1} (taken for initial and cured DCBA/PEth blends) was used as the internal standard.

2.2.2. Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) measurements were performed with a Rheometrics Scientific

Table 1
Chemical structures and characteristics of the monomer and additives

Component	Chemical structure	Molar mass, M (g mol^{-1})
Dicyanate ester of bisphenol A (DCBA)		278
Polyoxytetramethylene glycol (PTMG)		1000
Polyoxypropylene glycol (PPG)		1050
Triethylamine	$(C_2H_5)_3N$	101

dynamic mechanical thermal analyzer (MK II). The samples were measured in the bending mode at a fixed frequency of 1 or 10 Hz from −100 to 300°C using a heating ramp of 4°C/min. The strain was ×4. Some samples were additionally measured in the torsion mode using another dynamic mechanical thermal analyzer (RDAII-Rheometric) with the same conditions.

2.2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) thermograms were obtained using a Mettler TA3000 instrument under argon and over the temperature range from −120 to 320°C, at a heating rate of 20°C min^{-1}. The OCN-conversion (α) was calculated by Eq. (1)

$$\alpha = (\Delta H_T - \Delta H_R)/\Delta H_R \quad (1)$$

ΔH_R (the residual heat of reaction taking into account the PEth content) is deduced by integrating the area between the heat flow curve (exothermic peak) and the base line and ΔH_T (the total heat of the cure reaction) is determined in the same way by integrating the reaction exothermic peak of an initially unreacted specimen ($\Delta H_T = 710$ J g^{-1} [27]).

2.2.4. X-ray analysis

Small-angle X-ray scattering (SAXS) data were obtained with a Kratky camera (KRM-type diffractometer). The primary beam intensity was controlled with a monitoring channel in the scattering angle range from 3 to 5°. Copper Kα radiation and nickel filtering of the primary beam were used. Recording of the scattered radiation with a scintillation counter and digital conversion was performed using the step-by-step scanning regime.

2.2.5. 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/PEth composition. The theoretical value of gel fraction ($w_{g\ theor}$) was calculated [4] using Eq. (2) and obtained with the help of Monte Carlo simulation and with the conjecture that the linear PPG was completely extracted

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

α is the OCN-conversion (FTIR data) and w_{PEth} is the weight fraction of PEth in the initial composition.

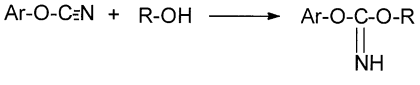
2.2.6. Tensile strength

At room temperature, the strength characteristics were measured using a Heckert FU-1000 test machine at a cross-head speed of 70 mm min^{-1} and specimens with dimensions of 40 × 5 × 1.2 mm^3.

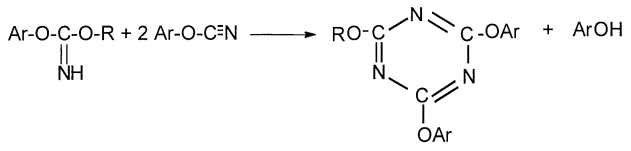
3. Results and discussion

3.1. Chemical structure characteristics

According to some publications [2,25–28], cyanic esters react with compounds containing phenolic or hydroxyl groups with formation of the iminocarbonate as in Scheme 2 (intermediate iminocarbonate formation).



Scheme 2.



Scheme 3.

Li and Kohn [26] noted that they have managed to synthesize the polyiminocarbonate in solution, but the main reaction in the bulk is polycyclotrimerization of the dicyanate ester with formation of the polycyanurate network, especially at high temperature. It is known [28,29] that iminocarbonate formed from an aryl cyanate and an alcohol in the presence of triethylamine participates in triazine ring formation with the abstraction of a phenol.

The phenol abstracted can also react with cyanate groups giving a fully aromatic iminocarbonate followed by cyanurate formation [2,4] (Schemes 2 and 3 (reaction scheme for mixed cyanurate cycle formation), where R = Ar). In the present study, we have analyzed the resulting products of cure at 150–180°C of mixtures of the dicyanate ester of bisphenol A with the hydroxyl groups in polyoxypropylene glycol. Typical FTIR absorption for pure PCN, PCN/PPG (45/55, wt%) and PCN/PTMG (58/42, wt%) are shown in Fig. 1a–c, respectively. In all spectra one can see strong absorption bands at 1370 and 1570 cm^{-1} arising from the vibrations of the cyanurate rings (triazine peak and phenyl-oxygen-triazine stretching peak, respectively. Weak absorption bands with maxima at 2236–2272 cm^{-1} arising from the stretching vibrations of the residual cyanate groups [28]

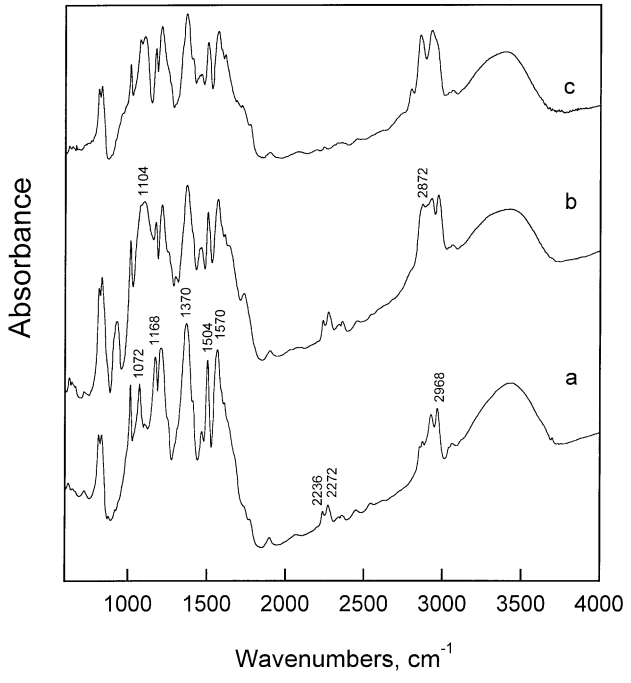


Fig. 1. FTIR spectra for the PCN homonetwork and a PCN/PEth composition: (a) pure PCN; (b) 45:55 PCN/PPG and (c) 58:42 PCN/PTMG (wt%).

Table 2
Conversion of DCBA as a function of composition

Composition PCN/PPG (wt% PPG)	OCN-Conversion, α (%)	
	FTIR data	DSC data
PCN (homonetwork)	95	96
5	97	97
10	95	96
26	95	95
31	94	96
34	94	96
37	95	98
42	98	97
47	93	94
55	93	93

are observed just for PCN and PCN/PPG (Fig. 1a and b). The degree of OCN-conversion for pure PCN and PCN/PPG blends studied are presented in Table 2. On the contrary, no cyanate group absorption bands at 2236–2272 cm^{-1} were found for the FTIR spectra (not shown) of all the PCN/PTMG blends. They showed the practical full conversion of OCN-groups in these blends. This fact can be explained by higher reactivity of the primary OH-groups of PTMG than the secondary OH-groups of PPG toward the DCBA and higher availability of OCN-groups in PCN/PTMG composition at high OCN-conversion than in PCN/PPG blend because of steric hindrance because of CH_3-substituent along the PPG polymer chain. The kinetic and diffusion limitations of PCN/PEth synthesis are under current investigation.

Other relevant peaks in the spectra of PCN/PEth blends are associated with the presence of PPG, i.e. absorption bands at 930, 1104 and 2872 cm^{-1} (Fig. 1b) or PTMG, absorption bands at 2857 and 2798 cm^{-1} from the CH_2-groups and at 1105 cm^{-1} from the C–O–C-links). Only small differences in the positions of these absorption bands compared with pure cured DCBA (PCN) and pure PPG were observed. We have established that the main reaction product in cured blends is the PCN, and no traces of iminocarbonate structures have been found. We have not detected the absorption band at 1675 cm^{-1} associated with the intermediate iminocarbonate in the spectra of PCN/PEth blends.

The specific character of the subsequent reaction of the iminocarbonate into the triazine ring lies in the possibility of exchange of the hydroxyl and cyanate groups between the monomer units [4]. Grigat and Putter [30] observed that the most acidic phenol was released, and thus, a substituted triazine ring should be obtained with the liberation of a monophenol deriving from DCBA. In the case of such an exchange, the alkyl dicyanate derived from PEth has to be obtained simultaneously (taking in account that there is an excess of DCBA in all the blends studied). Thus, three kinds of cyanate molecules, i.e. DCBA, monocyanate ester of bisphenol A and alkyl dicyanate will participate in the polycyanurate network formation.

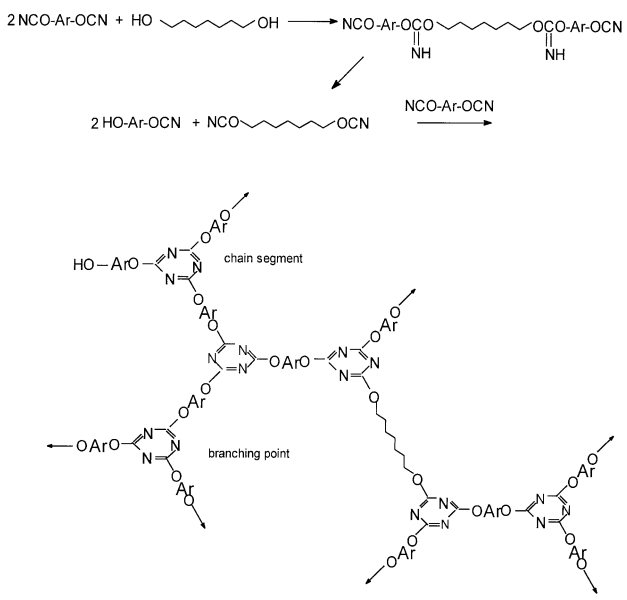
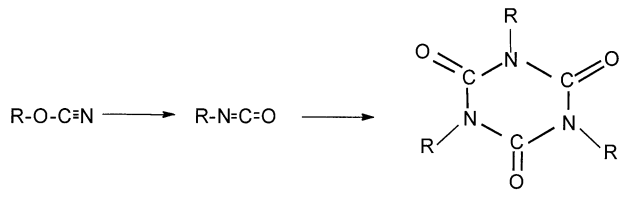


Fig. 2. Monomer structure and network formation.

Similar to the co-reaction of dicyanates with diphenols [2,4], we would propose the scheme (Fig. 2), where the fragment $-O\sim\sim\sim\sim\sim\sim O-$ is incorporated into a network chain and all substituents on the triazine rings, which are not network chains, are hydroxyl-terminated.

Comparison of the FTIR spectra of the gel and sol fractions of the cured compositions showed clear differences. The sol fraction mainly consisted of pure PEth and traces of the product, which has the absorption band at 1730 cm^{-1}. The gel fraction basically consisted of cured DCBA (PCN), PPG or PTMG (obviously incorporated) and some fragments, which have an absorption band at 1712 cm^{-1}. Certainly, the alkyl cyanate formed participates in cyanurate cycle formation side-by-side with the aryl cyanate (Fig. 2), but also partly isomerizes to the isocyanate with subsequent trimerization to isocyanurate [2,28]. So, the appearance of absorption bands at 1712 cm^{-1} in the gel fraction can be explained by there occurring traces of such side products (fragments) with isocyanurate rings [30] (Scheme 4, aliphatic cyanate isomerization to isocyanate with subsequent isocyanurate ring formation).

Besides, the isocyanate formed can also react with hydroxyl-containing compounds with the formation of urethane linkages. Such urethanes with a carbonyl absorption band at 1730 cm^{-1} could be the side product found in the sol fraction [30].



Scheme 4.

3.2. Gel fraction and incorporated PEth content

As was noted above, no unreacted OCN-groups have been found in the sol fraction of pure PCN and PCN/PEth blends. Thus, one can suppose that unreacted cyanate groups are trapped inside the polycyanurate network. It can be explained that topological limitations at the end of the DCBA cure prevent reaction of cyanate groups spatially separated from each other, because of the high connectivity of the final network [31]. The theoretical calculation of gel fraction of PCN, by the use of Eq. (2), has shown that for PCN with OCN-conversion ≥93% (the lowest experimental value of OCN-conversion of PCN in the PCN/PPG blends. See Table 2) the value of gel fraction must be ≥99.4%. Thus, we have assumed that DCBA is integrated into the PCN completely. The assumption that the whole of the DCBA participates in network building allows us to calculate the quantity of PEth integrated into the network structure by comparison of the experimental and theoretical values of gel fraction. In Table 3, the compositions and their gel fractions as well as the calculated incorporated PEth content (incorporation degree) in the gel fraction, and PEth conversion at incorporation are shown.

As can be seen from Table 3 for PCN/PPG blends, the experimental values of gel fraction, $w_{g\ exp}$, decreases from 99.8 to 62.1% with increasing PPG content (2–55%) in the initial composition. From the comparison of $w_{g\ theor}$ and $w_{g\ exp}$, it can be concluded that not all of the PPG transfers into the sol fraction. So some part of PPG is chemically connected (incorporated) to the polycyanurate network. The PPG conversion by incorporation into polycyanurate network decreases from 95 to 31% with increasing PPG content in initial composition from 2 to 55%. However, at low PPG content in initial composition (less then 20 wt%) the incorporated PPG content in the gel fraction slowly increases from 0.01 to 0.06 mol mol^{-1} of DCBA, apparently because of the insufficient quantity of PPG for maximum possible incorporation. With increasing PPG content up to 27 wt%, the incorporation degree in the gel achieves a value approximately equal to 0.1 mol mol^{-1} of DCBA and stays constant with increasing PPG content in initial composition up to 55 wt%.

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 the PCN component in PCN/PPG blends were calculated by Eq. (2), where $\alpha = 1$. As can be seen from Table 3, the gel fraction decreases from 99.9 to 76.8% with increasing PTMG content from 0 to 42% in the initial composition. From the comparison of the theoretical and experimental values of the gel fraction, it is concluded that not all the PTMG transfers into the sol fraction. Thus, some part of PTMG is also chemically incorporated into polycyanurate network. The conversion of

Table 3
Gel fraction of cured DCBA/PPG blends as a function of composition

PEth content in initial composition (wt%), w_{PEth}	Gel fraction (wt%), w_g		Gel fraction composition		PEth conversion at incorporation (wt%), $\Delta w_g{}^a/w_{PEth}$
	$w_{g\ exp}$	$w_{g\ theor}$	PEth incorporation degree (wt%), $\Delta w_g{}^*/w_{g\ exp}$	Incorporated PEth moles[b], $(\Delta w_g/M_{PEth})/(w_{g\ theor}/M_{DCBA})$	
PPG					
0	99.9	99.8	–	–	–
2	99.8	97.9	1,9	0.01	95
5	99.8	94.9	4,9	0.01	98
10	98.5	89.8	8,8	0.03	87
15	97.5	84.8	13,0	0.04	85
20	97.0	79.8	17,7	0.06	86
26	97.0	73.8	23,9	0.09	89
29	96.3	70.8	26, 5	0.09	88
31	92.1	68.7	25,4	0.09	75
34	91.0	65.7	27,8	0.10	74
37	87.1	62.8	27,9	0.11	66
42	81.2	58.0	28,6	0.11	55
47	72.6	52.8	27, 3	0.10	42
55	62.1	44.8	27, 9	0.10	31
PTMG					
26	94.8	74.0	22.0	0.08	80
29	95.0	71.0	25.3	0.09	83
31	92.0	69.0	25.0	0.09	74
34	90.0	66.0	26.7	0.10	71
38	82.1	62.0	24.5	0.09	53
42	76.8	58.0	24.5	0.09	45

[a] $\Delta w_g = w_{g\ exp} - w_{g\ theor}$.
[b] Per mol of DCBA.

PTMG at incorporation decreases from 80 to 45% with the increase of PTMG content in initial composition from 26 to 42 wt%. However, the molar ratio of incorporated PTMG/DCBA, similarly to PPG/DCBA, in the gel is constant and equal to approximately 0.1 mol PTMG per mol of DCBA.

As was noted above, an aryl cyanate reacts with an alcohol to form a cyanurate ring with an abstraction of phenol (Schemes 2 and 3). By a certain time of reaction, sufficient amounts of the more active phenol should have been formed and this reaction could go much faster than the one involving alcohol [32]. So, PCN modified with a oligomeric additive, PEth (partly incorporated chemically) has been synthesized.

3.3. Dynamic mechanical thermal properties

The morphology and miscibility of two polymer components in a polymer blend can be assessed from DMTA data. 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 [33]. An intermediate degree of miscibility results in a broad transition. This microheterogeneous morphology is often used to develop good damping materials [34]. The parameters of interest in this study were the loss factor peak (tan δ) location and height as well as a value for the loss factor at the inter-transition region (half-distance between the T_gs of the individual polymers). These parameters will help to assess the miscibility and phase morphology of polymer blends as function of components content.

The loss factor (tan δ) versus temperature plots for the homonetwork PCN and the PCN/PTMG series with different compositions are shown in Fig. 3 and T_g values are presented in Table 4. 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 a 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 [35]. 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 compositions 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

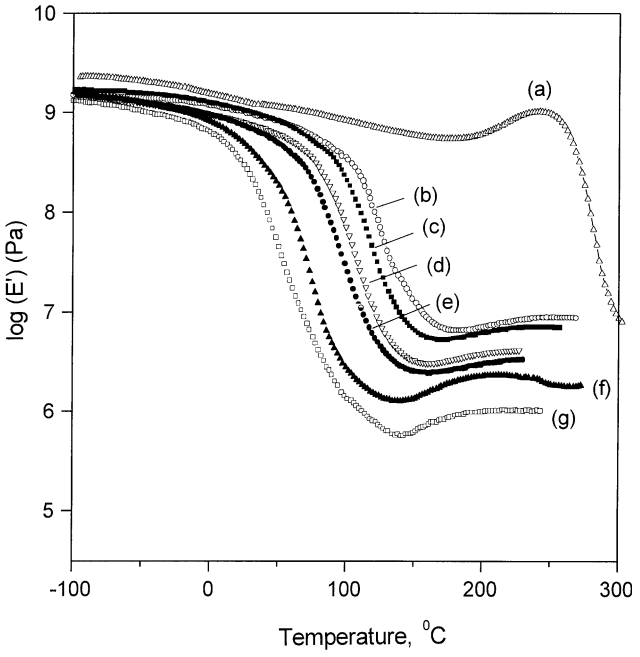


Fig. 3. Loss factor (tan δ) versus temperature for the PCN/PTMG blends (bending mode, 10 Hz): (a) pure PCN; (b) 74:26; (c) 71:29; (d) 69:31; (e) 66:34; (f) 62:38 and (g) 58:42 PCN/PTMG (wt%).

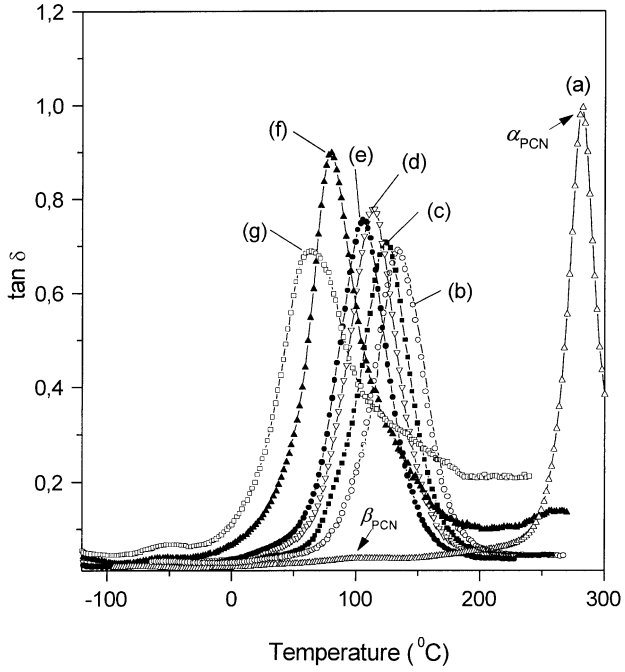


Fig. 4. Log storage modulus (E') versus temperature for the PCN/PTMG blends (bending mode, 10 Hz): (a) pure PCN; (b) 74:26; (c) 71:29; (d) 69:31; (e) 66:34; (f) 62:38 and (g) 58:42 PCN/PTMG (wt%).

storage moduli (E') versus temperature plots presented in Fig. 4 confirm 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 possible incorporated structure of the PTMG into the PCN due to the participation of PTMG molecules in PCN formation through the iminocarbonate 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 a 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 loss modulus (E'') for PCN/PTMG blends presented in Fig. 5, 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 a 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 than −120°C. This relaxation could be attributed to the crankshaft motion of the $(-CH_2-)_4$ segments in the PTMG component (γ relaxation) [35].

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

Table 4
DMTA data (bending mode, 10 Hz) for PCN/PTMG blends as a function of composition

PCN/PTMG compositions		T_g (tan δ_{max}) (°C)	Tan δ_{max} (width at 1/2 height)
(mol mol^{-1})	PTMG (wt%)		
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

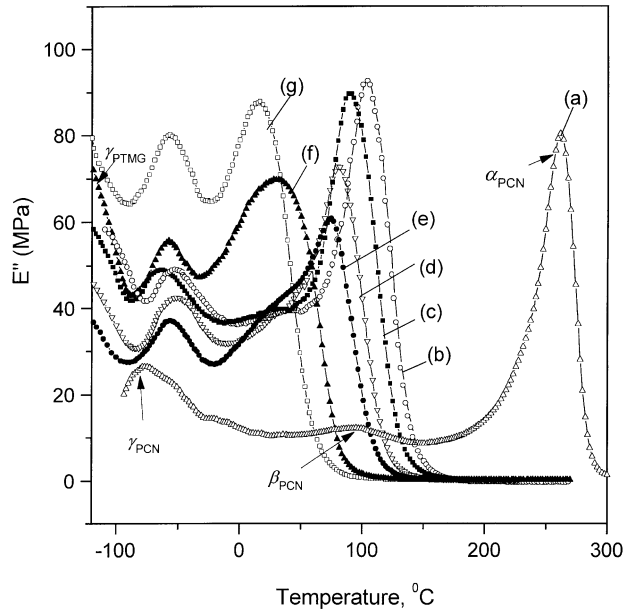


Fig. 5. Loss modulus (E'') versus temperature for the PCN/PTMG blends (bending mode, 10 Hz): (a) pure PCN; (b) 74:26; (c) 71:29; (d) 69:31; (e) 66:34; (f) 62:38 and (g) 58:42 PCN/PTMG (wt%).

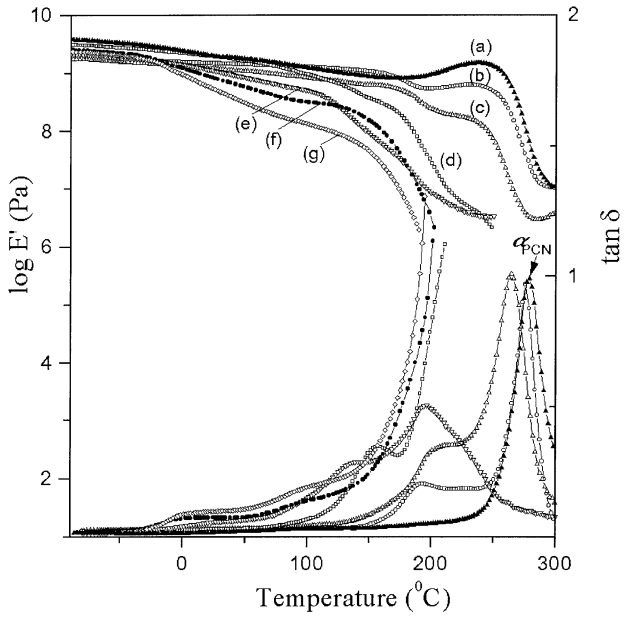


Fig. 7. Log storage modulus (E') and loss factor (tan δ) versus temperature for the PCN/PPG compositions (bending mode, 1 Hz): (a) pure PCN; (b) 98:2; (c) 95:5; (d) 90:10; (e) 85:15; (f) 69:31 and (g) 63:37 PCN/PPG (wt%).

of the PCN/PTMG blends could be obtained according to the Fox [38] relationship

$$1/T_g = W_1/T_{g1} + W_2/T_{g2} \quad (3)$$

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. Fig. 6 shows the change of T_g 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 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 [33,39].

The storage modulus (E') and loss factor (tan δ) as well as loss modulus (E'') versus temperature plots for the PCN/PPG series are shown in Figs. 7 and 8. Both the step-drop mechanism in the storage moduli and well-separated loss

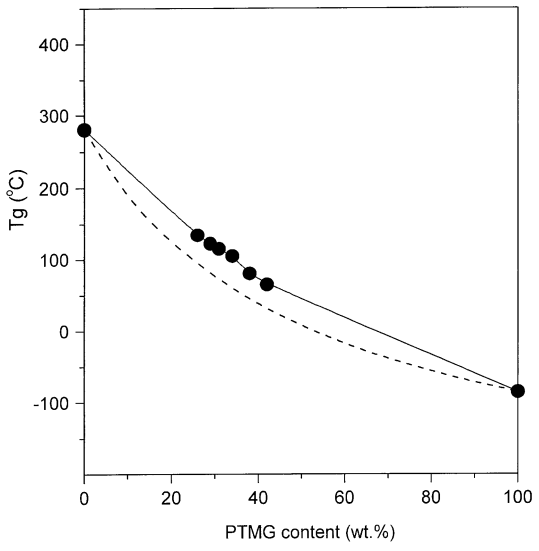


Fig. 6. T_g values determined by DMTA and calculated from the Fox equation for the PCN/PTMG compositions: (●) T_g determined by DMTA; (- - -) T_g calculated from Fox's equation.

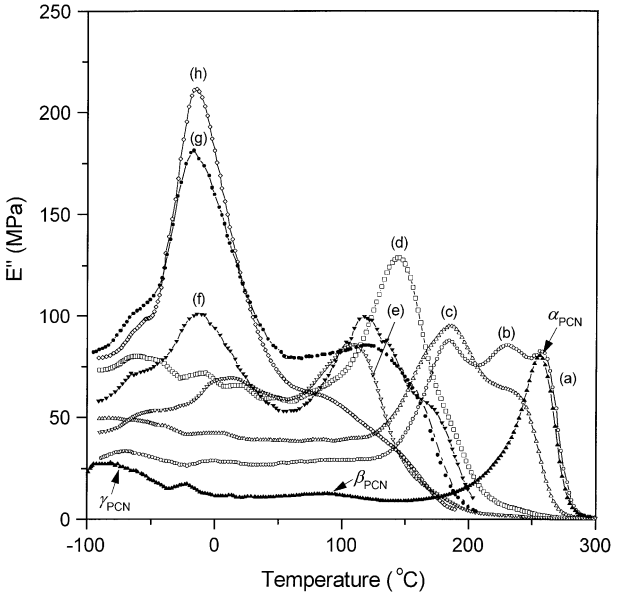


Fig. 8. Loss modulus (E'') versus temperature for PCN/PPG composition (bending mode, 1 Hz): (a) pure PCN; (b) 98:2; (c) 95:5; (d) 90:10; (e) 85:15; (f) 74:26; (g) 69:31 and (h) 63:37 PCN/PPG (wt%).

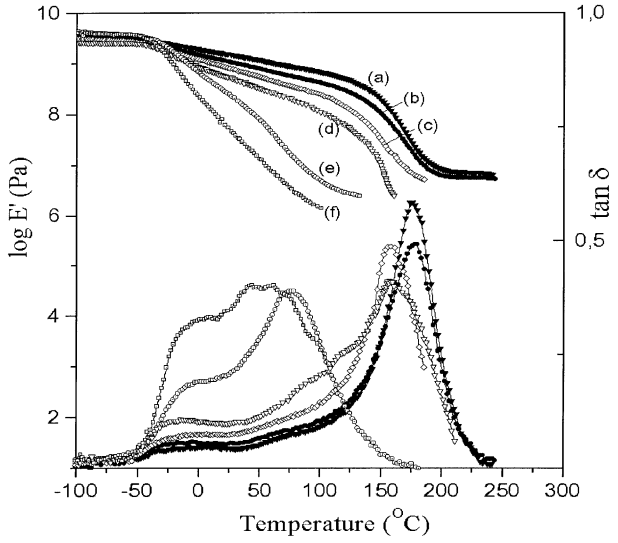


Fig. 9. Loss moduli (E'') versus temperature for the PCN/PPG compositions (torsion mode, 1 Hz): (a) 74:26; (b) 69:31; (c) 66:34; (d) 78:42; (e) 53:47 and (f) 45:55 PCN/PPG (wt%).

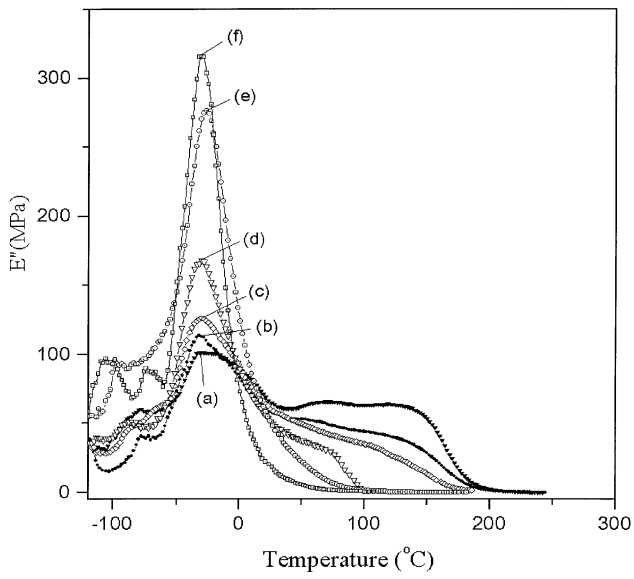


Fig. 10. Log storage moduli (E') and loss factor (tan δ) versus temperature for PCN/PPG composition (torsion mode, 1 Hz): (a) 74:26; (b) 69:31; (c) 66:34; (d) 78:42; (e) 53:47 and (f) 45:55 PCN/PPG (wt%).

factor transitions indicate gross phase separation in the PCN/PPG blends. As it was impossible to measure correctly the tan δ values for compositions with higher PPG contents by the bending mode, an additional DMTA study was carried out using the torsion mode. The dependencies of log E', tan δ and E'' (torsion mode) versus temperature for the PCN/PPG series with higher PPG contents are shown in Figs. 9 and 10.The shift of the glass transition temperature T_g (obtained from the tan δ maximum or the half height of the step-drop in log E') takes place for both polymers with changing composition. It is known that pure PPG has its T_g in the region from -75 to -60°C [37]. As can be observed from Figs. 7–10, there are at least three main glass transition regions that indicate the formation of three phases of dissimilar composition, differing in properties from the pure components. These are the phase rich in PCN-network, the mixed phase of PCN/PPG components and the phase rich in the linear PPG component. Their values of T_g and the tan δ maxima are given in Table 4. With increasing PPG weight fraction, the plateau between the PPG T_g and the PCN T_g moves to lower storage moduli, E', reflecting the change in phase morphology with composition (Figs. 7 and 9). The loss modulus, E'', versus temperature shows two or three distinct transitions depending on composition (Figs. 8 and 10). Similarly to the results from the loss factor data, the increase in PPG content leads to decreasing T_g values for the PCN-rich and PPG-rich phases, as well as for the PCN/PPG mixed phase.

The mentioned decreases in the transition of PCN-rich phase and in the transition of PCN/PPG mixed phase at higher PPG contents indicate that the PCN segments are freer to move in the blends than in the PCN homonetwork. Reasons for this could be an increase of PCN-network defect content due to a decrease in its crosslink density in PCN/PPG composition. There are two main reasons, which can decrease the crosslink density of PCN during its formation in the presence of a linear component: (1) incorporation of linear PPG into the PCN (See Fig. 2), (2) decrease in the final degree of OCN-conversion.

One can assume that the increase in degree of PPG incorporation will contribute to the enhancement of phase mixing in PCN/PPG blends due to the increase in the network structure defects and the affinity of the PPG-modified network to non-incorporated PPG. The above conclusion is confirmed by the analysis of the loss factor peak height of both components (See Table 5). The loss factor peak heights of the PCN and PPG components do not decrease linearly with decreasing content. We consider that it is due to the involvement of some part of each of the components in the formation of PCN/PPG mixed phase. The loss factor peak height usually gives an indication of phase continuity [33] in a polymer blend, with the component exhibiting the higher peak representing the continuous phase. Thus, it can be concluded from the data in Table 5 that a phase inversion will take place at PPG contents higher than 55 wt%. The loss factor values of the inter-transition region were taken at an intermediate temperature (104°C) between the PCN and PPG glass transitions. Generally, the inter-transition loss factor value increases with increasing linear PPG content in the blends, which indicates the increase of component mixing in these blends.

The relationship between T_g and the OCN-conversion in the PCN/PPG blends was studied using DSC measurements.

3.4. Differential scanning calorimetry

It is known [40], as for epoxy networks, that topological limitations at the end of the DCBA cure might prevent

Table 5
DMTA (1 Hz) data for PCN/PPG blends as a function of composition

PCN/PPG compositions (wt% PPG)	T_g (°C)[a]			tan δ_{max}		Inter-transition height at 104°C
	PCN-rich phase	PCN/PPG mixed phase	PPG-rich phase	PCN-rich phase	PPG-rich phase	
Bending mode						
0	278	–	–	0.99	–	0.03
2	274	191	–	0.83	–	0.03
5	263	189	–	1.00	–	0.05
10	199	150	–	1.60	–	0.08
15	194	139	20	0.51	0.05	0.17
20	178	133	14	–	0.05	0.16
26	174	77	−6	–	0.06	0.17
31	172	65	−12	–	0.07	0.15
34	162	51	−12	–	0.07	0.18
37	157	53	−13	–	0.10	0.20
Torsion mode						
26	176	58	−28	0.59	0.05	0.10
31	177	57	−30	0.49	0.06	0.11
34	160	56	−25	0.48	0.08	0.15
42	155	47	−23	0.41	0.10	0.21
47	76	32	−13	0.39	0.19	0.26
55	60	16	−18	0.40	0.33	0.26

[a] At the tan δ_{max} or half height of step-drop log E'.

unreacted cyanate groups spatially separated from each other reacting, due to the high connectivity of the final network. However, the separation of cyanate groups can be increased due to the presence of the second component in the blend, especially when it is at a high percentage. As was shown above (see Table 2), the final conversion of cyanate groups slightly decreases at high PPG content in the PCN/PPG blends. The OCN-conversion calculated above by the FTIR spectroscopy technique is the true conversion, obtained without any assumption, because this technique allows detection of the presence of all the unreacted cyanate groups. Whereas by using the DSC technique it is possible to detect all functional groups liable to react. Fig. 11 presents typical DSC scans for pure PCN and the PCN/PPG blends with different compositions. As was shown by Georjon et al. [40] for pure PCN, the exothermic process starting above 220°C should be attributed to completion of PCN cross-linking reaction. The values of the OCN-conversion for pure PCN and PCN/PPG blends calculated from DCS data by Eq. (1) are presented in Table 2. Note that no residual heat of reaction was observed on the second heating of the samples. One can see that the values of OCN-conversion calculated from FTIR spectroscopy and DSC data are nearly the same. Georjon et al. [40] have investigated in detail the influence of OCN-conversion on T_g of PCN. Based on their data, one can suppose that the T_g of PCN will decrease approximately from 280 to 225°C as the conversion changes from 98 to 93%. However, from the DMTA data presented in Table 5, the decrease of PCN-component T_g in compositions studied is much greater.

Summarizing all data discussed above it can be concluded that the lowering of the glass transition temperature of the modified network matrix with increasing PPG content is due to: (a) PPG incorporation, (b) a decrease of final OCN-conversion and (c) an increase in the percentage of non-incorporated PPG, which then acts as a plasticizer.

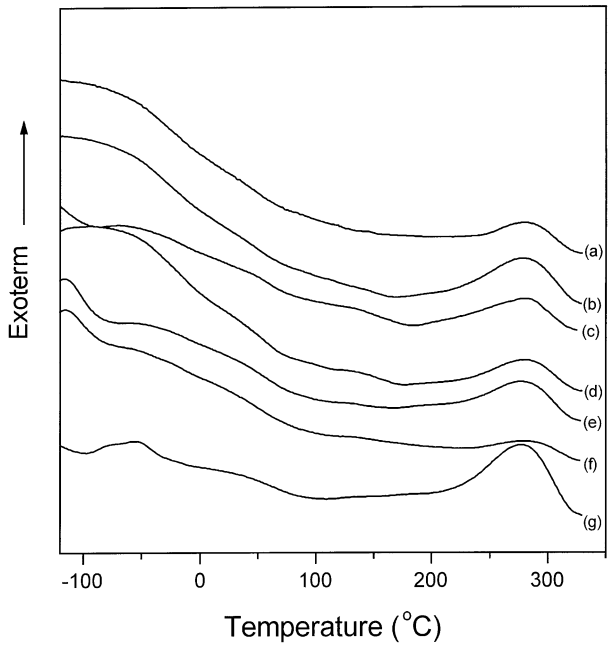


Fig. 11. Typical DSC thermograms for the PCN/PPG compositions: (a) pure PCN; (b) 74:26; (c) 71:29; (d) 69:31; (e) 66:34; (f) 63:37 and (g) 45:55 PCN/PPG (wt%).

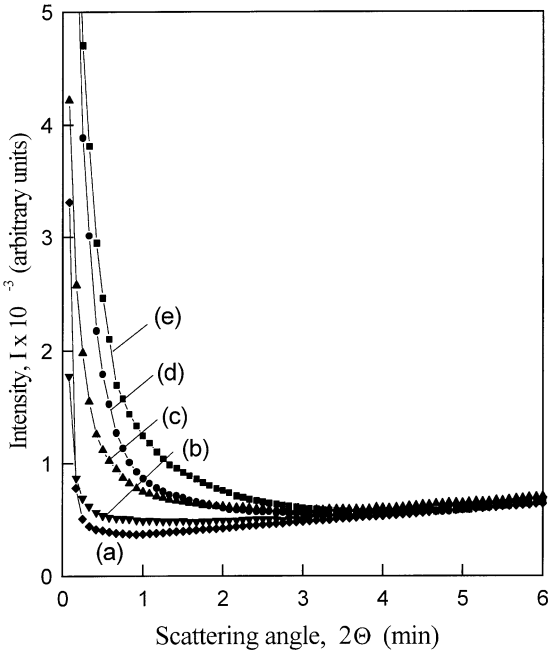


Fig. 12. SAXS curves for the PCN/PPG compositions: (a) pure PCN; (b) 90:10; (c) 80:20; (d) 66:34 and (e) 45:55 PCN/PPG (wt%).

3.5. X-ray analysis

The above conclusions are in agreement with the SAXS analysis of the PCN/PPG series. The X-ray scattering intensity versus scattering angle plots for pure PCN and for the PCN/PPG series are shown in Fig. 12. It can be seen that the X-ray scattering intensity of pure PCN is very small, indicating that it is almost homogeneous in structure (Fig. 12a). The value of X-ray scattering intensity of the PCN/PPG blends is higher and increases with growth of PPG content. This leads to greater heterogeneity (Fig. 12b–e). It is known that the electron density fluctuations within the phases can be considered to produce additional intensity components in the small-angle region because of the internal structure of the phases. One can assume that the increase of X-ray scattering intensity for PCN/PPG blends shows the presence of microphases with electron density differing from that of the homogeneous pure PCN and PPG components. This means that the PCN/PPG blends consist of the microphases with different compositions, in addition to the PCN and the PPG microphases. As was discussed above, we consider that there are PCN-rich and PPG-rich microphases as well as a mixed PCN/PPG microphase.

3.6. Structure–property relationships

The tensile strength (σ) and elongation at break (ε) versus modifier (PPG, PTMG) content for cured (unextracted) PCN/PEth series are shown in Fig. 13. The concentration dependence of tensile strength passes through a maximum. The elongation at break increases slightly up to a certain concentration of PEth and then dramatically increases. It is clearly seen that the sharp change of σ and ε values (i.e. the cusp) corresponds to a composition with PEth content equal to the maximum incorporation degree (26–28% in Table 3). Thus, the incorporation of PEth into PCN significantly improves the network properties, but dissolution of non-incorporated PEth (at higher PEth contents) in the modified polycyanurate network leads to the opposite effect. In general, the tensile strength of compositions with PEth content up to 40% is higher than for pure PCN. From the point of view of technological applications, we see excellent possibilities to obtain composites with the desired properties by changing the oligomer modifier content. For example, in the region of small content (<10%) of PPG, it is possible to produce the thermosets with high values of T_g (270–263°C) and tensile strength (35–50 MPa), which are higher than for pure PCN.

4. Conclusions

The possibility of modification of brittle PCN, based on DCBA with various amounts of oligomeric additive, hydroxyl-terminated PEth such as PPG and PTMG has been investigated. It is proposed that PEth incorporate into the PCN structure through mixed cyanurate ring formation and abstraction of phenol-terminated compounds. The maximum value of incorporated PEth content is near 0.1 mol mol^{-1} of DCBA irrespective of PEth type and it does not increase with further growth of the PEth content in initial composition. It is assumed that by a certain time of reaction sufficient amounts of the more active phenolic

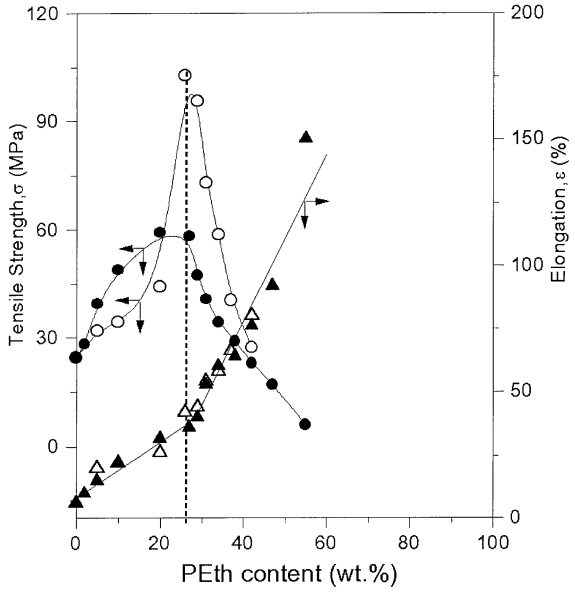


Fig. 13. Tensile strength, σ (●, ○) and elongation at break, ε (▲, △) for the PCN/PEth compositions as a function of modifier (PEth) content: (●, ▲) PPG; (○,△) PTMG.

groups should have been formed and this reaction could go much faster than the one involving hydroxyl groups.

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

The formation of multiphase polymer systems due to microphase separation of the components occurring at DCEBA/PPG curing has been observed by DMTA analysis. The formation of very finely divided morphologies with highly interpenetrating phases, viz. a phase rich in PCN-network, a mixed phase of PCN/PPG components and a phase rich in linear PPG component is discussed.

The PEth incorporation decreases the crosslink density of network matrix and contributes to improve the component miscibility due to increasing affinity of the PEth-modified network to non-incorporated PEth. The non-incorporated PEth is dissolved in the network matrix, playing the role of plasticizer in these PCN/PEth blends.

It is supposed that the rate of the incorporation reaction in the case of PTMG is faster than in PPG. Thus, the growing PCN has no time to phase separate. This conclusion requires experimental verification.

The introduction of PEth into PCN improves the mechanical properties of the latter to maximum extent at the PEth content of 26–28%, corresponding to the maximum PEth incorporation degree. The use of small additions of oligomeric modifier PPG ($<10\%$) allows production of thermosets with high T_g and good tensile strength properties.

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