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Structure–property relationships in brittle polymer networks modified by flexible cross-links

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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 was determined by gel fraction measurements. Earlier morphological and thermal transition studies indicated a non-crystalline structure, considerable nanostructural heterogeneity and a wide dispersion of glass transition temperatures of the hybrid networks. The present paper reports on a continued investigation of structure-property relationships and employ dielectric techniques to focus on molecular dynamics. Two secondary relaxations of PCN, one secondary relaxation of PTMG and a single, broad α relaxation (dynamic glass transition) were detected in the hybrids. The α relaxation was studied in detail over wide ranges of temperature and frequency. The results were systematically analyzed in terms of time scale, relaxation strength and shape of the response, and are discussed in terms of plasticization, presence of nanostructural heterogeneities (composition fluctuations) and hybridization. A distinctly different behaviour, observed for the hybrid with 30% PTMG, is explained in terms of a more pronounced nanoheterogeneous structure. Finally, stress-strain measurements were performed and their results are discussed in terms of structure and molecular dynamics.

Key words: *modified polycyanurate network; polyoxytetramethylene glycol (PTMG); dielectric spectroscopy; main* α *relaxation*

1. Introduction

Polycyanurate (PCN) networks, typically synthesized by cyclotrimerization reaction of dicyanic ester of bisphenol A (DCBA) [1, 2], are characterized by high glass

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transition temperature (T_g) and high thermal stability, good mechanical properties, excellent adhesion to various substrates, chemical resistance, low electric permittivity and loss values, and low water uptakes. These and other good properties make them suitable for applications in high performance technologies, in particular as matrices for glass and aramid fiber-reinforced plastics in electronic and aerospace industries. A primary drawback of PCNs, restricting their more extensive applications, is, next to high prices, low room temperature toughness [1, 2].

PCNs may be toughened by (i) physical modification through the addition of thermoplastics and the formation of so-called semi-interpenetrating polymer networks (IPNs) [3]; (ii) chemical modification by co-reaction with monomers or oligomers containing active hydrogens, such as phenols, diamines, diepoxides, ethers and esters [1, 2, 4–7]; (iii) combination of physical and chemical modification by use of a reactive co-monomer and a non-reactive rubber or a thermoplastic or a rubber or a thermoplastic containing reactive chain ends [8–12].

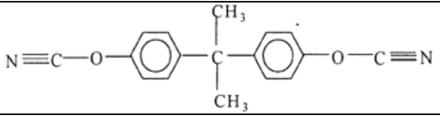
Much attention has been recently paid to modification of PCNs by hydroxyl-terminated polyethers. PCNs were synthesized in the presence of different contents of polyoxypropylene glycol (PPG) and polyoxytetramethylene glycol (PTMG), and the effect of the type of the oligomeric modifier, initially miscible with DCBA, on the chemical structure, glass transition behaviour, phase morphology and mechanical properties of the modified PCN was studied [4–6]. The results indicated the formation of very finely divided morphologies with three highly interpenetrated phases, a PCN -rich, a PPG-rich and a mixed PCN/PPG one, in the case of PCN/PPG network [4, 5]. On the other hand, PCN/PTMG cure compositions proved to be more homogeneous, exhibiting a single broad glass transition in dynamic mechanical analysis (DMA) measurements [6]. Miscibility in multicomponent polymeric systems is, however, an intriguing subject and experimental results may depend on the technique used [13]. Dynamic techniques, such as dielectric relaxation spectroscopy (DRS), nuclear magnetic resonance (NMR) and depolarized light scattering (DLS), have proved sensitive to dynamic and spatial heterogeneities in macroscopically homogeneous polymeric systems [12].

In an attempt to further investigate the effect of PTMG modifier on the phase structure, molecular dynamics and final properties of PCNs, several series of PCN/PTMG cure compositions with varying molar mass and content of PTMG were synthesized and studied. By employing a variety of experimental techniques, the results provide information on structure–property relationships which is essential for optimizing composition and processing (cure) conditions to meet specific end-use requirements. In the first paper of this series, next to FIR 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 [14]. The results revealed a non-crystalline structure, considerable nanostructural heterogeneity and a wide dispersion of glass transition temperatures of the hybrid networks. In the present paper, we continue that study. We employ broadband dielectric relaxation spectroscopy (DRS) and thermally stimulated depolarization currents (TSDC) techniques to investigate details of molecular dynamics. Mechanical properties are investigated by stress–strain measurements and discussed in correlation with the results of structural and dynamic studies.

2. Experimental

Materials. The cyanate monomer used in the present work was dicyanate ester of bisphenol A (DCBA, >98% purity). Triethylamine (99% purity) was used as cure catalyst (1 mol %). DCBA and triethylamine were used as received. Poly(oxytetramethylene) glycol (PTMG) with the molar mass M_n = 1000 g/mol was used as the modifier. PTMG was dried at 80 ºC under vacuum for 6h. The materials used in this study are summarized in Table 1. Samples with weight ratios of PCN/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, degassed at 80 ºC for 0.5 h and then poured into a PTFE-coated mould. The curing cycle consisted of three stages: 10 h at 150 ºC, 8 h at 180 ºC and 3 h at 210 ºC.

Table 1. Chemical structures 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 particular due to their high reactivity towards OH end groups of PTMG. Similar to the co-reaction of dicyanates with phenols [15], we would propose a scheme [4], where the fragment $O–[(CH_2)_4–O]_{14}–$ is incorporated into a network chain and all substituents on the triazine rings which are not network chains are hydroxyl terminated (Scheme 1).

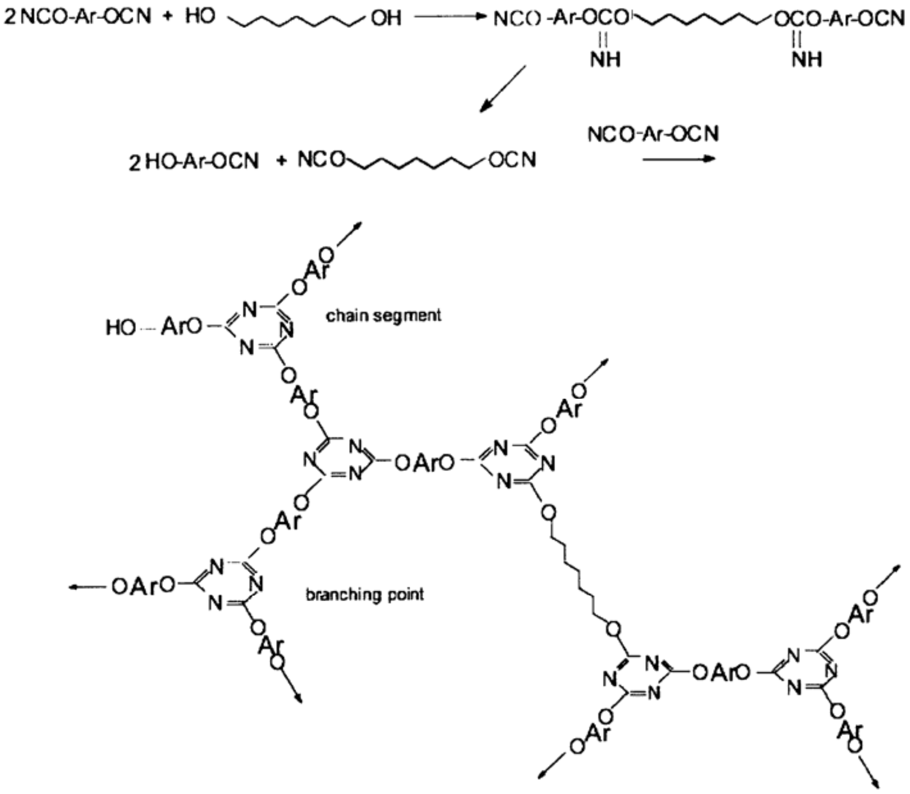
The sol-gel analysis (compare ref. [4] for details) was used to determine the fraction of PTMG incorporated into the PCN network. This can be calculated by comparison of experimental and theoretical values of the gel fraction, as the whole of DCBA participates into the network formation (FTIR results) [4]. In Table 2, the compositions and their gel fractions, as well as the incorporated PTMG content (degree of incorporation) in the gel fraction and PTMG conversion at incorporation are shown. It follows that PTMG conversion by incorporation into the PCN network decreases from

97% to 78.8% when the PTMG content in the initial composition increases from 10 to 40 wt. %. 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 1).

Table 2. Gel fraction results (wt. %) for the pure PCN and the hybrid networks PCN/PTMG

PTMG content in initial composition w_{PTMG}	Gel fraction w_g		PTMG incorporation degree $\Delta w_g^*/w_{g\,\mathrm{exp}}$	PTMG conversion at incorporation $\Delta w_g^*/w_{\mathrm{PTMG}}$
	$w_{g\mathrm{exp}}$	$w_{g\mathrm{theor}}$		
0	99.9	100	–	–
10	99.7	90	9.70	97.0
20	99.4	80	19.5	97.0
30	95.7	70	26.8	85.7
40	91.5	60	34.4	78.8

$^*\Delta w_g = w_{g\mathrm{exp}} - w_{g\mathrm{theor}}$



Scheme 1. Monomer structure and network formation

Techniques. A Novocontrol sample cell (for TSDC measurements) in combination with the Novocontrol Quatro cryosystem and a 617 Keithley electrometer were used for thermally stimulated depolarazation currents (TSDC) [16]. Broadband dielectric relaxation spectroscopy (DRS) measurements [17] 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 (High Wycombe, Bucks, England).

3. Results and discussion

3.1. Overall dielectric behaviour

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

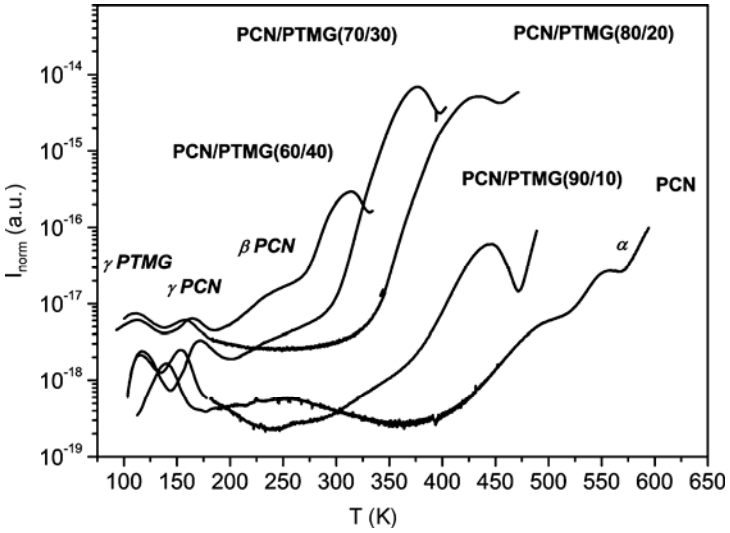


Fig. 1. TSDC thermograms measured on pure PCN and the hybrid networks. The depolarization current is normalized to the electric field applied and the surface area of the sample

For pure PCN we observe four peaks. The peaks located at 143 and 256 K are associated with secondary relaxations, attributed to short range motions of PCN chains, as they are detected at temperatures lower than that of the main α relaxation associated with the glass transition, while the double peak at higher temperatures is associated with the glass transition of regions with different crosslinking density. 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 [18]. 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 motions of chain fragments between the network junctions. DMA measurements on the PCN network of the present study give three loss peaks [4]: 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 those described by Georjon et al. [18].

Bearing in mind a lower equivalent frequency of TSDC measurements, as compared to DMA, the location (on the time scale) of the γ PCN relaxation detected by TSDC is in a 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 results ([12] and present work) with DMA ones [4, 18] 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.

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 of regions with different crosslinking density, in consistency with the results of DSC and CRS obtained on the same samples [14]. 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 [4].

In 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 cannot be detected in the pure PCN network. More specifically, this relaxation is attributed to damped oscillations of ether segments around their equilibrium positions (local mode [19]). 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. It should be noted that all the hybrid networks show a single peak at higher temperatures shifting to lower temperatures (towards the glass transition temperature of pure PTMG (188 K)) with increasing PTMG content, in agreement with the results of DMA [4], DSC and CRS (creep rate spectroscopy) [14] 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. This apparent miscibility might be attributed to the participation of PTMG in PCN formation. One can assume that the incorporation of PTMG will improve the miscibility of the components due to increased affinity of the modified PCN/PTMG network to non-incorporated PTMG.

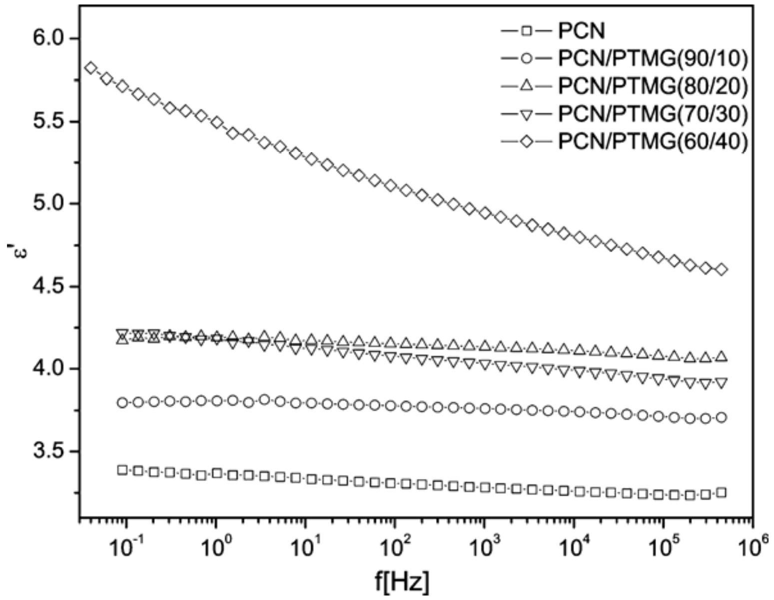


Fig. 2. Frequency dependences of the real part of dielectric function ε', measured at 298 K. The compositions of the samples are indicated in the plot

Figure 2 shows the results of DRS measurements at room temperature (298 K): frequency dependences of the real part of dielectric function $\varepsilon'(f)$. At the temperature of measurements all the samples are in the glassy state, as is indicated by the TSDC results of Figure 1, and only secondary relaxations contribute to the spectra. For the pure PCN network ε' is low and practically independent of frequency, indicating a suitability of PCN for applications in microelectronics [1, 2]. The increase of $\varepsilon'(f)$ on addition of PTMG has probably contributions arising from both the polar PTMG component and the increased flexibility of the PCN network. This point can be further followed by systematic investigation of various polarization (relaxation) mechanisms contributing to $\varepsilon'(f)$. It is striking in Figure 2 that for the PCN/PTMG (70/30) network $\varepsilon'(f)$ does not further increase with respect to the PCN/PTMG (80/20) network. This composition shows a distinguished behaviour also in other respects, to be discussed later, indicating non-monotonous changes of properties with PTMG content, in agreement with the results of morphological characterization [14]. Finally, a large dispersion of $\varepsilon'(f)$ is observed for the PCN/PTMG (60/40) network, indicating, in agreement with dielectric loss $\varepsilon''(f)$ and ac conductivity $\sigma_{ac}(f)$ plots (not shown here) a long-range connectivity of PTMG-rich regions [12]. Future measurements at high frequencies would help to separate the contribution to the increase of $\varepsilon'(f)$ in the PCN/PTMG (60/40) network dipolar from the space charge/conductivity contribution.

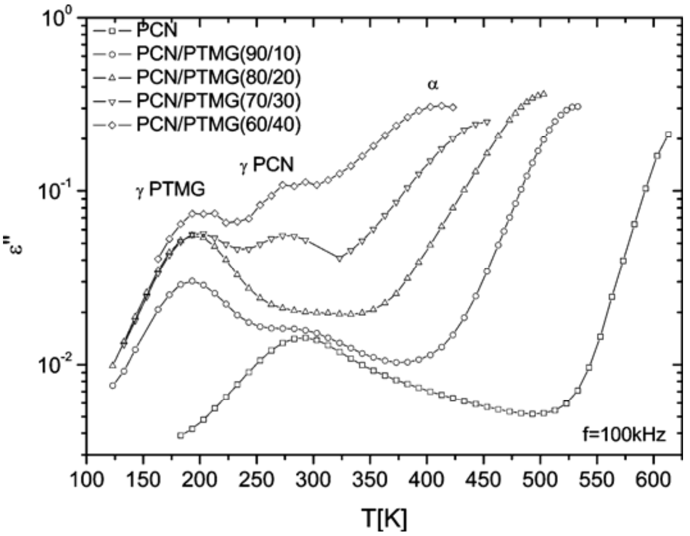


Fig. 3. Temperature dependences of dielectric loss ε'', measured at 100 kHz for pure PCN and the hybrid PCN/PTMG networks indicated in the plot

The relaxations detected by TSDC (Fig. 1) were studied in detail by means of DRS measurements over broad temperature and frequency ranges. Temperature dependences of dielectric loss, $\varepsilon''(T)$, at a constant frequency of 100 kHz are presented in Figure 3, in order to show an overall dielectric behaviour of the samples under investigation and make a comparison with the TSDC thermograms (Fig. 1). The results have been recorded isothermally and replotted as a function of temperature at a constant frequency. The latter is selected rather high, in order to avoid the contribution of conductivity (dominating at low frequencies), as will be shown later. We observe the same peaks as in the TSDC thermograms, shifted towards higher temperatures due to a higher frequency of DRS measurements. In the following we shall focus on the investigation of the main α relaxation.

3.2. The main α relaxation

Figure 4 shows dielectric loss $\varepsilon''(f)$ spectra in the PCN/PTMG (90/10) network at selected temperatures, measured in order to follow the α relaxation associated with the glass transition. The spectra are typical of PCN and the hybrid networks. The increase of ε'' with decreasing frequency, observed at low frequencies, is related to conductivity phenomena [12], while the α relaxation is observed as a peak at higher frequencies. The α relaxation in pure PCN and the hybrid networks was analyzed with respect to time scale, relaxation strength and shape of the dielectric response. The following expression, consisting of a sum of the Havriliak–Negami (HN) model function and a conductivity term [12, 17], was fitted to the experimental $\varepsilon''(f)$ data

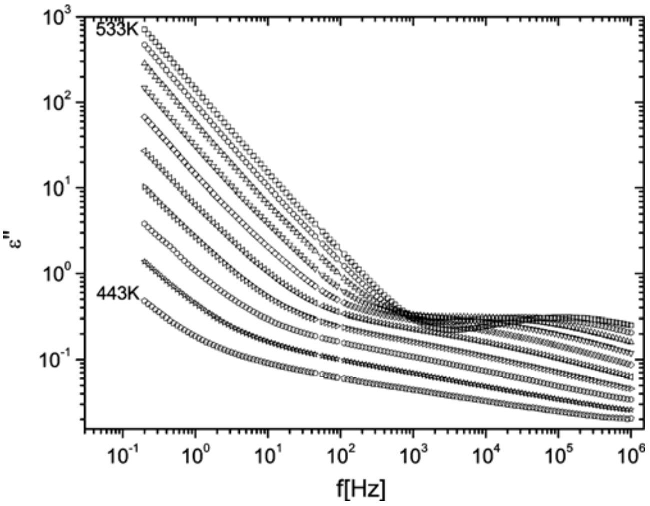


Fig. 4. Frequency dependences of dielectric loss ε'' in the region of the main α relaxation (from 443 to 533 K, in steps of 10 K) in the hybrid PCN/PTMG (90/10) network

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

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric relaxation strength with ε_s and ε_∞ being the limits of $\varepsilon'(\omega)$ for $\omega\tau << 1$ and $\omega\tau >> 1$, respectively. The relaxation time τ is related to the position of loss maximum by the equation $2\pi f_{\max} = 1/\tau$. The parameters α and β describe the symmetric and asymmetric broadening of the dielectric response, K and s are constants. 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 [12, 17].

Figure 5 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 the relaxation time of 100 s [12], are also included. For each sample we observe an α relaxation which, at each frequency, systematically shifts to lower temperatures with increasing PTMG content, towards the glass transition temperature of pure PTMG (188 K). These results confirm the previous ones obtained with DMA [12] and DSC and CRS [14] at a single frequency with similar PCN/PTMG networks and allow to extend them to a broad frequency range. A single Vogel–Tammann–Fulcher (VTF) equation, characteristic of the main α relaxation in polymeric systems [20]

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

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 for reducing the number of free parameters and improving the quality and reliability of fits [21], the parameter f_0 was fixed at 10^{13} Hz, the frequency of the order of lattice vibration frequencies. Reasonable values were obtained for the fitting parameters, with the pseudo-energy B increasing with increasing amount of PTMG and the Vogel temperature T_0 being located 50–70 K below the glass transition temperature determined by TSDC.

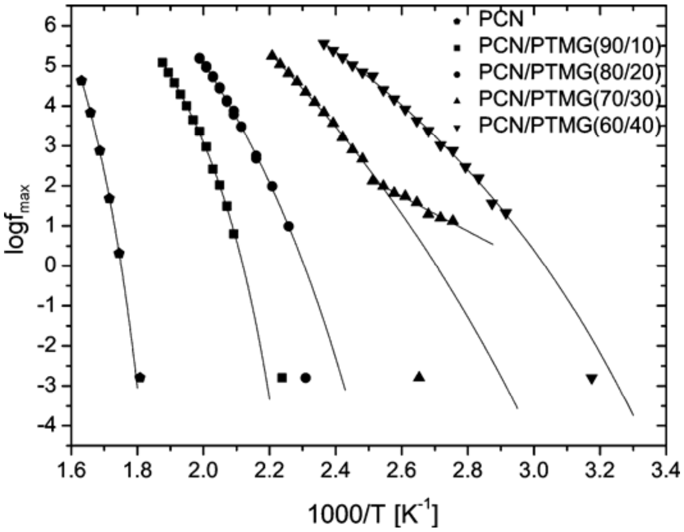


Fig. 5. Arrhenius plot of the α relaxation in pure PCN and in the hybrid networks indicated in the plot. TSDC data are included at the equivalent frequency of 1.6 mHz. The lines are fittings to the DRS data with the Arrhenius equation (Eq. (3)) for the hybrid network PCN/PTMG(70/30), and with the VTF equation (Eq. (2)) for other compositions

The data for the PCN/PTMG (70/30) network in Figure 5 cannot be fitted with a single VTF equation. This can be done, however, for the high temperature/frequency data, with reasonable values for the fitting parameters which follow the trends described above for the other samples. The temperature dependence of the data at lower temperatures/frequencies is satisfactorily described by the Arrhenius equation

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

The values of the fitting parameters obtained are 0.95 eV for the activation energy, E_{act}, 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 [22] 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 5 would suggest, at least in a middle temperature/frequency range, the contribution of both α and Goldstein–Johari β relaxation to the dielectric spectra [23, 24]. 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. It is interesting to note, however, that two well-separated relaxations have been detected for the PCN/PTMG (70/30) network by TSDC and that the higher temperature TSDC point is in good agreement with the DRS data for the α relaxation (Fig. 5) and that at lower temperatures (not shown in Fig. 5) to the DRS data for the Goldstein–Johari β relaxation. These results can be discussed in terms of the Adam–Gibbs theory for the glass transition [25], the increase of the cooperativity length, i.e. the characteristic length of the glass transition, with decreasing temperature [20] and the influence of a second component on the mobility of the polymer chains [26]. At high temperatures the relaxation occurs through a co-operative rearrangement of the polymeric chains. At lower temperatures, the cooperativity is suppressed and the relaxation occurs partly through cooperative rearrangements and partly through motions of isolated chains in regions of large free volume (islands of mobility) [20].

Results similar to those reported here for the PCN/PTMG (70/30) network have been obtained before with highly crosslinked sequential interpenetrating polymer networks (IPNs) of poly(ethyl acrylate) (PEA) and poly(ethyl methacrylate) (PEMA) [24]. A splitting of the α relaxation and the Goldstein–Johari β relaxation was observed in the PEMA networks, a single α relaxation in PEA-rich compositions and Arrhenius behaviour in middle compositions. The latter was explained by a suppression of cooperativity due to incorporation of PEA chains to the cooperative motions of the PEMA network shifting the α and Goldstein–Johari β relaxations to different extents, and hence resulting in changes in the shape of the spectrum in the merging zone. Thus, the distinct behaviour of the PCN/PTMG (70/30) network with respect to the other hybrids indicates a higher degree of heterogeneity of that network, which is consistent with the results of SAXS measurements on the same hybrids [14].

Figure 6 shows the results for the dependence of the dielectric strength $\Delta\varepsilon$ on the frequency of the α loss peak. The latter allows for comparison of samples with different glass transition temperatures. We observe in Figure 6 that $\Delta\varepsilon$ (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, $\Delta\varepsilon$ is lower in the PCN/PTMG (70/30) than in the PCN/PTMG (80/20) network, indicating constraints imposed on the motion of the polymer chains in the former network. DRS measurements in semi-interpenetrating polymer networks of linear polyurethane and PCN network with chemical crosslinks between the components showed an increase of $\Delta\varepsilon$ of the α relaxation with respect to that in pure polyurethane. These results suggest that the reason for the increase of $\Delta\varepsilon$ of the α relaxation in both systems is the hybridization effect resulting in loosened molecular packing of the chains and in an increase of free volume. $\Delta\varepsilon$ 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 [17, 20]. The dependence is approximately linear, in agreement with results obtained previously with both polymers and glass-forming liquids [27]. A different behaviour is observed for the PCN/PTMG (70/30) network, where $\Delta\varepsilon$ starts decreasing with decreasing loss peak frequency below ca. 100 Hz. This behaviour is in agreement with the results shown in Figure 5 (change of slope at approximately 100 Hz), and with the common observation that the relaxation strength of the Goldstein–Johari β relaxation decreases with decreasing temperature [20, 26], providing an additional support for the interpretation given above for the distinct behaviour of the PCN/PTMG (70/30) network.

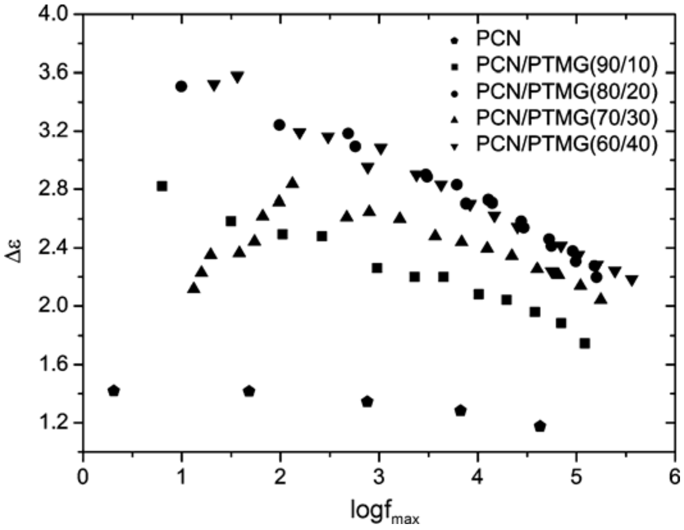


Fig. 6. Dielectric strength $\Delta\varepsilon$ against logarithm of maximum frequency $\log f_{\max}$ of the α relaxation in pure PCN and the hybrid networks indicated in the plot

Results for the shape of the α loss peak are given in Figure 7. The peak is asymmetric in the pure PCN network, whereas it is symmetric ($m = n$) in all the hybrids, in agreement with the results showing that constraints imposed by crystallites, increase of crosslinking density and geometrical confinement render the α relaxation more symmetric [28]. We observe in Figure 7 that m is practically independent of temperature (frequency) of the loss peak in pure PCN, whereas it systematically increases with increasing temperature in the hybrid networks, reflecting a decreasing influence of intermolecular interactions due to decrease of the cooperativity length, i.e. the size of the cooperatively rearranging regions within the Adam–Gibbs theory [25]. The parameter m is significantly smaller in the hybrids as compared to its value in the pure PCN network, reflecting the increasing influence of intermolecular interactions due to the existence of regions with compositions different from the mean composition. The composition fluctuations in the hybrids under investigation are due to the existence of regions with different density of rigid crosslinks, similar to those of the pure PCN network, resulting from the incorporation of PTMG into the network. The PCN/PTMG (70/30) network shows again a distinct behaviour, with *m* values comparable to those of the PCN/PTMG (60/40) network, suggesting a more nanoheterogeneous structure. The shape parameter *n* shows the same temperature dependence in the pure and the hybrid networks, increasing with increasing temperature (frequency) of loss peak, as is commonly observed in polymers and glass-forming liquids [17]. Interestingly, the PCN/PTMG (90/10) network shows the highest *n* values, even higher than in pure PCN, indicating a reduction of constraints in that network, in agreement with the results of SAXS measurements [14].

3.3. Mechanical measurements

Figure 8 shows the results of stress-strain measurements at room temperature. The values of elastic (Young) modulus, tensile strength, elongation at break and toughness

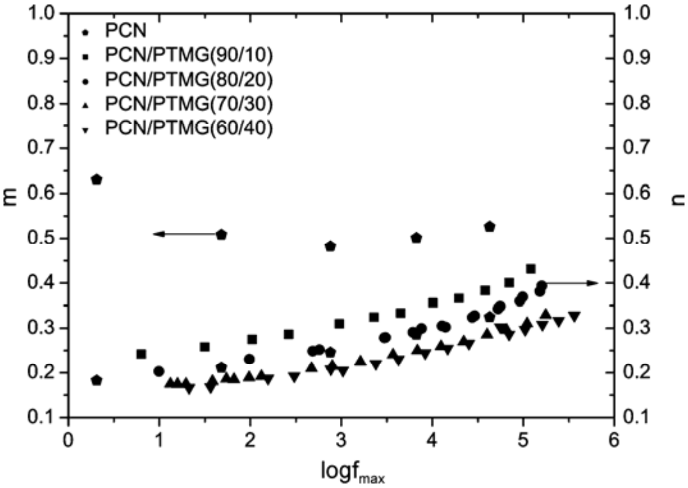


Fig. 7. Shape parameters *m* and *n* against the logarithm of maximum frequency logf_{max} of the α relaxation in pure PCN and the hybrid networks indicated in the plot

Table 3. Stress–strain results for the pure PCN and the hybrid networks PCN/PTMG

PTMG content in initial composition, w_{PTMG} (wt. %)	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

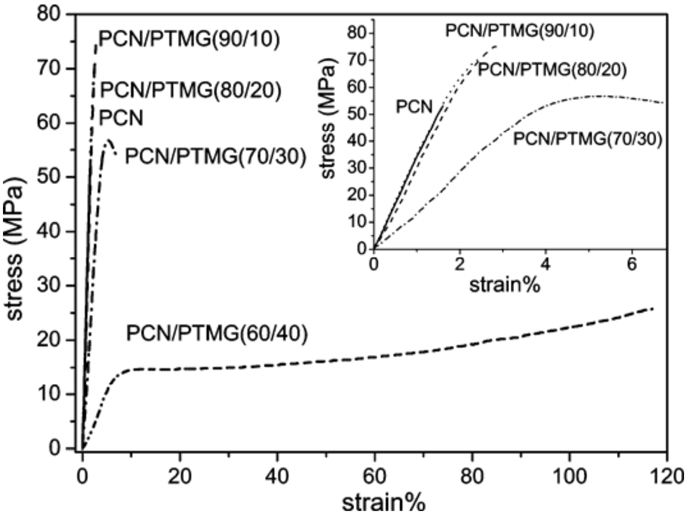


Fig. 8. Stress strain curves for pure PCN and the hybrid networks indicated in the plot. The inset shows details at low strain values

can be determined from these measurements, results for the first three parameters being shown in Table 3. The PTMG conversion by incorporation into the PCN network has also been included in Table 3. The results show that both the elastic modulus and the tensile strength decrease with increasing amount of PTMG, whereas the maximum elongation at break increases. Incorporating 10% of PTMG into the network does not practically affect the elastic modulus nor the elongation at break, whereas the tensile strength increases significantly. These results can be explained by microplasticity, detected by CRS on the same hybrids [14]. A change of the behaviour is observed in Figure 8 and Table 3 from a brittle material (pure PCN and hybrids with 10 and 20% PTMG) to a ductile material (hybrids with 30 and 40% PTMG). The behaviour of the PCN/PTMG (60/40) network is distinctly different from that of the other networks in Figure 8, showing a pronounced yield point, hardening and elongation at break. This behaviour can be due to a proximity of the temperature of measurements to the glass transition temperature of that network (TSDC, Figure 1). Future stress-strain measurements at variable temperature would be helpful to further clarify this point.

4. Final remarks

Molecular dynamics of hybrid polycyanurate/polyoxytetramethylene glycol (PCN/PTMG) networks 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 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. 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.

Two secondary relaxations of PCN (γ and β, in the order of increasing temperature), one secondary (γ) relaxation of PTMG and a single, broad α relaxation (dynamic glass transition) were detected in the hybrids. The α relaxation was studied in detail over wide ranges of temperature and frequency. By fitting appropriate model functions to experimental data, the results were systematically analyzed in terms of time scale, relaxation strength and shape of the response.

The time scale of the α relaxation is discussed on the basis of the Arrhenius plots and Vogel–Tammann–Fulcher fits to data. The relaxation shifts systematically to lower temperatures/higher frequencies with increasing amount of PTMG, indicating a miscibility of the two components and plasticization by PTMG. The relaxation strength increases in the hybrids. A comparison with the latter system indicates that this is a hybridization effect, which results in loosened molecular packing of the chains and an increase of free volume. The α loss peaks become symmetric and broader in the hybrids, reflecting an increasing influence of intermolecular interactions due to the existence of regions with compositions different from the mean composition (different density of rigid crosslinks, similar to those of the pure PCN network, resulting from the incorporation of PTMG into the network). A distinct behaviour is observed for the hybrid with 30% PTMG with respect to time scale (splitting of the α relaxation into an α relaxation and a Goldstein–Johari β relaxation), relaxation strength and shape of the response, and explained in terms of a more pronounced nanoheterogeneous structure. Finally, stress-strain measurements indicate a change from brittle behaviour at low PCN contents (PCN and hybrids with 10 and 20% PTMG) to ductile behaviour at 30 and 40% PTMG.

Several questions arise or are left open for further work, such as separation of the contributions of incorporated and non-incorporated PTMG to the effects described above and a possible influence of the molar mass of the PTMG used (here 1.000 g/mol). Also, stress-strain measurements at various temperatures would help to separate effects of morphology from effects of temperature of measurements with respect to glass transition temperature on mechanical properties.

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