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Dielectric relaxation of heterocyclic polymer networks: Effect of the ratio and nature of the heterocyclic rings

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Heterocyclic Polymer Networks (HPN) prepared by trimerization of 1,6-hexamethylene diisocyanate (HMDI) in presence of diglycidyl ether of bisphenol A (DGEBA) and triethylene diamine in two different regimes were characterized by dielectric spectroscopy in the 10^{-1}–10^5 Hz frequency range and in the 123 K–423 K temperature interval. The dielectric experiments reveal the existence of multiple composition dependent relaxation processes. The γ process, appearing at low temperatures only in partially cured systems is related to the presence of free DGEBA. The β process is associated to local motions of the carbonyl groups present in the isocyanurate and oxazolidone cycles. The α relaxation, which has its origin in the segmental motions above the glass transition temperature, tends to appear at higher temperatures with increasing network junction density and with the degree of curing. The fragility and cooperativity of the α relaxation is discussed in terms of recent relaxation approaches. © *2000 Kluwer Academic Publishers*

1. Introduction

Polymer networks containing isocyanurate and oxazolidone heterocycles belong to a special family of high-performance thermosetting polymers with outstanding thermal stability [1, 2]. Previous research on the field was focussed on the effect of chemical composition on the thermal stability [3, 4]. However, the relaxation behaviour of such networks, of interest as far as the mechanical properties are concerned, remains essentially unexplored. The dynamics of a great variety of chemically cross-linking networks has been investigated by different techniques including dielectric spectroscopy [5]. According to the classification of Fitz and Mijovic [5] heterocyclic polymer networks based on polyisocyanoureate-oxazolidones would belong to a kind of system in which dipoles present in the reactants react to form a new type of polar groups. Previous Dynamical Mechanical Analysis studies of polyisocyanurate-oxazolidones [6, 7] reveal the existence of composition-dependent multiple relaxations which are characteristic of these heterocyclic polymer networks (HPN). Different thermal analysis techniques were used to characterize cure kinetics and thermal transitions in thermally cured epoxy-isocyanate HPN systems of variable chemical composition [8–11].

The aim of the present work is to study, by means of dielectric spectroscopy, the effect of the relative content and the chemical nature of the heterocyles on the relaxation behaviour of HPN systems. It must be emphasized that conventional epoxy networks contain dielectrically active dipoles on both epoxy resin and hardener [12]. Furthermore, a unique feature of HPN systems is that, for high content of isocyanurates, the dielectric response is expected to arise from the dipoles located in a symmetric three-arm junction, while for high content of oxazolidone will be mainly due to those dipoles located in chain strands between the network junctions.

2. Experimental

2.1. Synthesis of the heterocyclic polymer networks (HPN)

For the synthesis of the HPN systems a slightly modified method as the previously described was used [8–11]. 1,6-hexamethylene diisocyanate (HMDI), diglycidyl ether of bisphenol A (DGEBA) molar mass 359 and triethylene diamine (TEDA)NR_3 were purchased from Aldrich Co. and used as received. In the present work, DGEBA was selected instead of the raw

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epoxy resin EPON-828, in order to assure that only each fifteenth molecule may be assumed to contain a secondary hydroxyl group. In this way the possibility of urethane formation and, hence, the occurrence of additional relaxation processes is minimized. Crystalline TEDA (reaction catalyst) was used here instead of volatile triethyl amine to reduce catalyst evaporation at high evacuation conditions.

Reaction mixtures with HMDI/DGEBA mass ratios 90/10, 70/30 and 50/50 and TEDA (0.3–0.5% w/w) were prepared by careful mechanical mixing of the components at room temperature and subsequently evacuated for 5 minutes. The initial ratios of isocyanate/epoxy groups for 90/10, 70/30 and 50/50 are 18.8/1, 4.9/1 and 2.1/1 respectively calculated as considered in ref [10] The mixtures were, then, placed between two parallel, specially treated glass plates for thermal curing. After curing, thin free standing films (0.15–0.18 mm thick) were obtained. The films were coated with circular gold electrodes (30 mm in diameter) by sputtering. As in our previous studies [8, 10], two different curing procedures were used for sample preparation:

1. In the first case (HPN-1), samples were prepared by slow heating up to the curing temperature ($T = 373$ K) and subsequent isothermal storage during 2.5 hours. In this case, the dominant primary reaction (Fig. 1) is assumed to be the isocyanate trimerization resulting in the formation of a network of six-membered, three arm isocyanurate heterocycles. As previously shown [13], the glass transition temperature of these samples steadily increases during curing reaching an asymptotic upper limit after about 2.5 hours of curing. In this case, HPN-1 can be regarded as a polymer network formed by polyisocyanurate with incomplete reaction of isocyanate groups and free DGEBA component (Fig. 1, Scheme 1).
2. In the second case, HPN-2, samples were prepared by a step-like heating of HPN-1 samples up to the curing temperature ($T = 493$ K). This ensures a maximum degree of functional group conversion. In this case, the

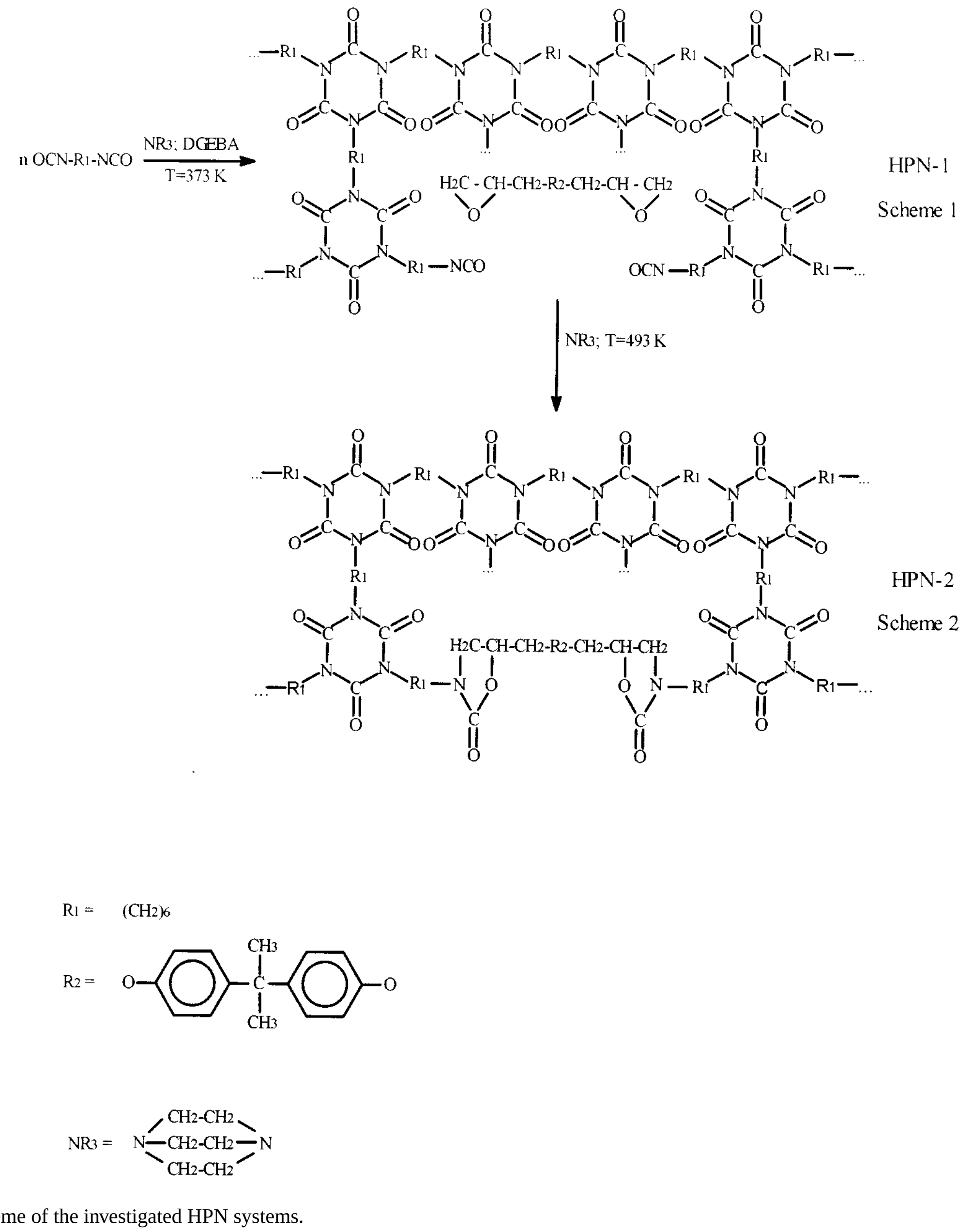

Figure 1 Scheme of the investigated HPN systems.

initial trimerization reaction of isocyanates is gradually taken over by a secondary reaction of oxazolidone heterocycles formation through a concomitant reaction between epoxy and isocyanate groups [2, 13–15]. As a consequence, HPN-2 samples can be regarded as homogeneous HPN systems with a variable content of heterocycles of different nature (Fig. 1, Scheme 2).

2.2. Technique

Measurements of the complex dielectric permittivity, $\epsilon^* = \epsilon' - i\epsilon''$, were performed over a frequency window of 10^{-1} Hz $< F < 10^5$ Hz, in a temperature range of 123 K $< T <$ 423 K. To cover the above frequency range, a Novocontrol system integrating a SR 830 Lock-in amplifier with a dielectric interface was employed. The temperature was controlled by a QUATRO system from Novocontrol providing a nitrogen jet with a temperature error, during every single sweep in frequency, of ±0.1 K.

2.3. Data analysis

The phenomenological Havriliak-Negami(HN) [16] formulation was used to describe the dielectric α relaxation. In this approach, the complex dielectric permittivity exhibits a frequency ($\omega = 2\pi F$) dependence of the form:

$$\epsilon^* = (\epsilon_\infty) + \frac{\epsilon_0 - \epsilon_\infty}{\left[1 + (i\omega\tau_o)^b\right]^c} \qquad (1)$$

where ϵ_0 and ϵ_∞ are the relaxed ($\omega = 0$) and unrelaxed ($\omega = \infty$) dielectric constant values, τ_0 is the central relaxation time of the relaxation time distribution function and b and c ($0 < b, c < 1$) are shape parameters which describe the symmetric and the asymmetric broadening of the relaxation time distribution function, respectively [16]. The relaxation strength is defined by $\Delta\epsilon = \epsilon_0 - \epsilon_\infty$ Equation 1 leads to a Debye single relaxation time equation when $b = c = 1$.

3. Results

The dielectric loss values, ϵ'', for two HPN-1 and HPN-2 samples with a ratio HMDI/DGEBA = 70/30 are shown in Fig. 2a and b respectively. In both cases the dielectric loss, ϵ'' reveals the existence of several relaxation processes. These processes appear as maxima in the dielectric loss measurements (Fig. 2a and b). At low temperatures, HPN-1(70/30) presents two broad processes labeled γ and β. In HPN-2(70/30) only the β process is clearly detected in this temperature range. A more prominent process is observed in both systems at higher temperatures, which on the basis of previous calorimetric studies, is related to the occurrence of the glass transition [8–10] and, therefore, it will be referred to as α. As frequency is increased the maximum loss peak for the relaxations shifts towards higher temperatures. The large increase of ϵ'' at higher temperatures and low frequencies is characteristic of a conduction process and will be labeled as σ.

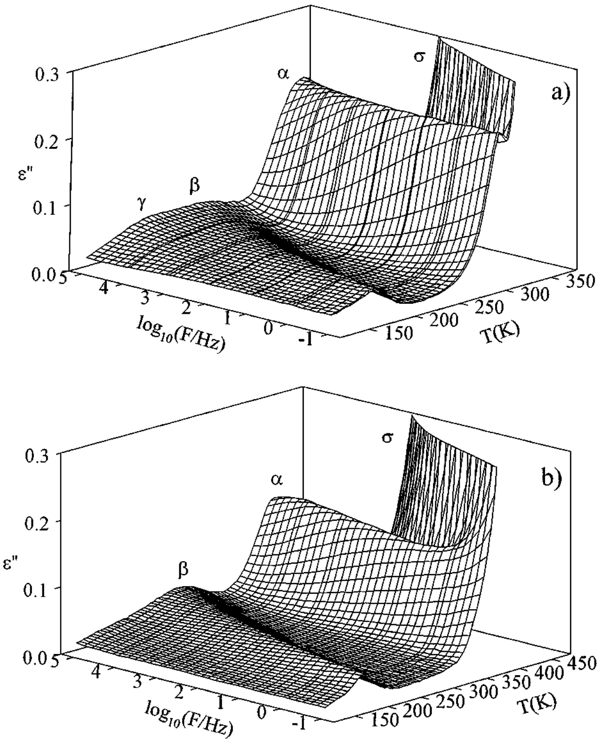

Figure 2 Dielectric loss as a function of temperature and frequency for HPN-1 70/30 HMDI/DGEBA (a) and HPN-2 70/30 (b).

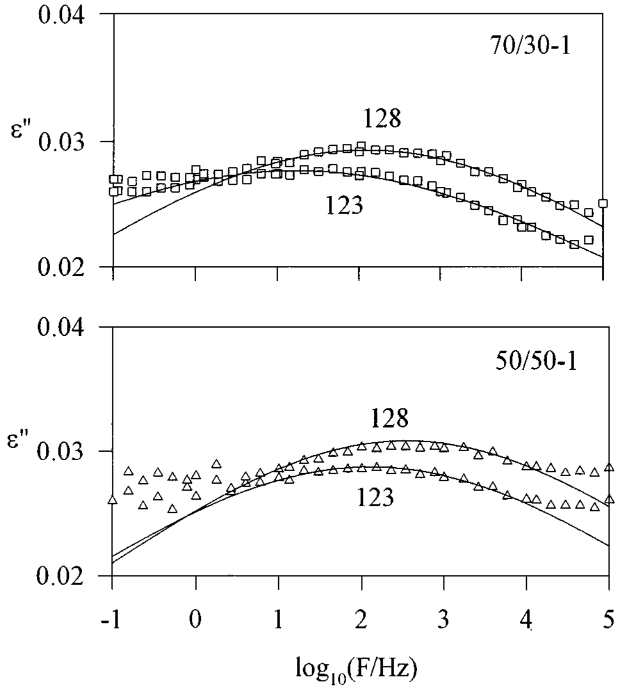

Figure 3 Dielectric loss as a function of frequency in the temperature region of the γ relaxation for two selected HPM-1 samples. HMDI/DGEBA ratios: 70/30 (upper) and 50/50 (lower). The best fits of the HN-analysis are shown by the solid lines.

3.1. HPN-1 systems

Fig. 3 represents the experimental ϵ'' data as a function of frequency in the temperature region of the γ relaxation for two selected HMDI/DGEBA ratios (70/30 Fig. 3 (upper) and 50/50 Fig. 3 (lower)). Although, the weakness of the γ relaxation induces a high signal-to-noise ratio at high and low frequencies a tentative analysis through the HN procedure can be

TABLE I HN parameters of sub-glass relaxations of HPN-1

Sample	T, K	$\Delta\varepsilon$	b	c	τ_{HN}, s
		γ-process			
70/30-1	123	0.559	0.126	1	9.72×10^{-3}
	128	0.508	0.146	1	1.32×10^{-3}
50/50-1	123	0.477	0.153	1	1.24×10^{-3}
	128	0.502	0.156	1	4.56×10^{-4}
		β-process			
	193	0.305	0.269	1	2.81×10^{-2}
90/10-1	203	0.268	0.309	1	4.67×10^{-3}
	213	0.221	0.331	1	1.35×10^{-3}
	183	0.381	0.277	1	5.32×10^{-2}
70/30-1	193	0.259	0.359	1	1.11×10^{-2}
	203	0.265	0.363	1	1.93×10^{-3}

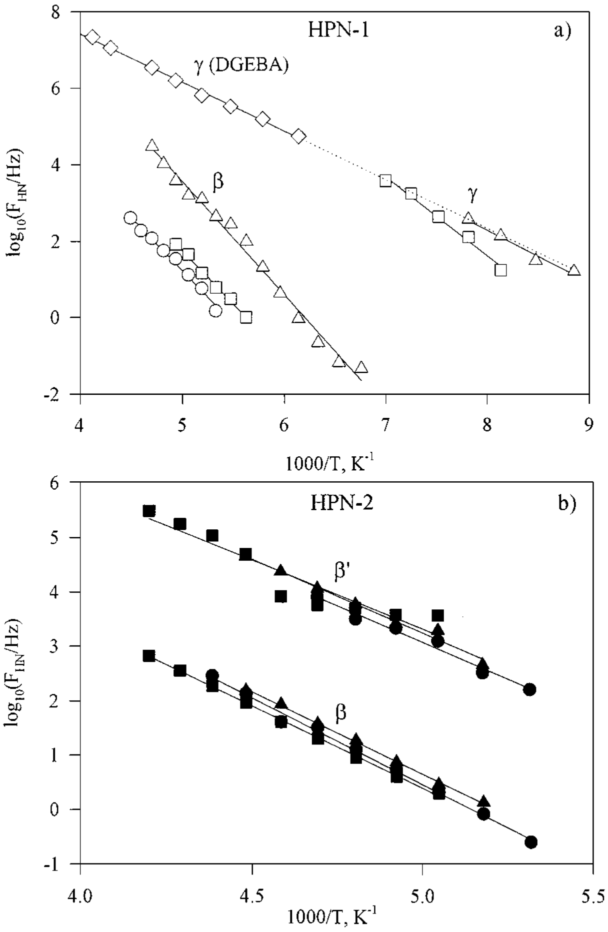

Figure 4 F_{HN} values as a function of the reciprocal temperature for (a) HPN-1 (open symbols) and (b) HPN-2 (full symbols) systems in the region of γ, β and β' processes. : HMDI/DGEBA: (○) 90/10, (□) 70/30 and (△) 50/50. ◇ Data for pure DGEBA taken from ref. [18].

accomplished. The best fit of the HN-analysis to the data is shown by the continuous lines. The parameters obtained (Table I) reveal that this process is symmetric ($c = 1$) and rather broad ($b \leq 0.2$). From this analysis a value of $F_{HN} = (2\pi\tau_{HN})^{-1}$ is obtained and the corresponding temperature dependence is shown in Fig. 4a. From the linearity of the Log F_{HN} vs. $1/T$ plots, values of the apparent activation energies of 25.9 kJ/mol for HPN-1(50/50) and of 39.3 kJ/mol for HPN-1(70/30) are estimated.

Fig. 5 shows the ϵ'' data as a function of frequency in the temperature region of the β relaxation for two HMDI/DGEBA ratios (90/10 Fig. 5 (upper) and 70/30 (lower) Fig. 5). The best fit HN-analysis of the data is shown by the solid lines. The corresponding parameters are given in Table I. Here the γ relaxation has been simulated by extrapolation to higher temperatures of the low temperature HN-parameters [17]. The β relaxation process also appears as a symmetric and relative broad one. The corresponding values for F_{HN}, shown in Fig. 4a, reveal also a linear dependence of Log F_{HN} with the reciprocal temperature. Values of the apparent activation energies of 56.5 kJ/mol, 53.3 kJ/mol and 53.5 kJ/mol were obtained for 50/50, 70/30 and 90/10 HMDI/DGEBA ratios respectively.

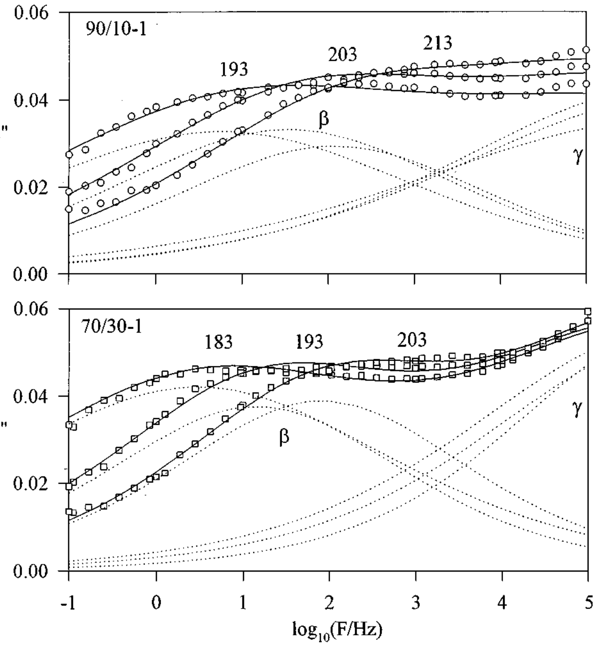

Figure 5 Dielectric loss as a function of frequency in the temperature region of the γ and β relaxations for two selected HPN-1 samples. HMDI/DGEBA ratios: 90/10 (upper) and 70/30 (lower). The best fits of the HN-analysis are shown by the solid lines. The dotted lines represent the separate contribution of different relaxations.

Fig. 6 shows the experimental ϵ'' data as a function of frequency in the temperature region of the α relaxation for three HMDI/DGEBA ratios (90/10, 70/30 and 50/50). The best fit of the HN-analysis to the data is shown by the solid lines. In agreement with other authors, owing to the existence of a conduction process (σ) a conduction term of the form $\sigma/(\epsilon_{vac}\omega^s)$ was added to ϵ''. Here ϵ_{vac} is the vacuum permittivity and "s" is an exponent which accounts for non-ohmic conduction phenomena [18, 19]. The corresponding parameters are shown in Table II. From the fitting parameters the value of $\tau_{max} = (2\pi F_{max})^{-1}$, where F_{max} is the frequency of maximum loss, can be obtained [20] from:

$$\tau_{max} = \tau_{HN} \sin^{-1/b}\left(\frac{b\pi}{(2+2c)}\right) \sin^{1/b}\left(\frac{bc\pi}{(2+2c)}\right) \tag{2}$$

where $\tau_{HN} = (2\pi F_{HN})^{-1}$. The corresponding values for τ_{max}, shown in Fig. 7, reveal a Vogel-Fulcher-Tamann (VFT) dependence of Log τ_{max} with the reciprocal temperature:

$$\tau_{max} = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{3}$$

TABLE II HN parameters of α-relaxation of HPN systems

Sample	T, K	$\Delta\varepsilon$	b	c	τ_{HN}, s	$\sigma_{\varepsilon''}$	$S_{\varepsilon''}$
HPN-1							
	358	1.233	0.271	0.575	8.30×10^{-2}	2.10×10^{-13}	0.792
90/10-1	368	1.182	0.303	0.492	6.16×10^{-3}	1.11×10^{-12}	0.948
	378	1.124	0.328	0.449	6.25×10^{-4}	3.85×10^{-12}	0.962
	328	2.127	0.251	1.000	4.90×10^{-4}	3.68×10^{-12}	0.965
70/30-1	338	1.996	0.263	0.969	5.53×10^{-5}	1.54×10^{-11}	0.970
	348	1.903	0.275	0.941	9.81×10^{-6}	6.17×10^{-11}	0.998
	338	1.932	0.234	1.000	5.86×10^{-3}	5.89×10^{-13}	0.862
50/50-1	348	1.821	0.241	0.990	3.25×10^{-4}	4.09×10^{-12}	0.991
	358	1.651	0.262	0.956	2.71×10^{-5}	2.61×10^{-11}	0.991
HPN-2							
	398	0.936	0.552	0.385	2.63×10^{-1}	2.20×10^{-13}	0.902
90/10-2	408	0.869	0.593	0.339	1.11×10^{-2}	8.35×10^{-13}	0.815
	418	0.834	0.607	0.315	9.48×10^{-4}	2.45×10^{-12}	0.728
	388	1.626	0.350	0.407	2.29×10^{-2}	2.83×10^{-12}	0.843
70/30-2	398	1.543	0.404	0.363	1.82×10^{-3}	9.04×10^{-12}	0.855
	408	1.470	0.437	0.367	2.21×10^{-4}	2.69×10^{-11}	0.851
	368	2.201	0.406	0.353	1.77×10^{-2}	6.15×10^{-12}	0.876
50/50-2	378	2.039	0.391	0.408	6.65×10^{-4}	1.08×10^{-11}	0.867
	388	1.944	0.395	0.439	5.53×10^{-5}	1.97×10^{-11}	0.861

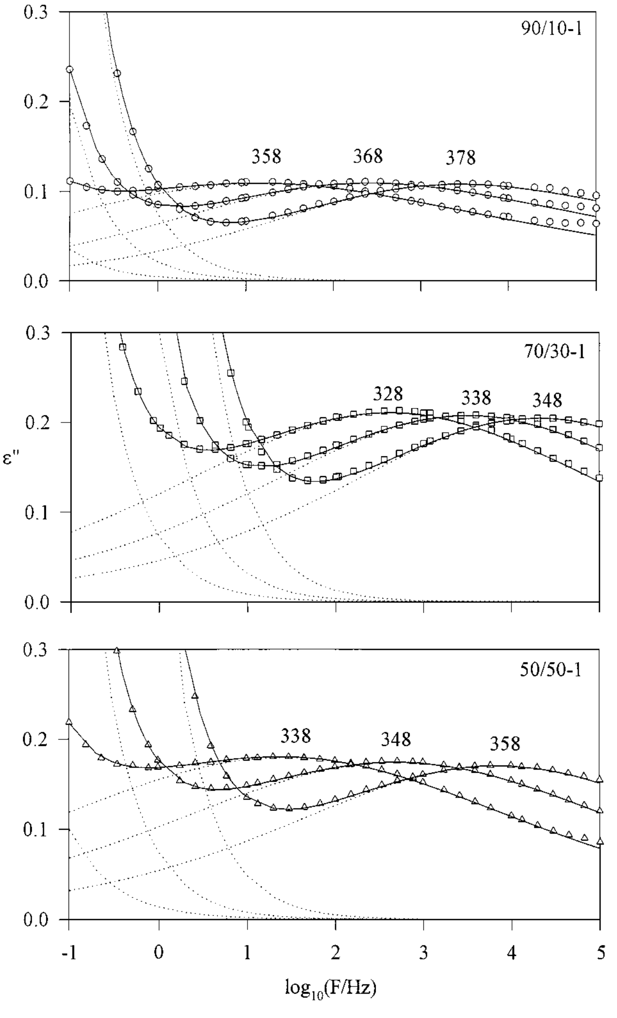

Figure 6 Dielectric loss as a function of frequency in the temperature region of the α relaxation for HPN-1 samples. (○) 90/10, (□) 70/30 and (△) 50/50. The best fits of the HN-analysis of the data are shown by the solid lines.

To reduce the effect of fitting over a limited frequency range a value of $\text{Log}_{10}\tau_0 \approx 14$ was assumed [21]. This assumption does not affect the quality of the data fit into the VFT equation but reduces the dispersion of fitting parameters. This dependence is expected for a segmental motion appearing above the glass transition temperature. Values of the VFT-parameters obtained for investigated systems are shown in Table III.

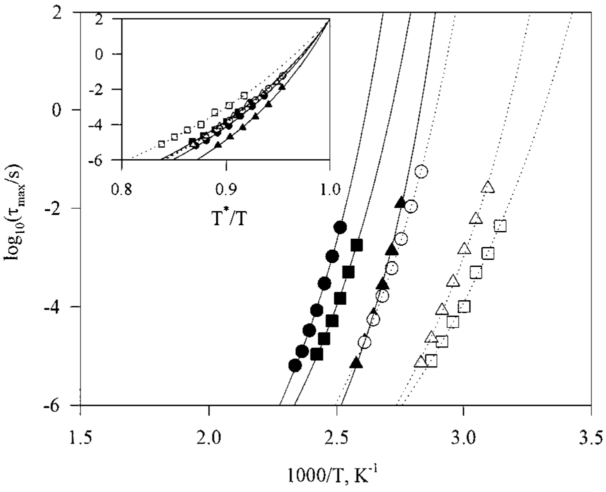

Figure 7 τ_{max} values as a function of the inverse temperature for (a) HPN-1 (open symbols) and (b) HPN-2 (full symbols) systems in the region of the α process. : HMDI/DGEBA: (○) 90/10, (□) 70/30 and (△) 50/50. Inset shows same data in a cooperativity plot fashion (Log τ_{max} versus T^*/T, where $\tau_{max}(T^*) = 10^2$ s). Solid and dotted lines are VFT fittings for HPN-2 and HPN-1 respectively.

3.2. HPN-2 systems

Fig. 8 illustrates the dependence of the experimental ϵ'' data as a function of frequency in the temperature region of the β relaxation for three HMDI/DGEBA ratios (90/10, 70/30 and 50/50). In these cases the β relaxation is accompanied by a higher frequency broad process that we label as β'. The best fit of the HN-analysis to the data is shown by the solid lines (see Table IV for parameters). In this case a superposition of two symmetric relaxations is considered. The corresponding F_{HN} values, shown in Fig. 4b, reveal a linear dependence of

Log F_{HN} with the reciprocal temperature. The values of the activation energies for the β process are 60.9 kJ/mol, 57.7 kJ/mol and 57.8 kJ/mol obtained respectively for the 50/50, 70/30 and 90/10 HMDI/DGEBA ratios. The corresponding values for the β' are 51.3 kJ/mol, 48.5 kJ/mol and 51.8 kJ/mol for the same HMDI/DGEBA ratios.

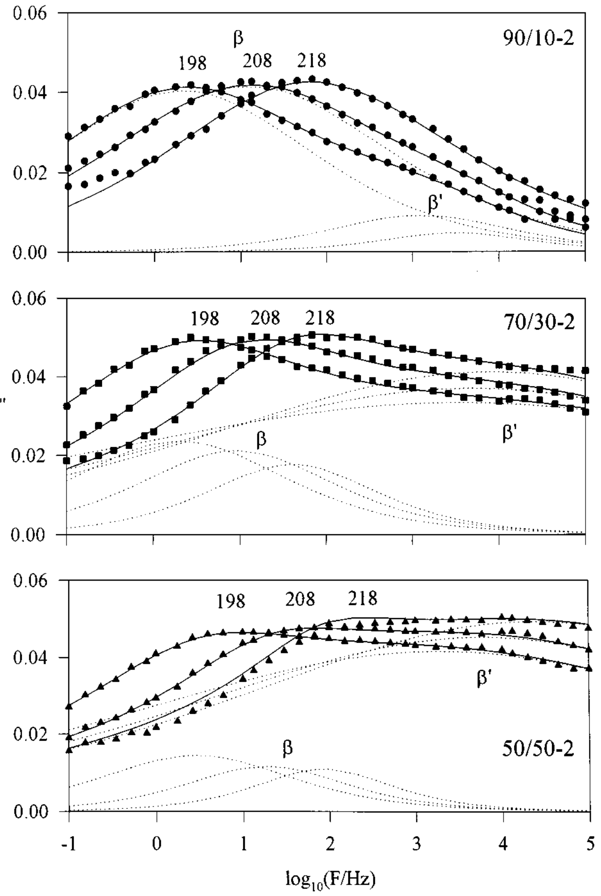

Figure 8 Dielectric loss as a function of frequency in the temperature region of the β and β' relaxations for HPN-2 samples. The best fits of the HN-equation are shown by the solid lines.

TABLE III α-relaxation VFT-parameters of HPN-1 and HPN-2 samples

HPN	τ_0, s	T_0, K	B	$F_{1/2}$
90/10-2	10^{-14}	306.1	2455	0.70
70/30-2	10^{-14}	287.9	2588	0.67
50/50-2	10^{-14}	295.0	1882	0.74
90/10-1	10^{-14}	272.6	2363	0.68
70/30-1	10^{-14}	220.8	2609	0.61
50/50-1	10^{-14}	247.5	2173	0.68

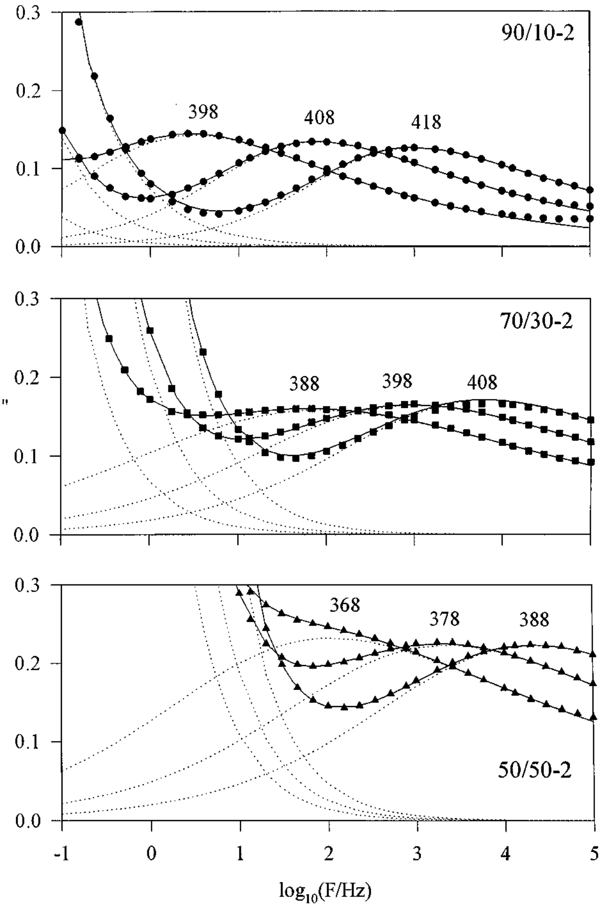

Figure 9 Dielectric loss as a function of frequency in the temperature region of the α relaxation for three selected HPN-2 samples. (○) 90/10, (□) 70/30 and (△) 50/50. The best fits of the HN-analysis are shown by the solid lines.

Fig. 9 shows the experimental ϵ'' data as a function of frequency in the temperature region of the α relaxation for three HMDI/DGEBA ratios (90/10, 70/30 and 50/50). The HN-analysis of the data, as described in the preceding paragraph, is shown by the solid lines and the corresponding parameters are collected in Table II. The corresponding values for $\tau_{\max}$, shown in Fig. 7, reveal also a Vogel-Fulcher-Tamann (VFT) dependence of Log $\tau_{\max}$ with the reciprocal temperature as expected for a segmental motion appearing above the glass transition temperature. Values of the VFT-parameters obtained for investigated systems are shown in Table III.

TABLE IV HN parameters of β- and β'-relaxation of HPN-2

		β relaxation			β' relaxation		
Sample	T, K	$\Delta\varepsilon_1$	b_1	$\tau_{\max 1}$, s	$\Delta\varepsilon_2$	b_2	$\tau_{\max 2}$, s
	198	0.250	0.397	7.66×10^{-2}	0.039	0.553	1.31×10^{-4}
90/10-2	208	0.274	0.374	1.27×10^{-2}	0.017	0.662	5.13×10^{-5}
	218	0.290	0.387	3.93×10^{-3}	-	-	-
	198	0.117	0.490	8.04×10^{-2}	0.585	0.145	4.41×10^{-5}
70/30-2	208	0.097	0.525	1.76×10^{-2}	0.530	0.177	3.23×10^{-5}
	218	0.071	0.591	3.96×10^{-3}	0.545	0.191	1.96×10^{-5}
	198	0.064	0.539	5.54×10^{-2}	0.602	0.175	8.30×10^{-5}
50/50-2	208	0.044	0.621	8.56×10^{-3}	0.611	0.187	2.74×10^{-5}
	218	0.035	0.706	1.87×10^{-3}	0.669	0.186	6.86×10^{-6}

As one can see, as the HMDI/DGEBA ratio increases the α process shifts towards higher temperatures in accordance with the previously reported trend followed by the calorimetric T_g in these systems [8–10].

4. Discussion

4.1. Relaxation processes associated with local motions

4.1.1. The γ relaxation process

Sub-glass relaxation processes are frequently associated with local motions of dipolar groups attached to the polymeric chain. In the HPN-1 systems investigated, the activation energy values (Fig. 4a), suggest that the underlying mechanism for the γ relaxation in HPN-1 series is a local motion of small molecular species, presumably DGEBA. In previous measurements on DGEBA, Casalini *et al*. [22] reported an activation energy for the γ process of pure DGEBA of 23.8 kJ/mol [22]. The values of F_{HN}, calculated from ref. [22], are shown in Fig. 4a for comparison with our own measurements on HPN-1. The agreement between both measurements seems to indicate that the DGEBA moiety present in HPN-1 systems (see Scheme 1) is responsible for the γ relaxation. The relative higher values of the activation energy found by us can be explained by considering that the mobility of DGEBA species in HPN-1 series (see Fig. 1 Scheme 1) is hindered by the local environment: either through dipole-dipole interactions between epoxy groups of DGEBA with isocyanurate heterocycles, and/or by hindrances to the local mobility of DGEBA caused by the HPN itself. In this case higher activation energies are expected as the HMDI/DGEBA ratio increases as experimentally observed. In fact, no clear evidence of γ relaxation is observed in the whole HPN-2 series and it only appears for HPN-1(90/10) as a high frequency contribution to the β relaxation (Fig. 5).

4.1.2. The β relaxation process

Inspection of the chemical nature of the investigated HPN systems (Fig. 1) reveals that the dielectrically active dipoles are located in the following moieties:

1. In the symmetrical isocyanurate heterocycle, because the atoms of oxygen and nitrogen are negatively charged while a large positive charge is concentrated in the carbon atoms.
2. In the asymmetrical oxyzolidone heterocycle which exhibits a similar charge conjugation as the isocyanurate but the existence of an additional oxygen within the ether group that may act like a molecular swivel.

The conjugation of carbonyl groups with nitrogen is typical for polyamides and polyurethanes. However, the amine groups (protons bonded to nitrogen atoms) providing capability of intermolecular hydrogen bonding in the latter are absent in the HPN systems. Considering the asymmetricity of the oxazolidone heterocycle and the presence of an oxygen it should be expected that a local motion in this unit will be less hindered by the environment than that associated to the isocyanurate heterocycle. In the light of the activation energy values for both the β and the β' processes (Fig. 4) we can attempt to assign the β' process (50 ± 1.5 kJ/mol) to the local motion of dipoles in the oxazolidone heterocycle and the β process (59.3 ± 1.5 kJ/mol) to that occurring in the isocyanurate heterocycle. Similar apparent activation energies were reported for the β process in aliphatic polyamides (58.5–62.7 kJ/mol) [23], and in aromatic polyetherimides (53.1, 57.7 and 58.9 kJ/mol) for oscillations of aromatic rings and benzimide cycles [24]. Analogous activation values are obtained for HPN-1 and HPN-2 although systematically lower values are observed for the former. This result can be explained by both, the plasticizing action of free DGBEA and by the incomplete trimerization of HMDI rendering a fraction of isocyanurate remaining as fragments with end groups of the type -$(CH_2)_6$-NCO in the HPN-1 under-cured systems.

4.2. The α relaxation process

When comparing the HPN-1 with the HPN-2 series the main effect on the α relaxation process is the higher temperature shift of this relaxation as the degree of curing increases. A second effect well observed in HPN-2 systems is the shift towards higher temperatures as the amount of isocyanurate heterocycles versus that of oxazolidone cycles increases, i.e as the HMDI/DGEBA ratio increases. For HPN-1 series, although 90/10 exhibits a higher temperature α relaxation than 70/30 and 50/50, an inversion of this tendency is observed for the two last samples. On the one hand, a possible interpretation of this effect might be associated with a solvent effect. Considering that HPN-1 samples contain free low-molecular mass DGEBA there must be a kind of solvent effect making that 50/50, with more DGEBA than the 70/30 sample, exhibits a lower temperature α relaxation than 70/30 sample. On the other hand, epoxy resin in HPN-1 may form a catalyst unit pairing with TEDA increasing the reactivities of HMDI increasing the degree of network conversion at the first step of polymerization [13].

As far as the shape of the α relaxation is concerned, the broadening parameters, b, for the HPN-1 under-cured samples are systematically lower than those of the HPN-2 systems (Table II). In contrast, the asymmetry parameter, c, is close to unity for HPN-1 series while is well below 1 for series HPN-2 (Table II). This observation suggests different patterns for the α relaxation of the two investigated series. The above mentioned broadening effect caused by defective curing process is reflected in the systematic lower values observed for HPN-1 as compared with those of HPN-2 series. In view of the physical meaning of “b” as a phenomenological measure of the width of the relaxation time distribution function the above data can be tentatively explained in the following way. On the one hand, at high HMDI/DGEBA ratios the major reaction is the trimerization of HMDI while DGEBA acts as a catalyst. Thus, the reaction product can be envisioned as a class of semi-interpenetrating polymer network of isocyanurate heterocycles mixed with linear DGEBA. Hence, the low b-values for HPN-1 series suggest an unusually wide relaxation time distribution function. This is presumably due to the broad spectrum of different structural units involved including linear and cyclic isocyanurates and DGEBA. Based on similar arguments, the higher b-values obtained for HPN-2 series can be interpreted as due to a reduction of the structural complexity provoked by a higher degree of curing rendering an effective conversion of linear isocyanurate into corresponding to heterocycles accompanied by a reduction of the amount of free DGEBA. On the other hand, at lower HMDI/DGEBA ratios the reaction between the epoxy groups of DGEBA and the isocyanate (or isocyanurate [2]) groups of HMDI becomes increasingly important. In this case the reaction product can be visualized as a HPN system containing two structurally different heterocycles: i) six-membered, three arm isocyanurate cycles and ii) five membered two arm oxazolidone cycles. Accordingly the decrease of b with decreasing HMDI/DGEBA ratio observed for the HPN-2 systems can be undestood in so far as the initial trimerization reaction of HMDI is gradually taken over by the formation of oxazolidone heterocycles.

In contrast with the sub-glass above discussed relaxations, the temperature variation of τ_{max} follows the VFT dependency as expected for cooperative relaxations. The τ_{max} values can be plotted as a function of a normalized temperature such that $T^* = T(\tau_{\mathrm{max}} = 10^2\ \mathrm{s})$ in order to build up a cooperativity plot (inset of Fig. 7) [20]. By doing so, it is possible to define a fragility index taking account of the cooperativity of the relaxation as $F_{1/2} = 2T^*/T_{1/2} - 1$, where $T_{1/2} = T(\tau = 10^{-6}\ \mathrm{s})$. The fragility or cooperativity of the relaxation increases as the $F_{1/2}$ value increase [20]. The calculated $F_{1/2}$ values (Table III) suggest that fragility increases, regardless of the HMDI/DGEBA ratio, with the extension of the secondary reaction, i.e. formation of oxazolidone cycles in the network structure. However, no systematic dependence of fragility is observed as the HMDI/DGEBA ratio changes. It should be expected that decreasing the HMDI/DGEBA ratio would provoke a decrease of the $F_{1/2}$ value due to the decrease of the network junction concentration. However, this effect can be compensated by a loss of flexibility due to an increase of the amount of aromatic structures present in DGEBA as observed for Poly(methyl phenyl siloxane) PMPS [5]. Preparation of model compounds in which the topological effects are separated from the chemical heterogeneity is in progress and will help to shed some light to this respect.

5. Conclusions

In summary, dielectric relaxation experiments of Heterocyclic Polymer Networks (HPN) containing isocyanurate and oxazolidone rings in the 10^{-1}–10^5 Hz frequency range reveal the existence of multiple composition dependent relaxation processes. The γ process, appearing at low temperatures only in partially cured systems, is related to the presence of free DGEBA. The β process, occurring at higher temperatures, is associated with local motions of the carbonyl groups present in the isocyanurate and oxazolidone cycles according to the measured values of the activation energies. The α relaxation, which has its origin in the segmental motions above the glass transition temperature, tends to appear at higher temperatures with increasing degree of network formation.

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