Synthesis of Inhomogeneous Modified Polycyanurates by Reactive Blending of Bisphenol A Dicyanate Ester and Polyoxypropylene Glycol

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SUMMARY: A series of polycyanurate networks (PCN), based on the dicyanate of bisphenol A monomer (DCBA), was synthesized in the presence of different contents of polyoxypropylene glycol (PPG). 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. It is supposed that the lowering of the glass transition temperature of modified network matrix at increasing PPG content is due to a) PPG incorporation, b) decrease of the final DCBA conversion and c) the increase of percentage of non-incorporated PPG, which acts as plasticizer.

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 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. Currently, this polymerization and the physical properties of the resulting polymers have attached 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)]. To improve this particular aspect dicyanate esters are modified by reactive co-monomers[3-11)] with homogeneous materials formation or by rubbers or thermoplastics which are able to form the dispersed phase in polycyanurate matrix[7,12-15)]. The most interesting case is the polymer

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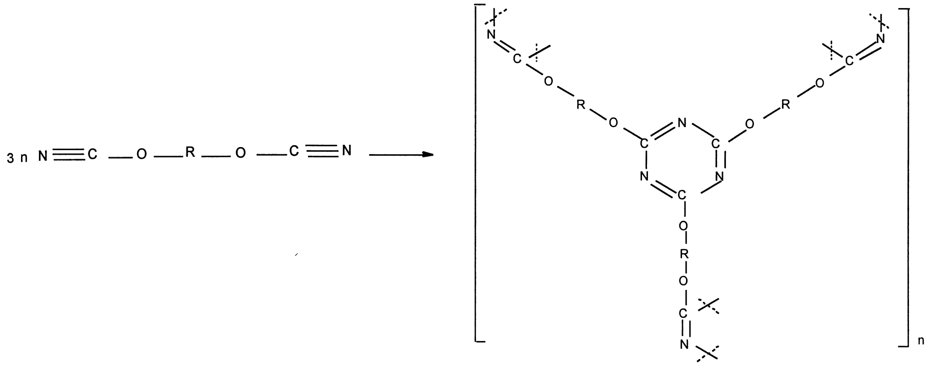
system with a certain degree of heterogeneity where the phases formed are linked chemically[7,14,15].



Scheme 1. Monomer structure and polycyanurate network formation

The aim of present research is to study the formation and structure of polycyanurate networks modified with polyoxypropylene glycol, their phase morphology, glass transition behaviour, and some mechanical properties.

Experimental

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 (3 mol.% per DCBA). The DCBA and triethylamine were used as received. Polyoxypropylene glycol (PPG, molar mass 1050 g/mol^{-1}) was used as the network modifier. PPG was dried at 80°C under vacuum for 6 h. Samples with component ratios of DCBA/PPG from 98/2 to 45/55 wt.% were prepared and studied. It was impossible to prepare the film samples with DCBA/PPG ratio smaller than to 45/55 wt.%. 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.

Techniques

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 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/PPG blends) was used as the internal standard.

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 1 Hz from –100 to 300°C using a heating ramp of 4 K/min. Some samples were additionally measured in the torsion mode using a Dynamic Mechanical Thermal Analyzer (RDAII-Rheometric Inc.) at the same conditions.

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 vacuum at 70°C. The experimental values of gel fraction ($w_{g\,exp}$) were defined as the weight fraction of the insoluble part of PCN/PPG composition. The theoretical value of gel fraction ($w_{g\ theor}$) was calculated using equation 2[4] obtained with the help of Monte Carlo simulation and with assumption that the linear PPG was completely extracted.

$$w_{g\,theor} = (1-w_{PPG}) \times (2\alpha-1)/\alpha^2 , \qquad (1)$$

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

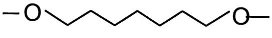
Density. The densities (average value of three measurements) of the cured samples were determined using the Archimedes's method at room temperature.

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 specimens with dimensions of 40 x 5 x 1.2 mm^3.

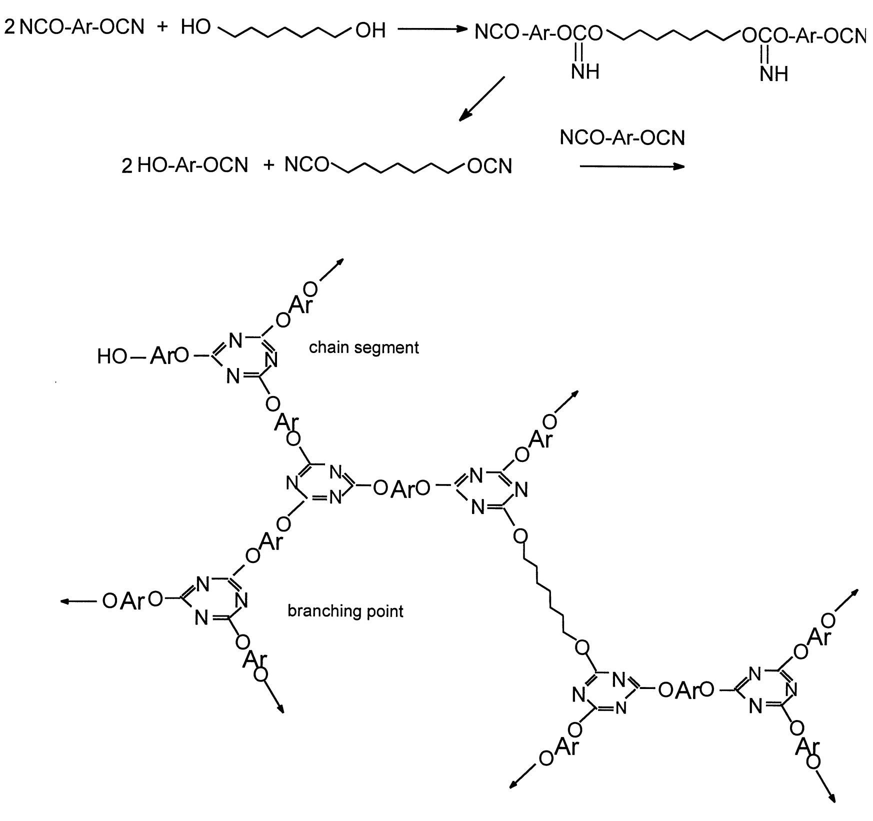
Chemical structure

A few papers only have been published[15,16,17] concerning the modification of cyanate esters with hydroxyl-terminated compounds and there is no clear understanding of the chemistry and how these compounds can be incorporated into the network.

In FTIR spectra we have found 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) and weak absorption bands with maxima at 2236-2272 cm^{-1} arising from the stretching vibrations of the residual cyanate groups[18]. Other relevant peaks in the spectra of cured DCBA/PPG blends are associated with the presence of PPG, i.e. absorption bands at 930, 1104 and 2872 cm^{-1}. 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 polycyanurate network, 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 cured DCBA/PPG blends.

Similarly to the co-reaction of dicyanates with diphenols[2,4), we would propose the scheme, where the fragment 

is incorporated into a network chain and all substituents on the triazine rings, which are not network chains, are hydroxyl-terminated.



Scheme 2. Modified network formation

Gel fraction and incorporated PPG content

No unreacted OCN-groups have been found in the sol fraction of pure PCN and PCN/PPG blends (FTIR data). Thus, one can suppose that unreacted cyanate groups are trapped inside the polycyanurate network. It can be explained by topological limitations at the end of the DCBA cure, which prevent reaction of cyanate groups spatially separated from each other, because of the high connectivity of the final network[19)]. The theoretical calculation of gel fraction of PCN (see Eq. 1*)* has shown that for PCN with OCN-conversion ≥93% (the lowest experimental value of OCN-conversion of PCN in the PCN/PPG blends) 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 PPG integrated into the network structure by comparison the experimental and theoretical values of gel fraction. In Table 1, the compositions and their gel fractions as well as the calculated incorporated PPG content (incorporation degree) in the gel fraction, and PPG conversion at incorporation are shown.

As can be seen from Table 1 for cured compositions, the experimental values of gel fraction, $w_{g\ exp}$, decreases from 99.8 to 62.1% with increasing PPG content in the initial composition from 2 to 55%. From 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 polycyanurate. The PPG conversion at 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 gel fraction slowly increases from 0.01 to 0.06 moles per 1 mol 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 gel achieves the value equal approximately 0.1 mol per 1 mol of DCBA and stays constant with increasing PPG content in initial composition up to 55 wt.%. Aryl cyanate reacts with an alcohol forming a cyanurate ring with abstraction of phenol. 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 one involving alcohol[20)]. So polycyanurate network modified with a oligomeric additive, PPG (partly incorporated chemically) has been synthesized.

Table 1.Gel fraction of cured DCBA/PPG blends as a function of composition.

PPG content in initial composition, w_{PPG}	Gel fraction, w_g		Gel fraction composition		PPG conversion at incorporation,
	$w_{g\,\mathrm{exp}}$	$w_{g\,theor}$	PPG incorporation degree, $\Delta w_g / w_{g\,\mathrm{exp}}$	Incorporated PPG moles [a], $\dfrac{\Delta w_g / M_{PEth}}{w_{gtheor} / M_{DCBA}}$	$\Delta w_g{}^{b)} / w_{PPG}$
wt.%	wt.%	wt.%			wt.%
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

a) Per 1 mol of DCBA

b) $\Delta w_g = w_{g\,\mathrm{exp}} - w_{g\,theor}$

Morphology

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[21)]. An intermediate degree of miscibility results in a broad transition. This microheterogeneous morphology is often used to develop good damping materials [22)]. 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_g 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 modulus (E'') *versus* temperature plots for the PCN/PPG series are shown in Figs. 1 and 2.

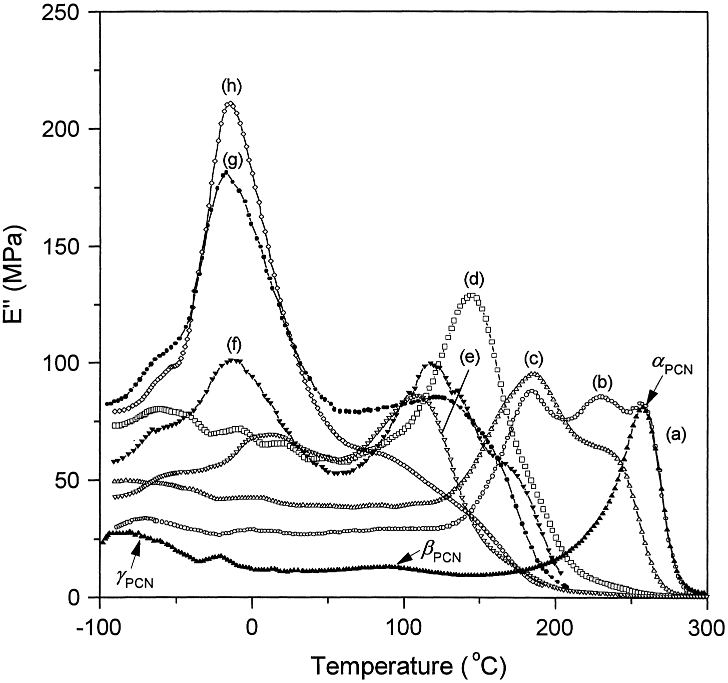


Fig.1: Loss modulus (E'') *versus* temperature for PCN/PPG composition (bending mode). (a) Pure PCN; (b) 98:2; (c) 95:5; (d) 90:10; (e) 85:15; (f) 74:26; (g) 69:31 and (h) 63:37 PCN/PPG (wt.%).

The PCN homonetwork exhibits the one main relaxation, denoted α, associated with the glass transition (T_g) at 278°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 associated with the motion of the phenylene groups present in the links between the planar

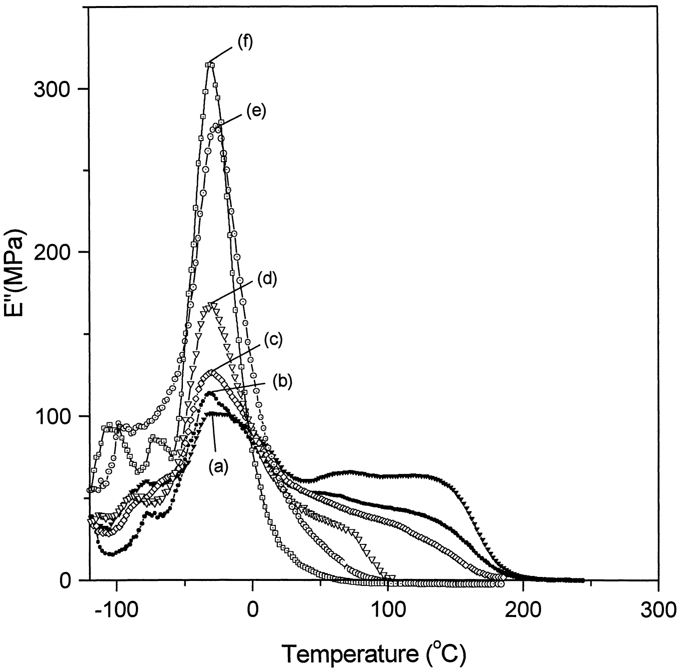


Fig.2: Loss moduli (*E''*) *versus* temperature for the PCN/PPG compositions (torsion mode). (a) 74:26; (b) 69:31; (c) 66:34; (d) 78:42; (e) 53:47 and (f) 45:55 PCN/PPG (wt.%).

six-membered three-arm cyanurate rings[23]. The β relaxation could be attributed to the motions of chain fragments between the network junctions. As was shown by Bauer et al.[24], this transition provides evidence about the presence of irregular network structures. 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 (See Table 2). It is known that pure PPG has its T_g in the region from –75 °C to –60°C[25]. As can be observed from Figs. 1 and 2 there are at least three main glass transition regions indicate the formation of three phases of dissimilar composition, differing in properties from the pure components. These are the phase riched in PCN-network, the mixed phase of PCN/PPG components and the phase riched in the linear PPG component. Their values of T_g and the height of the tan δ maxima are given in Table 2. As can be seen from Table 2, the transition of PCN–rich phase shifts to lower temperatures from 278°C to 60°C, as the PPG weight fraction increases from 0:100 to 55:45 PPG/PCN. The transition of PPG–rich phase consistently shifts to higher temperatures with increasing PCN weight fraction. The increase is near 40 K between the PPG transition in the 55:45 PPG/PCN (-18°C) and that in the 15:85 PPG/PCN (+20°C) blends. The decrease of T_g of the PCN/PPG mixed phase is also very significant with the differences of 175 K between its transition in 2:98 (191°C) PPG/PCN and 55:45 PPG/PCN (16°C). The loss modulus, E'', *versus* temperature shows two or three distinct transitions depending on composition (Figs. 1 and 2).

The mentioned decrease 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 Scheme 2). 2) Decrease in the final degree of OCN-conversion.

One can assume that the increase of PPG incorporation degree will contribute to expansion 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 2). The loss factor peak heights of the PCN and PPG components do not decrease linearly with decreasing their 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 continuity21) 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 2 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 growth of component mixing in these blends.

Georjon et al.26) have investigated in details 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 2, the decrease of PCN-component T_g in compositions studied is much

Table 2. DMTA (1 Hz) data for PCN/PPG blends as a function of composition.

Compositions (wt.% PPG)	Tg (°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 tanδ_{max} or half height of step-drop log E'.

greater. Summarising 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 of percentage of non-incorporated PPG, which then acts as a plasticizer.

Structure-Property Relationships

The density (ρ), tensile strength (σ) and elongation at break (ε) *versus* modifier (PPG) content for PCN/PPG series are shown in Fig. 3. It can be seen that the density value does not change with the composition according to the additive blend law (Fig. 3 a). The low density of PPG, 0.998 g/cm^3, contributes to the decrease in the ρ of the modified PCN. However, the decrease in experimental density as the modifier content was increased appears lower than predicted by the additive blend law. This result is perhaps due to the partial filling the empty volumes of modified networks by non-incorporated PPG.

The concentration dependence of tensile strength (σ) passes through a maximum (Fig. 3 b). The elongation at break (ε) increases slightly up to a certain concentration of PPG and then

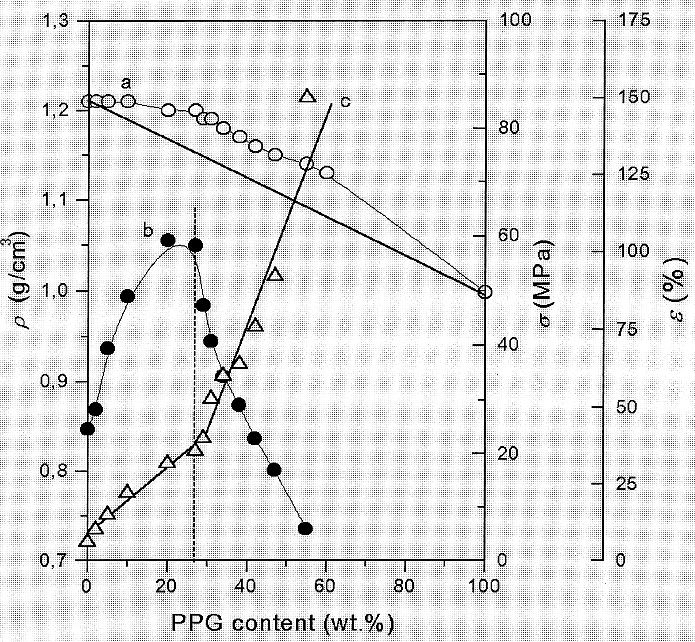


Fig.3: Density, ρ (a), tensile strength, σ (b), and elongation at break, ε (c), for the PCN/PPG compositions as a function of modifier (PPG) content.

dramatically increases (Fig. 3 c). It is clearly seen that the sharp change of values σ and ε (i.e. the cusp) corresponds to composition with PPG content equal to the maximum incorporation degree (26-28% in Table 1). Thus the incorporation of PPG into PCN significantly improves the network properties, but dissolution of non-incorporated PPG (at higher PPG contents) in modified polycyanurate network leads to the opposite effect. In general, the tensile strength of modified compositions studied is higher than for pure PCN (excluding the compositions with > 40 % of PPG). From the point of view of technological applications, we see excellent possibilities to obtain composites with the desired properties by change 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 (30-50 MPa), which are significantly higher than for pure PCN.

Conclusion

1. The possibility of modification of brittle PCN, based on DCBA with various amount of oligomeric additive PPG has been investigated. It is proposed that PPG might be incorporated into the PCN structure through mixed cyanurate ring formation and abstraction of phenol-terminated compounds. The maximum value of incorporated PPG content is near 0.1 mol per 1 mol of DCBA and it does not increase with further growth of the PPG content in initial composition. It is assumed that by a certain time of reaction sufficient amounts of the more active phenolic groups should have been formed and this reaction could go much faster than the one involving aliphatic hydroxyl groups.
2. The formation of multiphase polymer systems due to microphase separation of the components occurring at DCEBA/PPG composition curing has been observed by DMTA analysis. The formation of morphologies with highly interpenetrating phases, viz. a phase rich in PCN-network, the mixed phase of PCN/PPG components and the phase rich in linear PPG component is discussed. The PPG incorporation decreases the crosslink density of network matrix and contributes to improve the component miscibility due to increasing affinity of the PPG-modified network to non-incorporated PPG. The non-incorporated PPG is dissolved in the network matrix, playing the role of plasticizer in these PCN/PPG blends.
3. The introduction of PPG into PCN improves the mechanical properties of the latter to maximum extent at the PPG content of 26-28%, corresponding to the maximum PPG

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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