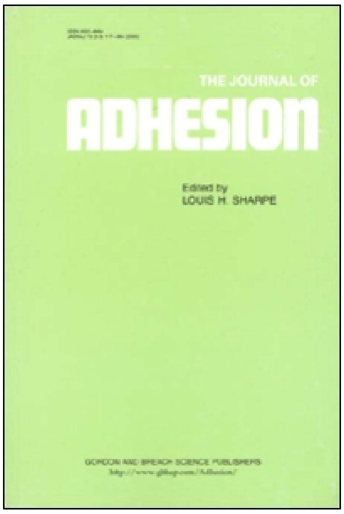

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Molecular Mobility in Semi-IPNs of Linear Polyurethane and Heterocyclic Polymer Networks*

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A study of the thermal and mechanical properties of new semi-interpenetrating polymer networks (IPN's) based on linear polyurethane (PU) and crosslinked trimerized dicyanate (TDC) reveals the existence of structures characterized by the absence of chemical interactions. Two distinct glass transitions are observed in the thermograms, as an indication of the fact that the two polymeric components preserve their molecular structure. The interpenetration affects markedly the glass transition temperatures revealed in the pure components in consequence of modifications in the local environments of the relaxing molecular units in the two phases. The primary and secondary relaxations of these systems show features which can be explained by accounting for the free-volume decrease due to the inclusion of PU in the network of TDC. Below the glass transition two molecular relaxations have been observed which have been ascribed to the secondary relaxation motions characterizing each polymeric component. Both relaxations exhibit a marked non-exponentiality which has been well accounted for in terms of a Gaussian distribution of relaxation times. The results of this analysis suggest that the local motions of TDC, ascribed to phenylene groups in the crosslinks between the cyanate units, are severely restricted by the inclusion of PU, while those of PU are slightly influenced by the presence of TDC.

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*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

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Keywords: Anelasticity; internal friction; anharmonicity; glass transition; polymers; crosslinked trimerized cyanate; primary and secondary relaxations; thermo mechanical properties

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I. INTRODUCTION

The structure and the molecular mobility of interpenetrating (IPN) polymer networks, used to bring together the properties of different polymers, have been subjected to intensive investigations in the last few years. An IPN is a combination of two polymers in network form, at least one of which is synthesized and/or crosslinked in the immediate presence of the other.

Motivation for this work was the preparation and the use of new materials with proper characteristics for a wide range of technological applications without requiring the synthesis of new polymers [1]. Crosslinked trimerized dicyanate (TDC) are polymeric materials which may be used as adhesives, compounds, coatings and binders for plastics for use at high temperatures and high stresses [2–5]. Since it is expected that the blend of the two different polymer networks does not change the morphology of the components, it is important to understand the phase behavior and the molecular movements characterizing the polymeric backbones. The study of the relaxation dynamics is useful to clarify the coupling mechanisms which are responsible for the mechanical and thermal characteristics of the whole network.

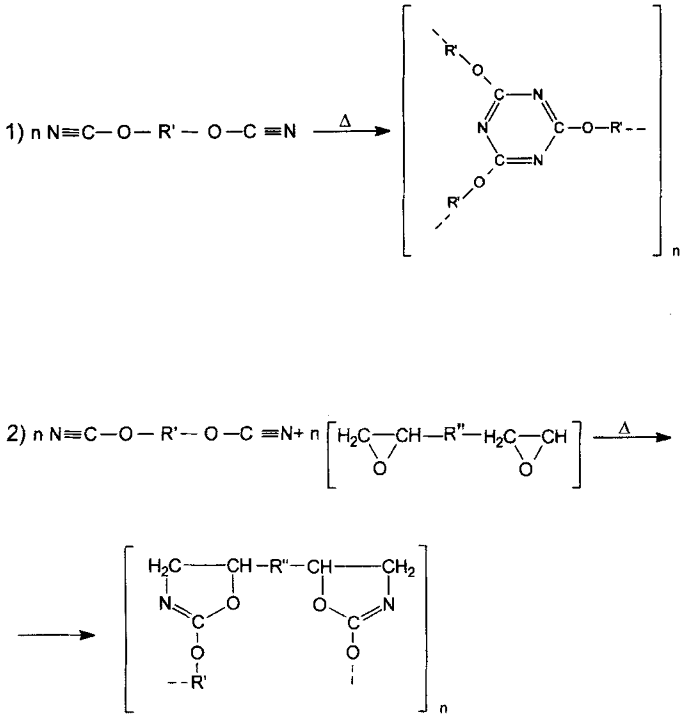
Previous mechanical studies of heterocyclic networks, blends with different molar ratio of hexamethylene-diisocyanate (HMDI) and epoxy resin (ER) [6], have emphasized the effect of ER which acts as a sort of "diluent" in the structure. It modifies the thermoelastic properties of the system giving rise to a softening monitored by the lowering of the rubber modulus. The chain interactions ensure the molecular homogeneity of the system producing the decrease of a single and well-defined glass transition with increasing ER concentration.

To find out whether the phase behavior of a new class of heterocyclic networks without chemical interactions is consistent with the predictions of a macroscopic structural homogeneity as opposed to some kind of local microscopic inhomogeneity, we have made mechanical investigations on semi-IPN based on linear polyurethane (PU) and cross-linked trimerized dicyanate (TDC). The low frequency elastic modulus and the internal friction exhibit temperature behaviors characterized by the presence of the γ- and α-relaxations, whose analysis permits one to obtain an insight into the structural phases which originate each relaxation and on their microscopic origin. It results that the interpenetration of the two polymers modifies the cooperative segmental dynamics associated with the α_a-relaxation but preserves the local arrangements of the relaxing centres, whose conformational transitions cause the low temperature γ-relaxations. The microscopic nature of relaxors remains as yet a puzzle, although some kind of local motion is believed to have significant mechanical activity for producing the γ-process.

II. EXPERIMENTAL DETAILS

II.1. Materials

Dicyanic ether of Bisphenol A (DCE) was purified according to the standard recommendations [7]; the melting point of purified DCE (354 K) was identical to the tabulated value [7]. Epoxy oligomer ED-20 (EO) was purified in argon flux during 2 hours (temperature: 373 K; pressure: 0.133 kPa). Linear polyurethane (PU) from 4,4′-diphenylmethane diisocyanate and oligomeric butylene glycol adipate (molar mass 1 kg/mol) was a commercial product (trade name VITUR T261, viscosity-average molar mass about 40 kg/mol). Semi-IPNs were prepared by the following scheme, see Figure 1. A mixture of DCE and ED (60/40 by weight, 2.3/1.0 by functional groups) with 0.5% of triethylamine was homogenized by heating to 423 K and stored in the flux of an inert gas. After 30 min. the reaction was stopped by cooling to room temperature; the product (oligooxazoline-cyanoureate, OCU) was dissolved in 15% solution of PU in cyclohexanone and the mixture was cast on glass slides treated with dimethylchlorosilane. The films obtained were heated to 423 K to remove the solvent; the cross-linking reaction of OCU was initiated by storage during 5 hours at this temperature, and completed by subsequent post-cure at 453 K during 3 hours. The extent of the cross-linking reaction of OCU in semi-IPNs obtained in this fashion could



R' — the residue dicyanic ester, R'' — the residue of epoxy resin

FIGURE 1 The formation of the trimerized dicyanate copolymer (TDC) by two main chemical reactions.

be checked by complete disappearance of characteristic IR absorption bands of stretching vibrations of —O—C≡N groups in the region of 2236–2272 cm^{-1}.

II.2. Methods

The mechanical characteristics (internal friction Q^{-1} and dynamic modulus E') were obtained in the 150–500 K temperature and 0.3–30 Hz frequency range by using the mechanical thermal analyzer

(DMTA) of the Polymer Laboratories driven in the bending mode. Before each run of measurement the sample were dried under vacuum of 10^{-4} mbar for ~ 12 h and then analyzed by maintaining the experimental chamber under a controlled atmosphere of nitrogen [8]. All the data were taken by using a running temperature with a rate of 2 K/min. The density was measured at room temperature by weighing the samples in air and in vaseline.

The thermograms of all the complexes were determined using a Perkin-Elemer DSC2 Differential Scanning Calorimeter at a heating rate of 20 K/min in the 320–450 K temperature interval. The magnitude of the features in the thermograms, as measured by the shift from the baseline, have been normalized by taking the weights of the samples (~ 4 mg) into account.

III. EXPERIMENTAL RESULTS

Pure TDC shows a single glass transition which occurs at a temperature of about 400 K, see Figure 2. The thermogram of pure PU has

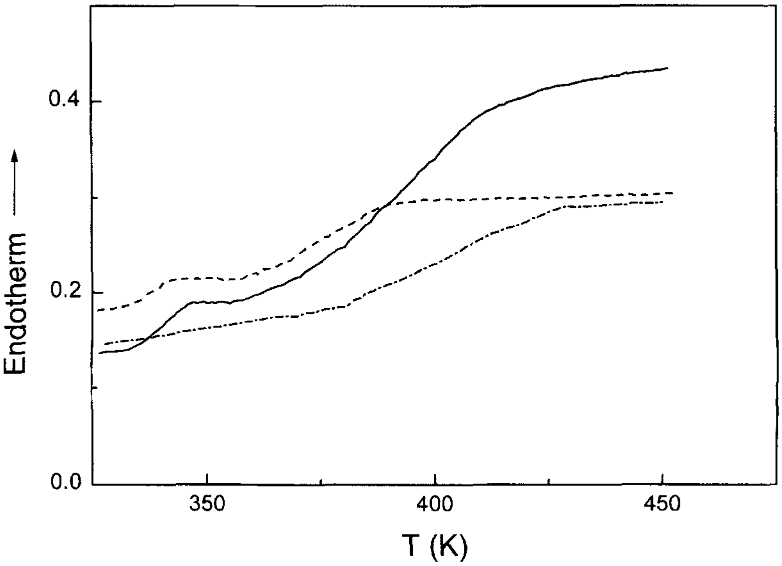


FIGURE 2 DSC traces of IPN (PU/TDC) samples through the glass transition temperature: (------) PU/TDC = 50/50; (——) PU/TDC = 25/75; (-.-.-.) PU/TDC = 0/100.

not been determined, because our DSC apparatus cannot work in the range below room temperature. By the indications of the mechanical results in the same sample (see Fig. 3), however, a calorimetric T_g lower than 273 K is expected. The endothermic features at about 330 K and 380 K, which characterize the thermograms of semi-IPN's, also inserted in Figure 1, are associated with the glass transitions of PU and TDC, respectively.

The temperature dependencies of the internal friction, Q^{-1}, and dynamic modulus, E', for pure PU and TDC between 120 K and

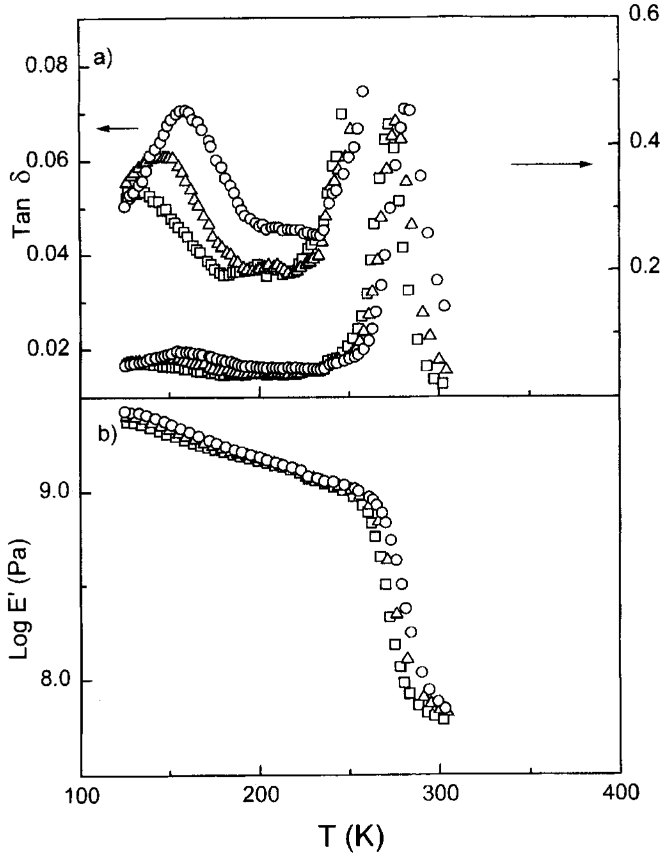


FIGURE 3 The effect of driving frequency on the temperature dependence of (a) internal friction and (b) dynamic modulus in pure PU.
(☐), 0.3 Hz; (Δ), 3 Hz; (○), 30 Hz. On the left hand-side of (a) the low temperature data are plotted by using an expanded scale.

550 K at selected frequencies are shown in Figures 3 and 4. As the temperature is increased from 120 K, tanδ, exhibiting the γ-relaxation peak, shows a transition up to about 200 K in PU and up to 300 K in TDC. Above these regions the loss shows in both the polymers the broad peaks typical of the glass to rubber transition, whose maximum shifts to higher temperatures as the mechanical driving frequency is increased. In Figures 3b and 4b the corresponding behaviors of the dynamic modulus for the same samples are presented. The modulus

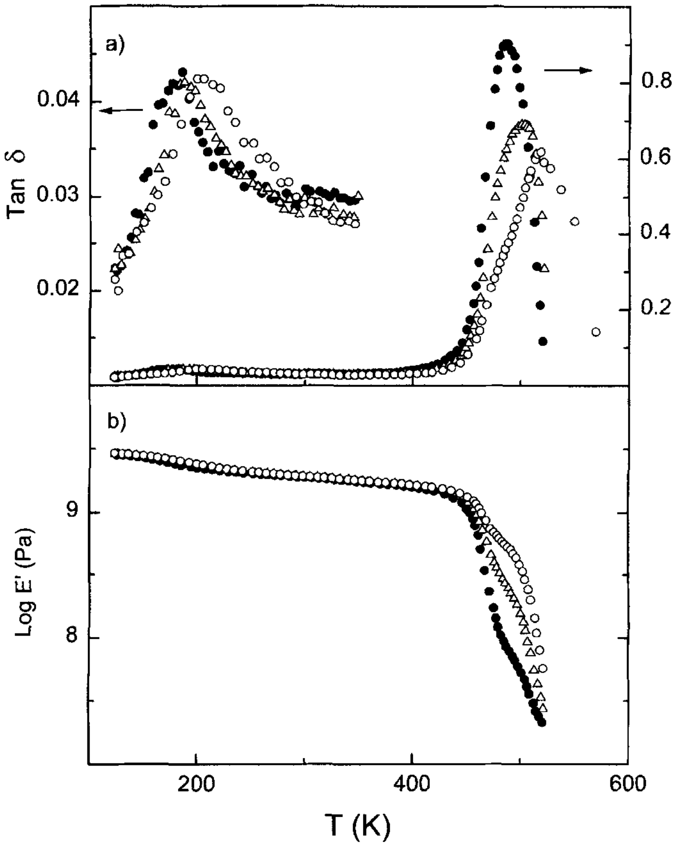


FIGURE 4 The effect of driving frequency on the temperature dependence of (a) internal friction and (b) dynamic modulus in pure TDC.
(●) 0.3 Hz; (c), 3 Hz; (○), 30 Hz. On the left hand-side of (a) the low temperature data are plotted by using an expanded scale.

exhibits a small inflection in the same temperature region, where the γ-peak is observed. With increasing temperature above this region, a linear decrease appears followed by sharp drops, which arise from the cooperative α_a-relaxation.

Figure 5 shows the mechanical spectra of two samples of PU analyzed by using two different experimental procedures. The sample labelled as "dry" was studied by applying the standard procedure, described in Sec. II.

The experiment for that labelled as "wet" was carried out in air and no special precautions were taken to prevent contact with water vapor.

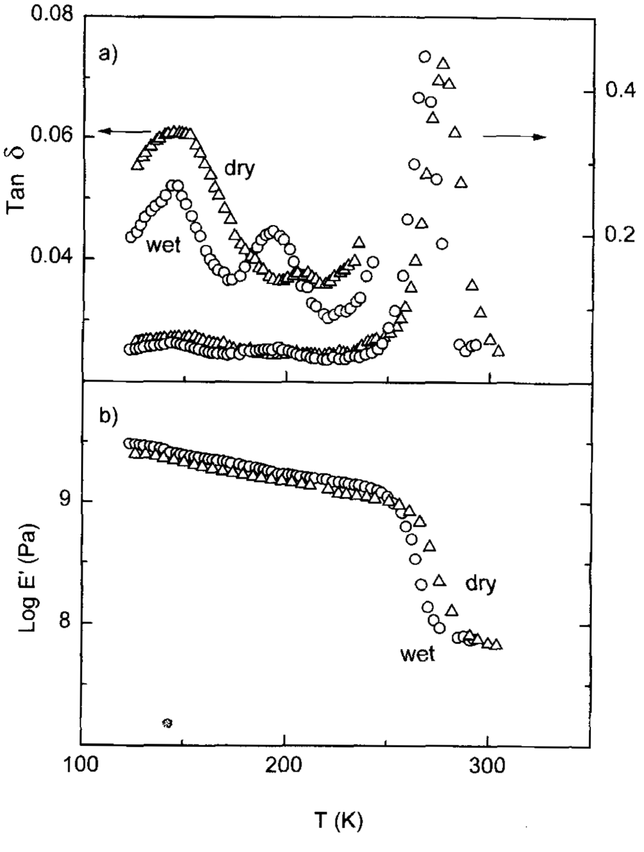


FIGURE 5 (a) Internal friction and (b) dynamic modulus in "dry" (Δ) and "wet" (○) pure PU samples. The mechanical frequency is 3 Hz.

In the wet sample the α_a-peak markedly shifts to lower temperatures and two well-defined peaks appear in the region where the dry sample shows a single γ-peak. Similar effects have been already observed in polyurethanes [9] and are ascribed to the presence of water absorbed in the polymer during its exposure to the air. The plasticization effect due to the absorbed moisture causes the lowering of T_g and the appearance of a second peak in the region of the low temperatures, usually defined as β-relaxation. This relaxation appears, to be severely suppressed in dry polymers. In contrast, the TDC polymer did not show any plasticization effects.

To illustrate the effects of the interpenetration, the experimental results for the temperature dependence of Q^{-1} and E' at 3 Hz in networks containing different molar ratios of PU and TDC (IPN50/50 and IPN25/75) are compared with those of pure polymers in Figures 6a and 6b. Broad peaks are observed at intermediate temperatures between those of pure PU and TDC which, as suggested by the presence of a shoulder in the low temperature tails, appear to be the result of the overlap of two close α_a-relaxations. The corresponding behaviors of the dynamic modulus show a linear decrease with increasing temperature followed by a first softening due to the α_a-relaxation of PU and a further sharp drop arising from the primary relaxation of TDC. In the low temperature region two well-defined peaks are revealed (Fig. 7), whose magnitudes can be roughly obtained by those of the γ-peaks in pure polymers scaled by the corresponding concentrations. The temperature of the peak, labelled γ_1, is almost coincident with that of the γ-peak in Pu, while that labelled γ_2 appears to be shifted to higher temperatures, as compared with the γ-peak in TDC; the magnitudes of these peaks decrease with decreasing content of the corresponding components. These features indicate that the molecular motions of TDC are affected by the interpenetrating chains of PU to a larger extent than the converse.

IV. DISCUSSION

The behavior of the thermal and mechanical characteristics of pure Pu and TDC in the region of the glass transition is typical of wholly amorphous polymers characterized by a high molecular homogeneity.

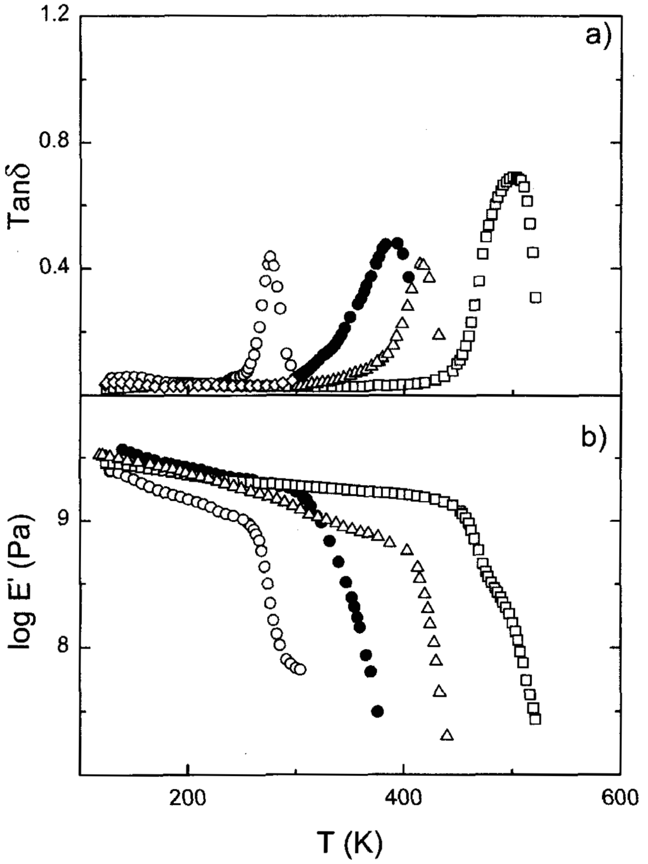


FIGURE 6 (a) Internal friction and (b) dynamic modulus as a function of temperature in IPN (PU/TDC) samples at 3 Hz: (○) PU/TDC = 100/0; (●) PU/TDC = 50/50; (Δ) PU/TDC = 25/75; (□) PU/TDC = 0/100.

Single glass transitions paralleled by well-defined α_a-loss peaks and drops in E' of about two orders of magnitude are present in the thermograms and in the mechanical spectra: the complete softening of these systems by crossing the glass transition and the lack of mechanical features arising from the melting of crystals ensure the absence of crystalline phases. The large difference in the Tg's of the two polymers reflects the nature of the chain interactions characterizing their structures:

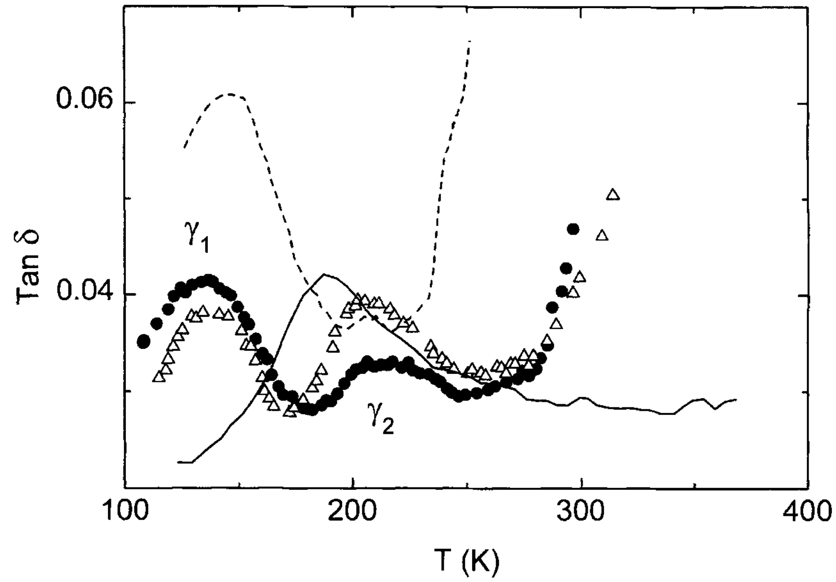


FIGURE 7 Comparison of the low temperature dynamical mechanical spectra of the IPN's at a frequency of 3 Hz: (----) PU/TDC = 100/0; (●) PU/TDC = 50/50; (Δ) PU/TDC = 25/75; (—) PU/TDC = 0/100.

PU is a linear polymer with weak interchain bonds, while TDC is a rigid, highly-crosslinked network.

The mixing of PU and TDC to build up the resulting semi-IPN's has the effect of giving rise to two T_g's and wider α_a-relaxations at temperatures which range between those of the pure polymers. It is argued that the presence of two transitions at the T_g's of both pure polymers is strictly connected 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. The smooth variations of the T_g with composition, as compared with those of the pure components, suggests a rather high affinity between PU and TDC, promoting their miscibility. They are to be ascribed to changes in the environment of the molecular units which alter the constraining effects on the long-range segmental motions. The mobility of PU chains is severely restricted by the stiffer and not yet relaxed molecular units of TDC, while the motion of the latter is favored by the soft and already relaxed PU chains. The concentration behaviors of the calorimetric T_g's and of the α_a-peak temperatures corresponding to the dynamical T_g's can be explained by the following considerations:

a) the large scale segmental motions of PU are constrained by the TDC crosslinked network whose channels confine the main chain of PU. The confinement reduces the free volume available for the chains, producing an elevation of T_g.
b) the inclusion of PU, increasingly soft with increasing temperature above 330 K, reduces the rigidity of the TDC cage which becomes more resilient as a result of the dilution effect. This circumstance should lead to a lowering of the requisite energy for the TDC cooperative motions enhancing the mobility of the molecular groups and correspondingly decreasing the T_g.

At temperatures below the glass transition region, the internal friction spectra of pure PU and TDC are characterized by a single γ-relaxation peak, while those of IPN's show two distinct peaks γ_1 and γ_2, which result from the secondary relaxation motions of the polymers building up the semi-IPN's. The mechanism involved is that the mechanical wave interacts with the relaxing centres and modifies their thermal equilibrium population so that a new equilibrium distribution is attained with a characteristic relaxation time, τ. All these peaks follow an Arrhenius behavior, as usually observed in polymers [8, 10], but are unexplainable in terms of a single relaxation time. In fact, due to the structural randomness of the polymer, there is a distribution of relaxation times. The relaxation loss has been analyzed using the following equation [8]

$$Q^{-1} = \sum_i \frac{A_i}{T} \int \exp\left(-\frac{(E - E_i)^2}{2E_{oi}^2} \right) \frac{\omega \tau_i(E)}{1 + \omega^2 \tau_i^2(E)} dE \tag{1}$$

where

$$A_i = \frac{N_i B_i^2}{\sqrt{32\pi}\, \rho c^2 K_B E_{oi}} \tag{2}$$

where the index i refers to γ_1 and γ_2 peaks. In Eq. (2), B_i is an average deformation potential that expresses the coupling between the mechanical stress and the system. The relaxation loss, Q_{rel}^{-1}, accounts for a relaxation time distribution, which arises from a Gaussian activation energy distribution and a single value for the characteristic time, τ_o. In Eq. (1) E_i and E_{oi} represent the most probable activation energy and the width of the distribution, $\tau(E) = \tau_o \exp(E/kT)$, N_i is the total number of relaxing particles per unit volume, ρ is the density, v is the sound velocity and the other symbols have the usual meanings.

The relaxation loss has been evaluated by subtracting an internal friction background, weakly temperature dependent, from the experimental curves at the highest frequencies. The values of E_i, E_{oi}, $N_i B_i^2$ and τ_{oi} were obtained by the least-square fits to the experimental data with a Minuit minimum search program.

Typical fits of the relaxation loss are shown by a solid line in Figure 8. The good fit to the shape of the experimental results and the finding that the theoretical parameters obtained from the fits at different mechanical frequencies are the same within a few percent prove the validity of this theoretical approach. The relaxation parameters,

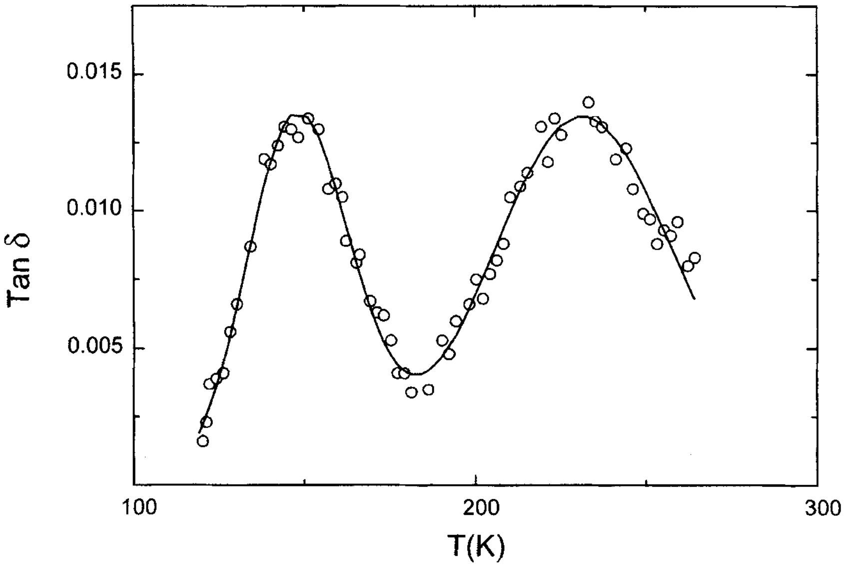


FIGURE 8 omparison between the experimental data and theoretical fit by Eq. (2) of the γ_i-relaxations in the IPN sample with $X = 0.25$. The mechanical frequency is 30 Hz.

resulting from this analysis, are given in Table I. The mean activation energy, E_1, appears to be quite independent from the PU concentration, while E_2 shows a defined increase by going from pure TDC to the semi-INP's. This finding strongly suggests that the local motion of the relaxing particles in PU is not affected by the interpenetration, while that in TDC is severely hindered, probably as a consequence of restrictions in free volume induced by the main chain of PU. It is expected, in fact, that the inclusion of Pu hinders the shrinkage of TDC on crosslinks which results in a reduction of the volume available for the transitions. The other striking feature of the results is that the products $N_1B_1^2$ and $N_2B_2^2$, involving the density of relaxing particles and the deformation potential for γ_1 and γ_2 relaxations, do not appear to scale proportionally to the decreasing concentrations of Pu and TDC, respectively. It is believed that this trend also reflects relevant changes of B_i with the concentration that partially cover the real variations of the relaxing particle number, N_i. It has been shown, in fact, that the deformation potential follows a roughly linear correlation with the glass transition temperature, T_g, for a wide range of amorphous materials [11]. Now, the glass transition temperatures of these polymers change markedly by interpenetration, producing a parallel change of the deformation potential. The fact that the product $N_iB_i^2$ results from variations in both the quantities N and B implies that the density of relaxing particles, N, could follow a quite different behavior from that observed for $N_iB_i^2$. A further important consideration needs to be made to justify the sharp reduction of $N_2B_2^2$ with decreasing TDC content. As more clearly explained in the following, it is thought that such a large decrease of the relaxation strength mainly results from severe restrictions imposed by the PU chains on the spatial ability to relax some TDC molecular groups.

Taken together, these two observations involving E_i and $N_iB_i^2$ support the conclusion that the relaxing particles are groups sited inside the main chain of PU or the crosslinks in the network of TDC. The formers are undisturbed from the inclusion of TDC, while the TDC motion appears to be severely restricted by PU chains. This explanation permits one to account also for the relevant reduction observed in the width, E_{o2}, of the γ_2-relaxation when PU is added to TDC. The pronounced suppression of the volume for the conformational transitions leads to the reduction of the configurations available for the

TABLE I Values of the parameters E_i, E_{0i}, and $N_iB_i^2$ for the γ-relaxations in semi-IPN's samples. The values of density, ρ, refer to room temperature

PU/TDC ratio	ρ ($g\,cm^{-3}$)	τ_1 ($10^{-14}sec$)	E_1 (eV)	E_{01} (eV)	$N_1B_1^2$ ($10^{19}\,eV^2cm^{-3}$)	τ_2 ($10^{-14}sec$)	E_2 (eV)	E_{02} (eV)	$N_2B_2^2$ ($10^{19}eV^2\,cm^{-3}$)
0/100	1.207	–	–	–	–	0.815	0.50	0.104	20.11
25/75	1.214	0.950	0.32	0.027	5.71	0.044	0.51	0.053	9.04
50/50	1.224	0.058	0.34	0.043	8.58	0.012	0.53	0.011	1.74
100/0	1.241	0.157	0.37	0.037	9.20	–	–	–	–

relaxors with a consequent relevant narrowing of the relaxation time distribution characterizing these local movements.

In the case of the γ_1-relaxation relative to PU there is a broad consensus [9, 12, 13] that the corresponding conformational transition is associated with the crankshaft motion of $(CH_2)_n$ groups between the hydrogen bonds. Concerning the local motions which have sufficient mechanical activity to induce the γ_2-transition in TDC, we note that the lack of direct microscopic information makes this analysis quite difficult. However, recent mechanical measurements have been made in copolymers built on sequence structures of BPA-PC and TMBPA-PC blocks in order to define the microscopic origin of the secondary relaxation in BPA-PC polymer [14]. The main chain of BPA-PC is built on phenylene groups whose local motions, correlated by the carbonate groups over distances involving more than one repeating unit, give rise to the γ-transition. By a systematic increase of the length of BPA-PC blocks, Jho and Yee [14] determined the γ-relaxation dependence on the correlation distance.

Since the same phenylene groups are present in the links between the planar six-membered three-arm cyanoureate rings of TDC, it is believed that the correlated motion of these groups could also be responsible for the γ_2-transition. The fact that the motion is strongly affected by the interpenetration of PU can be interpreted in terms of a decrease of the correlation distance due to the volume (and consequently the conformational transition) restrictions imposed on the relaxing units whose local environment has been modified by the inclusion of the PU chains.

V. CONCLUSIONS

New semi-interpenetrating polymer networks based on linear polyurethane and crosslinked trimerized dicyanate have been prepared in order to gain an insight into the interaction mechanisms which regulate the mechanical properties of these kinds of materials. The analysis of the temperature and frequency dependence of the mechanical characteristics reveals that the inclusion of PU softens the TDC rigid network which, on the contrary, affects the PU chain motion by restricting the cooperative long-range segmental dynamics. The softening of

TDC is interpreted by supposing that the penetration of PU chains hinders the shrinkage of TDC on the crosslinks. Two glass transitions are observed in the IPN's, whose temperatures change following the variations in the local environments of the relaxing units. 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.

This statement reflects also on a microscopic length-scale: two well-defined γ-relaxations corresponding to the local conformational transitions in both PU and TDC characterize the low temperature mechanical spectrum of semi-INP's. The analysis of these features in terms of parallel relaxations arising from a distribution of relaxation times suggests that the local motions in PU chains are slightly affected by the inclusion of TDC. On the contrary, the molecular motion of TDC is severely restricted by a marked reduction of the volume available for the relaxations of some groups, as a consequence of the presence of PU chains in the environments. It is concluded that this immobilizing effect due to PU chains introduces a reduction of the motional correlation of the phenylene groups, assumed as relaxors in TDC, which corresponds to a decrease of the mechanical relaxation activity of these molecular units.

Acknowledgments

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