Polymer Bulletin 58, 93–104 (2007)
DOI 10.1007/s00289-006-0616-1

Polymer Bulletin

Polycyanurate networks modified by polyoxytetramethylene glycol

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Received: 25 July 2005 / Revised version: 27 September 2005 / Accepted: 5 October 2005

Summary

We report results obtained within a collaborative project dealing with the preparation of hybrid polycyanurate/polyoxytetramethylene glycol (PCN/PTMG) networks and the investigation of their structure-property relationships by a variety of experimental techniques. The hybrids were prepared from PCN and PTMG (molar mass 1.000 g/mol) with 10, 20, 30 and 40 wt% PTMG. The degree of incorporation of PTMG into the PCN network was determined by gel fraction measurements. WAXS and SAXS studies had indicated that the materials under investigation are amorphous and exhibit nanostructural heterogeneity, which increases with increasing amount of PTMG. Stress-strain measurements show improvement of the mechanical properties for PTMG contents of 30 and 40%. The focus in this paper is on the detailed investigation of the α relaxation associated with the glass transition in wide ranges of frequency and temperature by dielectric techniques. A single α relaxation was observed in all the compositions shifting systematically to lower temperatures/higher frequencies with increasing PTMG content. The results were systematically analyzed in terms of time scale and relaxation strength of the response and are discussed in terms of plasticization, presence of nanostructural heterogeneities and hybridization. Co-operativity of the α relaxation, quantified in terms of fragility, was found to decrease with increasing amount of PTMG, in correlation with increasing level of nanoheterogenity.

Introduction

Polycyanurate (PCN) networks are synthesized by cyclotrimerization reaction of a dicyanate ester, typically dicyanate ester of bisphenol A (DCBA) [1, 2]. Pascault and

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Presented at 44th P.M.M. Microsymposium "Polymer Gels and Networks", Prague, 10–14 July 2005 coworkers investigated in detail the conversion in these networks and showed that there is an one to one relationship between the glass transition temperature of the network and the degree of conversion [3]. At full conversion, the PCNs are characterized by high glass transition temperature (T_g), in the range of 300 ^oC, and high thermal stability, as well as by some other good properties, which make them suitable for applications in high performance technologies. The primary drawback of PCNs for such applications is their low room temperature toughness [1, 2].

PCNs may be toughened by physical or chemical modification following various routes, such as the addition of thermoplastics and the formation of so-called semi-interpenetrating polymer networks (IPNs) [4], or the co-reaction with monomers or oligomers that contain active hydrogens (phenols, diamines, diepoxides etc) [1, 2,]. Perhaps a more perspective way is to combine physical and chemical modification by using a reactive co-monomer together with a rubber or a thermoplastic, or a rubber or a thermoplastic with functional chain ends reacting with the cyanate groups [5].

In previous work we used linear polyurethane as a modifier. Detailed investigations showed that the networks prepared in the presence of polyurethane were macroscopically homogeneous, with distinct heterogeneities at nanometer scale [6-8]. The results were explained in terms of the formation of a hybrid polycyanurate-polyurethane network due to chemical bonds between the components.

The next step was to use low molar mass polyethers or polyesters for PCN modification. PCNs were synthesized in the presence of different contents of polyoxypropylene glycol (PPG) and polyoxytetramethylene glycol (PTMG) and the effects of the type of the oligomeric modifier, initially miscible with DCBA, on the chemical structure, glass transition behavior, phase morphology and mechanical properties of the modified PCN were studied [9-11]. The results indicated the formation of very finely divided morphologies with three highly interpenetrated phases in the case of PPG [9, 10]. On the other hand, PCN/PTMG cure compositions proved to be more homogeneous, exhibiting a single, broad glass transition [11]. Miscibility in multicomponent polymeric systems is, however, an intriguing subject and the experimental results may depend on the technique used. Dynamic techniques, including broadband dielectric relaxation spectroscopy (DRS), have proved sensitive to dynamic and spatial heterogeneities in macroscopically homogeneous polymeric systems [8].

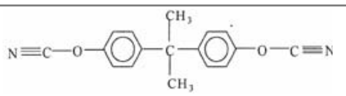
In the present paper we report results obtained within a project dealing with the preparation of hybrid PCN/PTMG networks, with varying molar mass and content of PTMG, and the investigation of their structure-property relationships by a variety of experimental techniques. In order to increase the final degree of PCN network curing and the degree of PTMG chemical incorporation harder curing conditions were applied with respect to the materials of ref. [9]. Thus, structure and properties of the polymer systems studied in the present paper may differ from those of the modified PCN networks of ref. [9]. In a first paper of this series, next to FTIR and sol-gel analysis, wide - and small-angle X-ray scattering (WAXS and SAXS, respectively), DSC and laser-interferometric creep rate spectroscopy (CRS) were employed to investigate nanostructure and segmental dynamics of PCN/PTMG compositions with PTMG molar mass 1.000 g/mol and content 10, 20, 30 and 40 wt% [12]. The results showed that the materials under investigation are amorphous and exhibit nanostructural heterogeneity, which increases with increasing amount of PTMG. In the present paper we continue that study. We employ stress-strain measurements to investigate mechanical properties. We then focus on the detailed investigation of molecular dynamics, in particular of segmental dynamics associated with the glass transition, by broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) techniques.

Experimental

Materials

Dicyanate ester of bisphenol A (DCBA, > 98 % purity) and triethylamine (99 % purity) as cure catalyst (1 mol %) were used, as received, for the preparation of the PCNs. Poly (tetramethylene glycol) (PTMG) with molar mass M_n=1.000 g/mol was used as the modifier. PTMG was dried at 80 °C under vacuum for 6 h. The materials are listed in Table 1. Samples with weight ratios of DCBA/PTMG 90/10, 80/20, 70/30, 60/40 and pure PCN were prepared and studied. The cyanate ester, catalyst and polyether were first mixed together, then degassed at 80 °C for 0.5h and then poured into a PTFE - coated mould. The curing cycle consisted of three stages: 10h at 150 °C, 8 h at 180 °C and 3 h at 210 °C. In the following the hybrids are designated by PCN/PTMG (X/Y), where X/Y is the weight ratio of DCBA and PTMG used.

Table 1. Chemical structure and characteristics of the materials used

Component	Chemical structure	Molar mass (g/mol)
Dicyanate ester of bisphenol A (DCBA)		278
Polytetramethylene glycol (PTMG)	$HO—[(CH_2)_4—O]_n—H$	1000
Triethylamine	$(C_2H_5)_3N$	101

Hybridization of the networks was confirmed by FTIR spectroscopy, which indicated practically full conversion of OCN- groups in the hybrid networks, in particular due to their high reactivity towards OH end groups of PTMG. Similar to the co-reaction of dicyanates with phenols [13], we would propose a scheme [9], where the fragment  is incorporated into a network chain and all substituents on the triazine rings, which are not network chains, are hydroxyl terminated.

Sol-gel analysis (compare ref. [9] for details) was used to determine the fraction of PTMG incorporated into the PCN network. This can be calculated by comparison of the experimental and theoretical values of gel fraction, as the whole of DCBA participates into the network formation (FTIR results) [9]. The results listed in Table 2 show that the degree of chemical incorporation of PTMG into the network decreases from 97 % to 78.8 % with increasing PTMG content, in the initial composition, from 10 to 40wt%. As a result, the hybrid networks studied include different contents of rigid triazine ring-aryl junctions and relatively flexible junctions, where triazine rings are chemically connected with flexible PTMG chains (Scheme in [12]).

Techniques

For thermally stimulated depolarazation currents (TSDC) [14] a Novocontrol sample cell for TSDC measurements was used, in combination with the Novocontrol Quatro cryosystem and a 617 Keithley electrometer. Broadband dielectric relaxation spectroscopy (DRS) measurements [15] were carried out by means of an Alpha Novocontrol analyzer, in combination with the Novocontrol Quatro cryosystem. Stress-strain measurements were performed at room temperature with an Instron 1121 tester (Buckinghamshire England).

Results and discussion

Mechanical measurements

The results of stress-strain measurements at room temperature are listed in Table 2. They show that both the elastic modulus and the tensile strength decrease with increasing amount of PTMG, whereas the maximum elongation at break increases. By incorporating 10 % of PTMG into the network, both the elastic modulus and the elongation at break are practically not affected, whereas the tensile strength increases significantly. These results can be explained by microplasticity, indicated by CRS on the same hybrids [12]. A change of the behaviour is observed in Table 2 from that of a brittle material (pure PCN and hybrids with 10 and 20 % PTMG) to that of a ductile material (hybrids with 30 and 40 % PTMG). Thus, the mechanical properties of the PCNs are improved by incorporation of PTMG and it is worth to further investigate the structure-property relationships of the hybrid networks.

Table 2. Stress-strain results for the pure PCN and the hybrid PCN/PTMG networks

PTMG content in initial composition (wt %), w_{PTMG}	PTMG conversion at incorporation (wt %)	Elastic Modulus GPa	Tensile Strength MPa	Elongation at break %
0	-	3.4	53	1.50
10	97.0	2.9	75	2.86
20	97.0	3.5	70	2.41
30	85.7	1.4	54	6.70
40	78.8	0.20	26	117

Overall dielectric behaviour

Figure 1 shows TSDC thermograms obtained with the pure PCN and the hybrid networks. The TSDC method corresponds to measuring dielectric losses as a function of temperature at constant low frequency (10^{-2} – 10^{-4} Hz) and provides an overview of the dielectric behaviour of the material under investigation.

For pure PCN we observe four peaks: two peaks at temperatures lower than T_g, located at 143 and 256 K and associated with secondary relaxations, attributed to short range motions of PCN chains, and a double peak at higher temperatures, associated with the glass transition. For comparison, Georjon et al. observed by dynamic mechanical analysis (DMA) measurements at 1 Hz two sub-glass relaxations in pure PCN networks, located at 168 K (γ relaxation) and 267 K (β relaxation), respectively [16]. The γ relaxation was ascribed to the motion of phenylene groups present in the links between the planar six-membered three-arm cyanurate structures. The β relaxation was attributed to the motions of chain fragments between the network junctions. DMA measurements on the PCN network of the present study give three loss peaks

[9]: two sub-glass loss peaks located, at 10 Hz, at 198 K and 373 K, γ and β relaxation, respectively, and a single one, the main α relaxation, located at 554 K. The secondary relaxations were ascribed to the same motions as described by Georjon et al. [16].

Bearing in mind the lower (equivalent) frequency of TSDC measurements, as compared to DMA, the location (time scale) of the γ PCN relaxation detected by TSDC is in good agreement with that observed by DMA. Thus, we adopt the same interpretation as for DMA measurements for the molecular motions responsible for the dielectric γ PCN relaxation. Results are less clear with respect to the β relaxation: intercomparison of dielectric ([8] and present work) and DMA results [9, 16] on various pure PCN networks indicate that the temperature location of this relaxation depends on both the experimental technique used and the structure of the network. Nevertheless, the molecular assignment of the β relaxation in all these studies to rotational motions of chain fragments between the network junctions is adopted here also for the TSDC β relaxation.

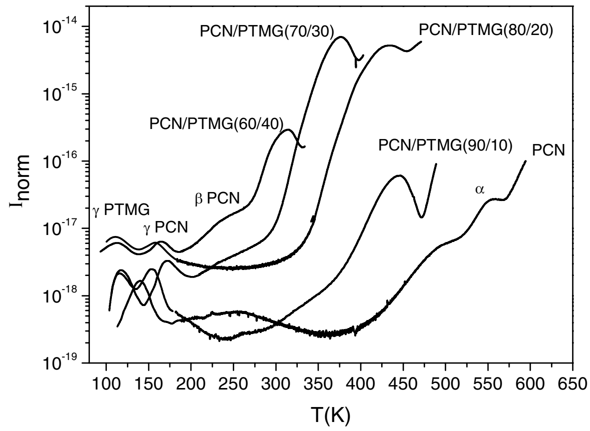


Figure 1. TSDC thermograms measured on pure PCN and the hybrid networks. The depolarization current is normalized to the electric field applied and the surface area of the sample

The two high-temperature peaks in the TSDC thermogram of pure PCN at 503 and 553 K are attributed to the main α relaxation, associated with the glass transition. Please note that the magnitude of the peak at 503 K, which is a measure of the number of relaxing units contributing to the peak, is by about one order of magnitude lower than that of the peak at 553 K. Thus, the TSDC peak at 553 K corresponds to the α relaxation of the main part of the PCN network, in agreement with the results of DMA measurements [9]. The peak at 503 K may be tentatively attributed to the glass transition of regions with lower cross-linking density.

In the TSDC thermograms obtained for the hybrid networks an additional secondary relaxation appears located at 125 K. This relaxation is attributed to local motions of the modifier PTMG, as it is not detected in the pure PCN network. More specifically, this relaxation is attributed to damped oscillations of ether segments around their equilibrium position (local mode [17]). The other two peaks observed in the hybrid networks at sub-glass temperatures are attributed to the modified γ and β relaxation of the PCN network, the latter being detected only in the thermograms of the hybrids with 30 and 40 % PTMG. All the hybrid networks show a single peak at higher temperatures, which shifts to lower temperatures with increasing PTMG content, in agreement with the results of DMA [9], DSC and CRS [12] and DRS to be reported later. The presence of a single α peak in the hybrid networks indicates miscibility of the two components at the molecular level. We will come back to this point later.

The relaxations detected by TSDC (Figure 1) were studied in detail by means of DRS measurements in broad temperature and frequency ranges. Isochronal (constant frequency) plots of dielectric loss against temperature, $\varepsilon''(T)$, at a constant frequency (not shown here) show the same relaxations as in Figure1. In the following we focus on the investigation of the main α relaxation associated with the glass transition.

The main α relaxation

The α relaxation was studied in detail by means of isothermal DRS measurements at several temperatures in the temperature range of interest. An example is given in Figure 2 for the PCN/PTMG (90/10) network. The spectra are typical for the PCN and the hybrid networks. The increase of ε″ with decreasing frequency, observed at low frequencies/high temperatures, is related to conductivity phenomena [8], not further studied here, whereas the α relaxation is observed as a peak at higher frequencies (located at about 10^5 Hz at 533 K). The α relaxation in pure PCN and the hybrid networks was analyzed with respect to time scale and relaxation strength of the dielectric response.

The following expression, consisting of a sum of the Havriliak - Negami model function and a conductivity term [8, 15], was fitted to the experimental $\varepsilon''(f)$ data

$$\varepsilon''(\omega) = \mathrm{Im}\left(\varepsilon_\infty + \frac{\Delta\varepsilon}{\left(1+(i\omega\tau)^\alpha\right)^\beta}\right) + K\omega^{-s} \qquad \mathbf{(1)}$$

where $\Delta\varepsilon=\varepsilon_s-\varepsilon_\infty$ is the dielectric relaxation strength with ε_s and ε_∞ the limits of $\varepsilon'(\omega)$ for $\omega\tau<<1$ and $\omega\tau>>1$, respectively. The relaxation time τ is related to the position of maximal loss by $2\pi f_{\mathrm{max}}=1/\tau$. The shape parameters α and β are related to the limiting behaviour of the dielectric response at low and high frequencies, the corresponding slopes in log-log plots being $m = \alpha$ and $n = \alpha\beta$, respectively [8, 15]. K and s are constants.

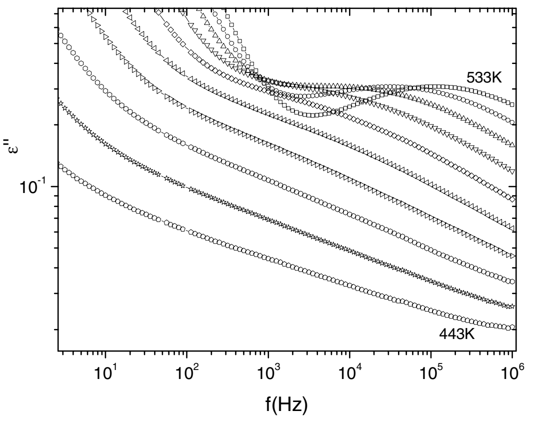


Figure 2. Dielectric loss ε'' against frequency *f* at selected temperatures in steps of 10 K in the region of the main α relaxation in the hybrid PCN/PTMG (90/10) network

Figure 3 shows the Arrhenius plot of the α relaxation in pure PCN and the hybrid networks. TSDC data determined by the peak temperature of the corresponding TSDC peak and the equivalent frequency of 1.6 mHz, corresponding to a relaxation time of 100 s [8], are also included. The positions of the γ and β relaxations of the pure PCN network are indicated by lines (without experimental points) for comparison. We observe in Figure 3 the systematic shift of the α relaxation to lower temperatures with increasing PTMG content, in agreement with previous results obtained with DMA [9] and DSC and CRS [12] at a single frequency, extended now to a broad frequency range. A single Vogel – Tammann - Fulcher (VTF) equation, characteristic for the main α relaxation in polymeric systems [18],

$$f_{\max} = f_0 \exp\left(-\frac{B}{T - T_0}\right) \qquad (\mathbf{2})$$

with temperature-independent empirical parameters f_0, B and T_0 (Vogel temperature), was fitted to the data, except for the PCN/PTMG (70/30) hybrid, which will be discussed later. Following common praxis f_0 was fixed to 10^{13} Hz [15]. Reasonable values were obtained for B and T_0, with B increasing from 2276 to 3733 K and T_0 decreasing from 495 to 204 K with increasing PTMG content. A change of the concavity of the plots with increasing amount of PTMG may be observed in the plots, which will be quantified later.

The data for the PCN/PTMG (70/30) network in Figure 3 cannot be fitted by a single VTF equation. However, this can be done for the high temperature/frequency data, with reasonable values for the fitting parameters. The temperature dependence of the data at lower temperatures/frequencies is satisfactorily described by the Arrhenius equation

$$f_{\max} = f_0 \exp\left(-\frac{E_{act}}{kT}\right) \qquad (\mathbf{3})$$

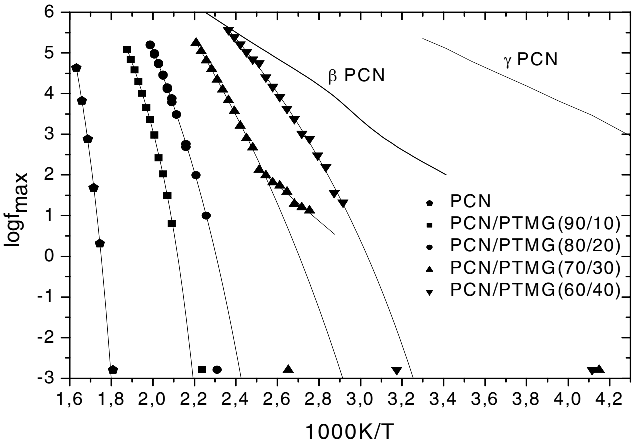


Figure 3. Arrhenius plot of the α relaxation in pure PCN and the hybrid networks indicated on the plot. TSDC data are included at the equivalent frequency of 1.6 mHz. The lines are fittings of the VTF equation (2) and the Arrhenius equation (3) (for the hybrid network PCN/PTMG(70/30)) to the DRS data for the α relaxation. The lines without experimental points indicate the positions of the γ and β relaxations of the pure PCN network

The values of the fitting parameters obtained are 0.95 eV for the activation energy, E_{act}, and 10^{14} Hz for the pre-exponential factor, f_0. These results suggest a change of the dynamics from a cooperative α relaxation at higher temperatures to a Goldstein-Johari β relaxation [19] at lower temperatures. It should be stressed that only a single HN expression was fitted to the data at each temperature, although the results in Figure 3 would suggest, at least in a middle temperature/frequency range, the contribution of both α and Goldstein-Johari β relaxation to the dielectric spectra [20, 21]. The results indicate that the main contribution to the dielectric response comes from the α relaxation at higher temperatures/frequencies and the Goldstein-Johari β relaxation at lower temperatures/frequencies. Support for this interpretation is coming from the data by the TSDC technique, which is characterized by high peak resolving power [14]: two well-separated relaxations have been detected for the PCN/PTMG (70/30) network by TSDC, the corresponding TSDC points being in rather good agreement with the DRS data for the α relaxation and for the Goldstein-Johari β relaxation. Two well-resolved relaxations have been detected by TSDC also for the PCN/PTMG (60/40) network (Figure 3), suggesting a splitting of the α relaxation into α and Goldstein-Johari β relaxation at low frequencies/temperatures. These results can be discussed in terms of the Adam-Gibbs theory for the glass transition [22], the increase of the co-operativity length, i.e. the characteristic length of the glass transition, with decreasing temperature [18] and the influence of a second component on the mobility of the polymer chains [23]. At high temperatures relaxation occurs through the co-operative rearrangement of the polymeric chains. At lower temperatures co-operativity is suppressed and relaxation occurs partly through co-operative rearrangements and partly through motions of isolated chains in regions of large free volume (islands of mobility) [18]. It would be interesting in future to further follow this point by extending the range of DRS measurements to lower frequencies towards the TSDC points in Figure 3.

Results similar to those reported here for the PCN/PTMG (70/30) network (and to some extent for the PCN/PTMG (60/40) network) have been obtained before with highly crosslinked sequential interpenetrating polymer networks (IPNs) of poly(ethyl acrylate) (PEA) and poly(ethyl methacrylate) (PEMA) [21]. Splitting of the α relaxation and the Goldstein-Johari β relaxation was observed in the PEMA networks, a sin-

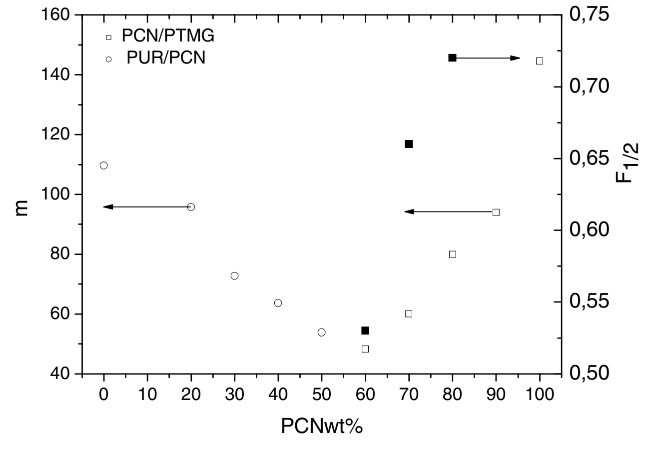


Figure 4. Composition dependence of the fragility index *m* and the fragility $F_{1/2}$ in PCN/PTMG and PUR/PCN hybrids

gle α relaxation in PEA-rich compositions and Arrhenius behaviour in middle compositions. The latter was explained by suppression of cooperativity due to incorporation of PEA chains to the cooperative motions of the PEMA network, which shifts the α and the Goldstein-Johari β relaxations to a different extent, inducing changes in the shape of the spectrum in the merging zone. Also measurements in natural rubber / silica nanocomposites indicate a splitting of the single α relaxation in the pure matrix into two relaxations, α and Goldstein-Johari β relaxation, in the nanocomposites (work in progress). Thus, the distinct behaviour of the PCN/PTMG (70/30) and (60/40) networks, with respect to pure PCN and the hybrids with lower PTMG content, indicates a higher degree of heterogeneity of those networks, which is consistent with the results of SAXS measurements on the same hybrids [12].

The suppression of cooperativity in the hybrids with respect to pure PCN, discussed on the basis of the Arrhenius plot in Figure 3, can be quantified in terms of fragility. The concept of fragility, i.e. deviation from the Arrhenius behavior in the activation diagram (Figure 3), introduced by Angell [24], has been much used in recent years to classify glass-forming materials with respect to kinetic and thermodynamic aspects of the glass transition. Several measures of fragility have been introduced. Two of them are used here, the steepness or fragility index m, defined by [24]

$$m = \left. \frac{d \log \tau}{d\left(\frac{T_g}{T}\right)} \right|_{T=T_g} \tag{4}$$

and the fragility $F_{1/2}$ defined by [25]

$$F_{1/2} = \frac{2T_g}{T_{1/2}} - 1 \quad \text{with} \quad \tau(T_{1/2}) = 10^{-6} s \tag{5}$$

Figure 4 shows the dependence of the two measures of fragility on the composition of the hybrids: independently of the measure used, fragility decreases, i.e. cooperativity is suppressed, with increasing PTMG content in the hybrids. We have included in the plot results obtained previously with the polycyanurate / polyurethane hybrids (PUR/PCN) [7] mentioned in the Introduction. Although the two systems are different, the results taken together suggest a minimum of fragility for the middle compositions. We can not grasp the significance of these results at present. It is interesting to note, however, that a similar dependence has been observed by DSC in polystyrene / poly(2,6-dimethyl-1,4-phenylene oxide) miscible blends [26].

Figure 5 shows results for the dependence of the dielectric strength Δε on the frequency of the α loss peak. The latter allows for comparison of samples with different glass transition temperatures. We observe in Figure 5 that Δε, which is a measure of the number of relaxing units contributing to the loss peak, increases significantly in the hybrids, as compared to the pure PCN network. Interestingly, Δε is lower in the PCN/PTMG (70/30) than in the PCN/PTMG (80/20) network, indicating constraints imposed to the motion of the polymeric chains in the former network. DRS measurements in semi-interpenetrating polymer networks of linear polyurethane and PCN network with chemical cross-links between the components showed increase of Δε of the α relaxation with respect to that in pure polyurethane [7, 8]. These results suggest that the reason for the increase of Δε of the α relaxation in both systems is the hybridization effect, which results in loosened molecular packing of the chains and increase

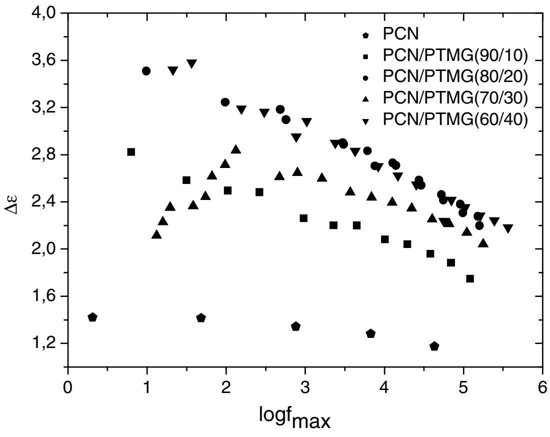


Figure 5. Dielectric strength Δε against logarithm of maximum frequency logf$_{max}$ of the α relaxation in pure PCN and the hybrid networks indicated on the plot

of free volume. Δε increases with decreasing loss peak frequency, i.e. with temperature decreasing towards the glass transition temperature, which is the behaviour typically observed for the α relaxation [15, 18]. A different behaviour is observed for the PCN/PTMG (70/30) network, where Δε starts decreasing with decreasing loss peak frequency below about 100 Hz. This behaviour is in agreement with the results shown in Figure 3 (change of slope at approximately 100 Hz) and the common observation that the relaxation strength of the Goldstein-Johari β relaxation decreases with decreasing temperature [18, 23], providing additional support for the interpretation given above for the distinct behaviour of the PCN/PTMG (70/30) network.

Several measures of the glass transition temperature T_g can be introduced by the techniques employed in the present and in a previous work [12] on the PCN hybrids. In Figure 6 we use three of them to describe the composition dependence of T_g in the hybrid networks: the peak temperatures of the α peak in the TSDC and the CRS thermograms and the temperature defined by the condition $\tau(T_g)$ = 100 s in DRS [8, 15]. The three measures are in rather good agreement with each other. Also, the composition dependence of T_g is rather well represented by the Fox equation for miscible blends [27]

$$T_g = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad \textbf{(6)}$$

bearing in mind the formation of chemical bonds between the two components. In Equation (6) T_g and w give the glass transition temperature and the mass fraction of the two components, respectively, and 188 K has been used for T_g of PTMG.

A final comment refers to the relation between the materials studied here and those of ref. [9]. The harder curing conditions applied in the present paper resulted in higher degree of chemical incorporation of PTMG into the network. No additional curing at high temperatures was observed by comparing TSDC first and second run measurements, whereas effects observed in DMA measurements in ref. [9] may be interpreted in terms of post curing. On the other hand, it is not clear how the final properties of the hybrid networks, such as T_g, depend, for the same PTMG content, on the degree of incorporated and non-incorporated PTMG. DMA measurements (the main technique

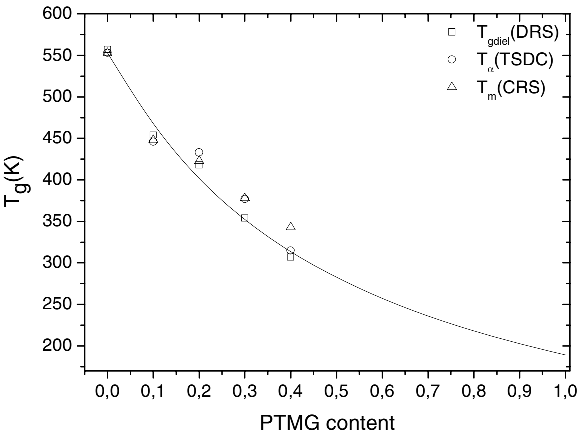


Figure 6. Composition dependence of the glass transition temperature T_g determined by DRS, TSDC and CRS. The line is the Fox equation (6)

applied in ref. [9], on the hybrids of the present study, now in progress, may shed more light on that point.

Conclusions

Hybrid polycyanurate / polyoxytetramethylene glycol (PCN/PTMG) networks were prepared from PCN and PTMG (molar mass 1.000 g/mol) with 10, 20, 30 and 40 wt% PTMG. The degree of incorporation of PTMG into the PCN network, determined by gel fraction measurements, was found to decrease with increasing PTMG content. Morphological and thermal transition studies in a previous work had indicated non-crystalline structure, considerable nanostructural heterogeneity and a wide dispersion of glass transition temperatures of the hybrid networks. In the present work molecular dynamics of the hybrids was studied in detail by broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) measurements, in an attempt to contribute to a better understanding of the structure-property relationships in these complex systems.

The α relaxation (dynamic glass transition) was studied in detail over wide ranges of temperature and frequency. By fitting appropriate model functions to the experimental data the results were systematically analyzed in terms of time scale and relaxation strength of the response. They suggest miscibility of the two components, as a result of hybridization, and plasticization by PTMG. The composition dependence of the glass transition temperature is rather well described by the Fox equation. Analysis of the results for the time dependence of the response in terms of fragility suggests suppression of cooperativity with increasing PTMG content of the hybrids. For the hybrids with the higher PTMG content of 30 and 40%, which show a change from brittle to ductile behaviour, the results of both the time scale (Arrhenius plot) and the relaxation strength of the response indicate a change from a single cooperative α relaxation at higher temperatures/frequencies to a non-cooperative Goldstein-Johari β relaxation at lower temperatures/frequencies. These results can be discussed in terms of the Adam-Gibbs theory for the glass transition, the increase of the co-operativity length with decreasing temperature and the influence of a second component on the mobility of the polymer chains. They indicate the existence of regions with different crosslinking density resulting from the incorporation of PTMG into the network. This spatial nanoheterogeneity is more pronounced in hybrids with a higher PTMG content, in agreement with the results of structural characterization. It may be expected that work in progress on the effect of molar mass of PTMG on molecular dynamics will help to further clarify these points.

Acknowledgements. The project is co-funded by the European Social Fund (75%) and Greek National Resources (25%) - (EPEAEK II) – PYTHAGORAS.

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