Anharmonicity and fragility in semi-interpenetrating polymer networks

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Abstract. Two series of semi-interpenetrating polymer networks (semi-IPN) based on the same linear polyurethane and two different heterocyclic polymer networks were characterized in terms of the complex dynamic modulus and the mechanical loss tangent, measured between 150 and 500 K at a frequency varying in the range between 0.3 and 30 Hz. The fragility and the deviations from exponentiality of the dynamics of the segmental motion of semi-IPNs in the glass transition interval have been obtained by modelling the mechanical α_a-relaxation. It was observed that the incorporation of linear polyurethane softens the heterocyclic polymer networks, lowers their resistance to the temperature-induced structural degradation, and increases the complexity of the long-range segmental dynamics. There has also been found a correlation between the fragility and the anharmonicity of the system, the most fragile polymer being characterized by the largest degree of anharmonicity. By extending the analysis to linear polymers, it was established that a growing anharmonicity is predictive of an increasing fragility.

1. Introduction

Non-exponentiality is the most salient phenomenological feature of the dynamics of segmental relaxation (DSR) in the glass transition interval of polymers (e.g., [1–3]). The extent of the deviations from exponentiality is believed [3–6] to depend both on the molecular structure and on the local environment of polymer chain segments. Single-phase, two-component polymer blends (PB) and interpenetrating polymer networks (IPN) are the obvious choices to study when investigating the effect of local environment on the DSR in polymers; however, the tendency of both PBs and IPNs to incipient microphase separation [7, 8] may become a problem.

The aim of the present paper is the experimental study of the DSR in the glass transition intervals of two series of semi-IPNs based on the same linear polyurethane (LPU) and two different heterocyclic polymer networks. Judging by the small-angle x-ray scattering, calorimetry, and dynamic mechanical analysis data [9–11], this new class of heterocyclic networks is consistent with a structural phase behaviour which shows a macroscopic structural homogeneity as opposed to some kind of local microscopic inhomogeneity. In contrast to the case for the addition of second-phase fillers to a polymer, such as carbon black or silica, which have very little effect on the glass transition temperature T_g [12], the incorporation of LPU in heterocyclic networks markedly changes both T_g and the cooperative DSR associated with

the α_a-relaxation. In particular, two glass transitions are revealed in semi-IPNs based on LPU and a copolymer of the trimerized dicyanic ether of bisphenol A and of the epoxy oligomer (DCE/EO): it is believed that the interpenetration of these two polymers gives rise to a double-phase amorphous network, each phase preserving the main morphological characteristics of the pure components.

Furthermore, the inclusion of LPU leads to an increase of both the fragility and the anharmonicity of the heterocyclic networks. This finding, examined in a more general context including amorphous linear polymers, leads us to conclude that the fragility of polymeric glass formers depends on their anharmonicity.

2. Experimental details

As already mentioned, a linear polyurethane (LPU) made from 4, 4-diphenylmethane diisocyanate and oligomeric butylene glycol adipate (molar mass $1000\,\mathrm{g\,mol^{-1}}$) was a common first component in both semi-IPN series. The second component (heterocyclic polymer network, HPN) was either the trimerized dicyanic ether of bisphenol A (DCE), in the semi-IPN-1 series, or a 60/40 (by weight) copolymer of the DCE and the epoxy oligomer (DCE/EO), in the semi-IPN-2 series (HPN-1 and HPN-2, respectively). Synthesis of semi-IPN-1 and semi-IPN-2 has been described in detail elsewhere [9, 10, 13]; therefore, only essentials need to be reported here. Monomeric DCE (or the DCE/EO prepolymer) was dissolved in a 15% solution of the LPU in cyclohexanone and the solution was cast at room temperature on glass slides treated with dimethyldichlorosilane. The films obtained were heated to 423 K to remove the solvent; the cross-linking reaction of the HPN was initiated by a storage for five hours at 423 K and completed by a subsequent post-cure at 453 K for three hours.

The complex dynamic modulus, $E^* = E' + \mathrm{i}E''$, and the mechanical loss tangent, $\tan\delta = E''/E'$ (where E' and E'' are the storage and loss components of the modulus, respectively) were measured under a controlled nitrogen atmosphere in the temperature interval between 150 and 500 K (heating rate: $2\,\mathrm{K\,min^{-1}}$; frequency range: 0.3–30 Hz) with a dynamic mechanical thermal analyser (Polymer Laboratories) [14]. Prior to measurement runs, each sample was dried at 353 K under a vacuum of 10 mbar for about 12 h.

3. Results and discussion

The peaks of $\tan\delta$ in the region of the main transition (α_a-relaxation or the dynamic glass transition) for LPU and both HPNs exhibited the familiar shifts to higher temperatures for higher driving frequency (figures 1(a), 1(b), and 1(c)); the higher values of T_g observed for HPN-2 are the obvious result of the network stiffening of a trimerized DCE with EO. The occurrence of a single glass transition for semi-IPN-1 (figure 1(d)) which is located midway between the T_g-values of the pure components (see table 1) is consistent with our earlier claim [11] of their single-phase state. Instead, the mixing of PU and DCE/EO to build semi-IPN-2 has the effect of giving rise to two calorimetric T_gs [9] and wider α_a-relaxations at temperatures which range between those of the pure polymers (figure 1(d)). It was argued [9] that the presence of two transitions could be related to the absence of chemical interactions between the two polymers, which form a double-phase network; in each phase the molecular structure and the microscopic homogeneity of the pure components are preserved. A more direct observation of two mechanical α_a-relaxations in semi-IPN-2 is provided by the temperature behaviour of the storage modulus E' in the sample with the HPN-2/LPU molar ratio equal to 75/25 (figure 2(a)). Two well-defined drops in the modulus are observed in the regions of temperature where $\tan\delta$
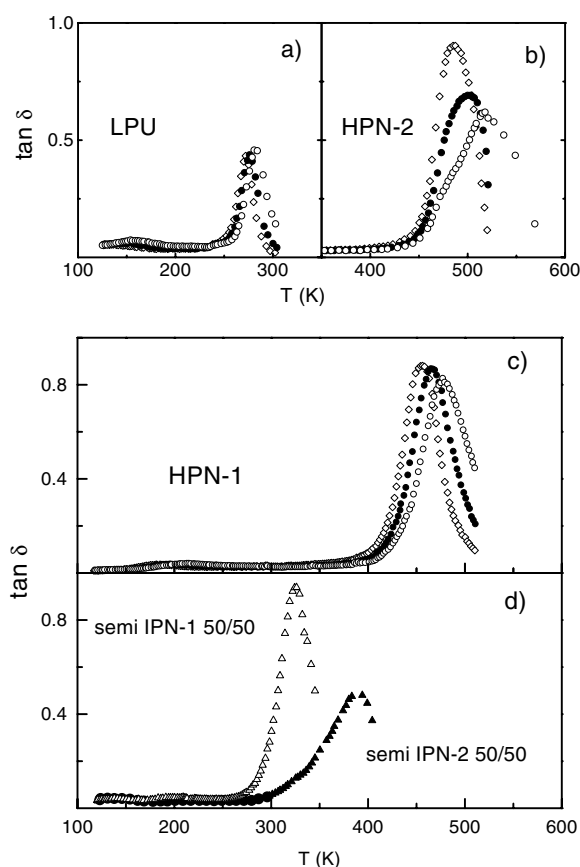
Figure 1. Mechanical loss tangent data for (a) LPU, (b) HPN-2, (c) HPN-1 at the driving frequencies (Hz) 0.3 (open diamonds), 3 (filled circles), and 30 (open circles); (d) comparison between the temperature behaviours of mechanical loss tangent data for semi-IPN-1 and semi-IPN-2 with a 50/50 HPNs/LPU molar fraction at a driving frequency of 3 Hz.

shows the main α_a-relaxation peak and the shoulder at lower temperatures. It is assumed that the small drop at lower temperatures is associated with the cooperative long-range segmental motion of LPU chains confined within the HPN-2 rigid network: the restriction in the segmental dynamics leads to an increase of the transition temperature, as compared to that of pure LPU. On the other hand, the lowering of the dynamical T_g observed on going from pure HPN-2 to the HPN-2 phase of this semi-IPN-2 can be explained in terms of the softening due to the penetration of LPU chains which hinder the shrinkage of HPN-2 on the cross-links. In contrast with what the evidence discussed would lead one to expect, only a single drop in $E'(T)$ for the semi-IPN-2 with the HPN-2/LPU molar ratio equal to 50/50 is revealed. It is believed that the further lowering of T_g for the HPN-2 phase (as revealed by calorimetric analysis [9]) leads the region of the mechanical α_a-relaxation to overlap with that of the LPU phase, preventing the observation of two distinct transitions in $E'(T)$. This makes it impossible to separate the contributions from the two phases and, consequently, also to perform a quantitative analysis of $E'(T)$ for this polymer.

As can be seen from figures 2(a) and 2(b), the initial (approximately linear) slow decrease with increasing temperature of the storage moduli E' of all samples studied in the temperature

Table 1. Calorimetric glass transition temperatures T_g, best-fit values of the parameters obtained by fitting the mechanical primary relaxation, and anharmonicity coefficients b' for semi-IPN polymers.

Sample		$10^3 b'$ (GPa K^{-1})	b^*	B (K)	T_0 (K)	M	β	T_g (K)
IPN-1								
HPN-1/LPU								
0/100		6.9	1.59	1612	213	89	0.32	255
30/70		10	1.67	1840	233	73	0.22	280
50/50		5.1	1.00	1748	236	62	0.2	311
100/0		2.3	0.49	3900	300	46	0.46	345
IPN-2								
HPN-2/LPU								
50/50	LPU phase							333
	HPN-2 phase							374
75/25	LPU phase			1946	241		0.29	335
		6.0	1.47					
	HPN-2 phase			3677	274	53	0.56	381
100/0		5.5	1.15	3314	351	45	0.35	404

interval below T_g is followed by a faster, non-linear drop (in some samples by over two decades) in a relatively narrow temperature interval around T_g. The drop moves to higher temperatures with increasing frequency as a consequence of the inherent dispersion (figure 2(c)); in the glassy region away from transitions, however, no significant variations of E' have been revealed in the frequency range explored.

As discussed elsewhere [14–16], the temperature dependence of E' in the region of the α_a-relaxation of polymers has been accounted for by the overlap of two different mechanisms:

(i) the anharmonic interactions of vibrational modes which cause a linear variation with the temperature of the elastic constants; and
(ii) the cooperative primary relaxation which produces the sharp drop in the modulus and the observed dispersion.

Of course this simple kind of approach can be applied to those polymers whose elastic behaviour within and below the glass transition temperature range is not affected by the presence of further dispersions arising from additional molecular relaxations which could mask the linear decrease and the α_a-relaxation drop of the modulus. As clearly shown in figure 2, and limiting the analysis to a restricted temperature range below T_g, the polymers analysed in this study represent a good example as regards the observation of the behaviour discussed.

In the approach used, the modulus $E'(\omega, T)$ in the region of the α_a-relaxation is given by the relation

$$E'(\omega, T) = [E_0 - b'(T - T_0')]_{anh} + \left[E_\infty' + \delta E' \int \frac{\mathrm{d}\phi(t)}{\mathrm{d}t} \cos(\omega t)\, \mathrm{d}t \right]_{rel}. \tag{1}$$

The first term on the right-hand side of equation (1) represents the temperature dependence of the elastic modulus due to the vibrational anharmonicity. E_0 is the value of E' at the lowest temperature T_0' in the experiment and the parameter b' is mainly determined by the Grüneisen coefficients which account for the anharmonic interactions between the vibrational modes [17].
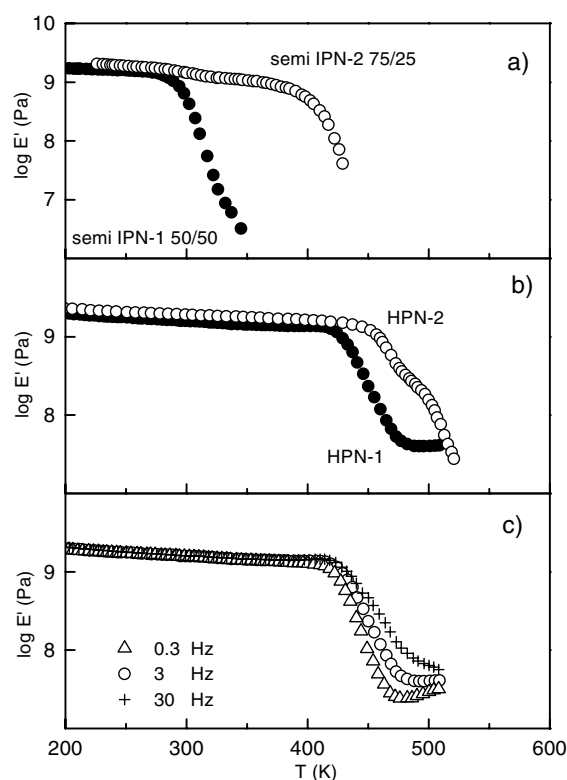
Figure 2. Temperature dependencies of the dynamic storage modulus E' at a driving frequency of 3 Hz in (a) semi-IPNs with 50/50 HPN-1/LPU and 75/25 HPN-2/LPU molar fractions and (b) pure HPN-1 and HPN-2. (c) $E'(T)$ at driving frequencies of 0.3 ($\triangle$), 3 ($\bigcirc$), and 30 Hz (+) in HPN-1.

The relaxation term is represented by the Fourier transform in the frequency domain of the stress relaxation function $E'(t)$ [18], where $E'(t) = E'_0 + (E'_\infty - E'_0)\phi(t)$; here, E'_∞ and E'_0 are the high-frequency (unrelaxed) and low-frequency (relaxed) storage moduli, respectively. In this expression, $\phi(t) = \exp[-(t/\tau)^\beta]$ is the Kohlrausch–Williams–Watt (KWW) 'stretched-exponential function' and $0 < \beta < 1$ is a phenomenological measure of the non-exponentiality (the width of the relaxation spectrum). Finally, the relevant relaxation time τ is expressed by the Vogel–Fulcher–Tammann (VFT) equation, $\tau = \tau_0 \exp[B/(T - T_0)]$, where τ_0 is the characteristic time and B and T_0 are empirical fitting constants.

The values of the parameters of equation (1) were determined by a minimum-search program that provides the simultaneous best fit of the experimental data at all the available frequencies for each sample. To reduce the number of fitting parameters, we used a fixed value of 3.1×10^{-14} s for the characteristic time τ_0. This value was derived by Brillouin scattering measurements on liquid polypropylene glycol of high viscosity [19] and was used as a quasi-lattice vibration frequency to set the short-time limit of the structural relaxation time in Angell's plot for polymers [20]. Furthermore, very narrow ranges of variability were imposed on the starting values of b', directly evaluated from the slope of $E'(T)$ in the glassy region, where the low-temperature γ-relaxation does not influence the linear trend of E'. The parameters resulting from this analysis are collected in table 1 and the quality of the data fit can be assessed from figure 3(a). Of course there is a strong coupling between some of the parameters, apart from β whose interval of variation cannot exceed ± 5–6%, because larger
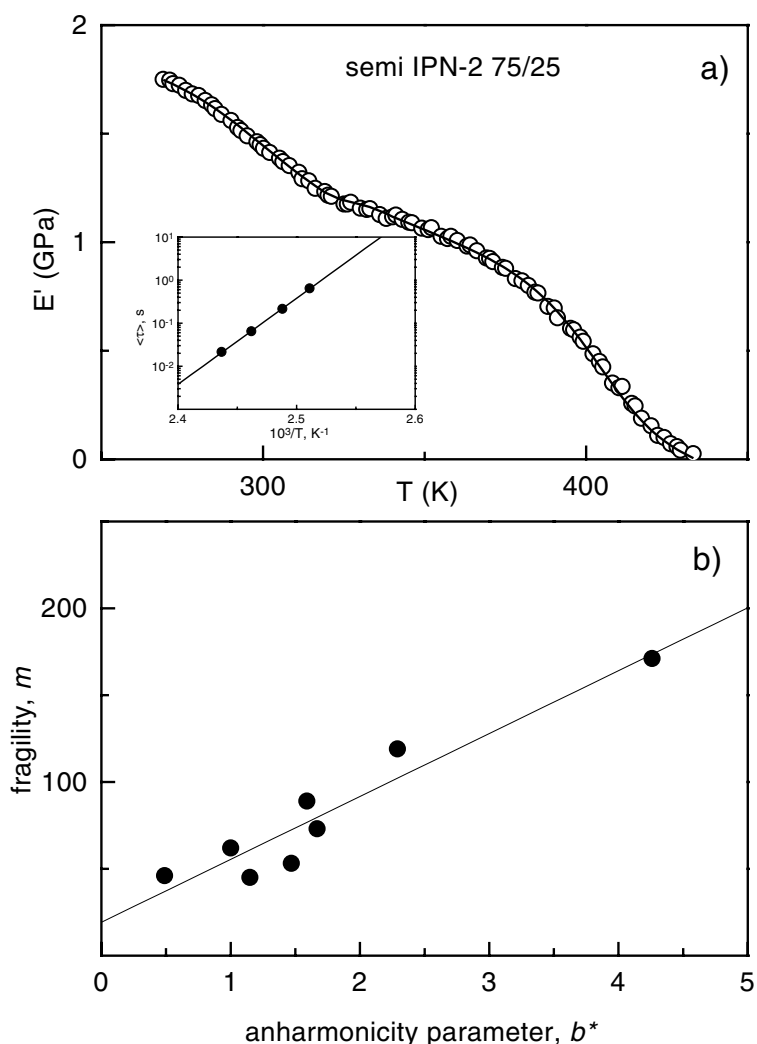
Figure 3. (a) The theoretical fit (solid line) with equation (1) of the temperature behaviour of the dynamic storage modulus in the regions of α_a-relaxations for the semi-IPN-2 sample with a 75/25 HPN-2/LPU molar fraction. The mechanical frequency is 3 Hz. In the inset the logarithm of the average relaxation time τ versus the inverse temperature is reported. A fit of the Arrhenius law to the τ-data deduced by mechanical experiments is shown as a solid line. (b) Fragility m plotted versus the anharmonicity parameter b^* for the polymers listed in tables 1 and 2. The solid line is a guide for the eyes only.

changes prevent reproduction of the experimental curve. Among the fit parameters, however, only the coefficient β is used, because through its value it is possible to correctly estimate the product $\omega\tau$ [21].

As could be expected, the smallest value of the anharmonicity factor b' was obtained for the densely cross-linked HPN-1 with presumably the tightest molecular packing; the concomitant loosening of the latter is reflected by the smooth increase of b' with LPU content in the IPN-1 series (table 1). As shown elsewhere [22], the network density of a trimerized aliphatic diisocyanate is decreased due to its 'internal dilution' with the EO; presumably, a similar effect

Table 2. Values of the thermal expansion coefficient α [25], the bulk modulus B [32], the specific heat C_p [33] and the density ρ [34] measured at room temperature. The values of the anharmonicity coefficients b' and b^* [26] and of the fragility m [6, 26] were determined using modulus measurements in the bending mode.

Sample	ρ (g cm^{-3})	T_g (K)	α (10^{-6} K^{-1})	C_p (J g^{-1} K^{-1})	B (GPa)	γ_{th}	m	b' (10^{-3} GPa K^{-1})	b^*
BPA-PC	1.20	418	65	1.207	4.57	0.60	119	11.0	2.29
PS	1.05	355	71	1.223	3.76	0.63	139	—	—
PMMA	1.18	374	62	1.376	5.81	0.66	145	—	—
PVC	1.268	320	74	0.950	5.41	1.00	171	27.3	4.26

is responsible for the higher value of b' for HPN-2 compared to HPN-1 (table 1). An interesting feature is the decrease exhibited by the parameter β_{LPU}, describing the non-exponentiality of LPU α_a-relaxation, on going from the pure component to the one confined within HPN-2 (semi-IPN-2 with 75/25). This reflects the effect of the constraints imposed on LPU amorphous chains by stiffer and not yet relaxed HPN-2 molecules, which restrict the cooperative movements of chain segments in their proximity and lead to a broadening of the segmental relaxation with an enhancement of its non-exponentiality.

Further insight into the relationship between glass-forming abilities and chemical composition of the systems studied can be obtained from comparison of values of the so-called 'fragility parameter' m which is defined by the following expression [6, 23, 24]:

$$m = \frac{\mathrm{d}\log\langle\tau\rangle}{\mathrm{d}(T_g/T)}\bigg|_{T=T_g}. \tag{2}$$

To evaluate the fragility of these polymers, the behaviour of the relaxation time in a temperature range above T_g has been derived from the curves of $E''(T)$ at different frequencies. Because of the restricted temperature range above T_g, τ follows an Arrhenius behaviour (see the inset in figure 3). The fragility can be calculated using the relation

$$m = E_A/(RT_g \ln 10) = -\log\langle\tau_A\rangle + \log\langle\tau_g\rangle$$

where E_A is the apparent activation energy of the process, $\langle\tau_A\rangle$ is the prefactor of the Arrhenius expression, and $\langle\tau_g\rangle = \tau(T_g)$ is usually taken as equal to 100 s [6].

As can be inferred from table 1, the fragility of the systems studied is lowest for both crosslinked components HPN-1 and HPN-2, and tends to increase in semi-IPN-1 systems (which appear to be single-phase systems) as the LPU content becomes higher. This increase of m can be explained within the fragility framework: in fact the term 'fragility' describes the inability of glass-former liquids to preserve the short- and medium-range order against the thermal degradation. It is believed that the trend revealed reflects the increasing number of internal degrees of freedom characterizing the mechanisms driving the structural rearrangements of large molecular groups in semi-IPNs, as compared to pure HPNs. The rigid structure of HPNs is weakened by LPU interpenetration and the resulting system, as a whole, tends to assume a less coherent structure whose resistance to the thermal degradation is gradually reduced with increasing LPU content. The same interpretation is also offered to explain the increase of m from pure HPN-2 to the HPN-2 phase in semi-IPN-2 with 75/25. The trend revealed appears to be in qualitative agreement with a rough linear correlation found between m and β [6]: higher values of m may be associated with the increased chemical complexity of a system, causing a broader distribution of relaxation times (i.e., smaller β).

A very interesting feature resulting from this analysis is the relation between fragility and anharmonicity, as weighted by the coefficient b' or, more properly for this kind of comparison,

by the dimensionless coefficient $b^* = (T'_g/E_0)b'$, whose values are also included in table 1. Strong glass formers, such as HPN1 and HPN2, show a lower anharmonicity than the fragile LPU. As discussed before, the anharmonicity factor depends on the Grüneisen coefficients [17], which can be quantified by the mean thermal Grüneisen parameter $\gamma_{th} = 3\alpha B^s/\rho C_p$, assuming that all vibrational modes have the same anharmonicity. In this expression α is the thermal expansion coefficient, ρ the density, B^s the isentropic bulk modulus, and C_p the specific heat measured at constant pressure. The densely cross-linked HPN1 and HPN2 are expected to exhibit smaller expansivity than the linear LPU, the other parameters defining γ_{th} being less sensitive, in the glassy region, to differences in the morphology. Consequently the behaviour of b' and b^* should reflect the decrease of the coefficient α—the most appropriate monitor of the vibrational anharmonicity—due to the presence of cross-links in the polymeric network. In polymers, in fact, the thermal expansion is determined by the overlap of the contributions of intrachain and interchain vibrations, which are controlled by covalent and van der Waals interactions respectively [25]. The introduction of cross-links in the polymeric network tends to suppress the interchain vibrations, which are responsible for large thermal expansions and vibrational amplitudes: *the system is driven towards a structural configuration which is more resistant to the thermal degradation of its molecular aggregation, as a consequence of a weaker temperature dependence of the vibrational amplitudes*. To establish that the correlation revealed represents a general feature of amorphous polymers, we have extended the analysis to a number of linear amorphous polymers, including PVC (poly(vinyl chloride), BPA-PC (bisphenol-A polycarbonate), PMMA (polymethylmethacrylate), and PS (polystyrene). In these materials the fragility has been determined by the same experimental method (dynamic modulus measurements) [6, 26] as is used in the present work: this provides a reliable scheme of classification where values of fragility, obtained in a homogeneous way in the range between 49 and 171, can be compared. Furthermore, all the parameters determining γ_{th} are known over a wide temperature interval [25]. In particular, for PVC and BPA-PC, b' has also been obtained from the temperature dependence of E' [26], this circumstance allowing a useful check of the existence of the claimed relation between b^* and γ_{th}. The values of γ_{th}, evaluated at 300 K, and of m for the cited polymers are included with those of b^* in table 2. It turns out that γ_{th} increases with increasing m, the most fragile glass former showing the highest anharmonicity and, even if the comparison is restricted to two polymers only (BPA-PC and PVC), the behaviour of b^* reflects that of γ_{th}. An m–b^* plot is reported in figure 3(b) and provides evidence for the existence of a roughly linear correlation between the two parameters of the polymers for which values are listed in tables 1 and 2. Thus it can be concluded that the class of amorphous polymers appears to be regulated by a correlation, which relates the 'fragile' or 'strong' character of these glass formers to a larger or smaller anharmonicity.

The present finding results in very close agreement with a recent model [27] which ascribes the deviation of the structural relaxation time from an Arrhenius behaviour ('the fragile character') to the anharmonicity of the intermolecular potential in glass-forming liquids. In this model the anharmonicity is reflected in the temperature dependence of the instantaneous (or infinite-frequency) shear modulus $G_\infty(T)$, which drives the average structural relaxation time away from an Arrhenius behaviour when the system goes across the glass transition region.

It is worth emphasizing that intimately linked to the present result are the considerations concerning two different groups of observations:

(i) the relation between picosecond anharmonicity and fragility [28], conjectured on the basis of the anomalous temperature behaviours exhibited at the glass transition by the mean square displacements of the particles of amorphous systems (the anomalous Debye–Waller factor);

(ii) the strong anharmonic effects, usually observed in the low-frequency region (a few meV) of neutron and Raman spectra of polymers, such as BPA-PC [29] and PVC [30], and also at temperatures quite far below the glass transition. They are often attributed to the occurrence of fast relaxations, causing the quasi-elastic scattering excess (QE), whose contribution is overlapped to that of only weakly anharmonic vibrations, responsible for the boson peak (BP).

In the context of the correlation between anharmonicity and fragility, we can speculate that the relaxational contribution to the spectrum should increase with increasing fragility, as a consequence of a larger anharmonicity characterizing the system. This conclusion agrees with the prediction of a recent theoretical model which tries to explain the anomalous features observed in low-frequency Raman and neutron scattering, the QE and the BP, in terms of the anharmonic coupling between relaxations and vibrations [31].

4. Conclusions

We have presented primary relaxation data for two series of new semi-interpenetrating polymer networks based on linear polyurethane and cross-linked trimerized dicyanate in order to study the mechanisms which regulate the relaxation dynamics of this kind of material. It has been observed that the inclusion of PU softens both the HPN-1 and HPN-2 rigid networks which, in contrast, affects the PU chain motion by restricting the cooperative long-range segmental dynamics. Single glass transitions are observed in semi-IPN-1, and indicate an affinity between LPU and HPN-1 and also a large-scale structural homogeneity.

In contrast to the case for semi-IPN-1, two glass transitions are observed in semi-IPN-2, where the absence of chemical intermolecular interactions is thought to give rise to a double-phase amorphous network, each phase preserving the main morphological characteristics of the pure components.

It has been shown that the LPU interpenetration in HPNs causes an increasingly fragile character of semi-IPNs which is paralleled by an enhanced non-exponentiality of the primary relaxation and an increasing anharmonicity of the vibrational modes. Extension of the analysis to data from the literature on amorphous linear polymers permits us to reveal the existence of a distinct correlation: a growing anharmonicity is predictive of an increasing fragility of polymers.

Acknowledgments

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