# Structure–Property Relationships in Thermoplastic-Apparent Interpenetrating Polymer Networks Based on Crystallizable Polyurethane and Styrene–Acrylic Acid Copolymer

A. KYRITSIS,<sup>1</sup> P. PISSIS,<sup>1</sup> O. P. GRIGORIEVA,<sup>2</sup> L. M. SERGEEVA,<sup>2</sup> A. A. BROUKO,<sup>2</sup> O. N. ZIMICH,<sup>2</sup> E. G. PRIVALKO,<sup>2</sup> V. I. SHTOMPEL,<sup>2</sup> V. P. PRIVALKO<sup>2</sup>

<sup>1</sup> National Technical University of Athens, Department of Physics, Zografou Campous, 15780 Athens, Greece

<sup>2</sup> Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, 253160 Kyiv, Ukraine

Received 10 July 1998; accepted 7 November 1998

ABSTRACT: Structure-property relationships in thermoplastic-apparent interpenetrating polymer networks (t-AIPNs), prepared by mechanical blending in a common solvent of crystallizable polyurethane (CPU) and styrene/acrylic acid random copolymer (S/AA), were investigated by means of wide-angle and small-angle X-ray scattering (WAXS and SAXS), dynamic mechanical analysis (DMA), thermally stimulated depolarization currents (TSDC) techniques, dielectric relaxation spectroscopy (DRS), and density, water uptake, deformation, and strength characteristics measurements. Several mechanical and dielectric relaxations of the pure components were characterized, and the effects thereupon induced by blending were followed. The two components show weak affinity to each other. The t-AIPNs can be classified into two groups with high and low contents of CPU, showing essentially the behavior of CPU and of S/AA, respectively. On the other hand, deviations from additivity in several properties indicate interactions between the two components, caused by the formation of H-bonds between their functional groups, and resulting in partial miscibility. In addition, significant changes are observed on some properties of the t-AIPNs on addition of small amounts of either of the components. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 385-397, 1999

**Key words:** thermoplastic-apparent interpenetrating polymer networks; local heterogeneity; relaxation; H-bonding; mixed microphase

# **INTRODUCTION**

Interpenetrating polymer networks (IPNs) received much attention in recent years.<sup>1,2</sup> IPNs may be defined as binary polymer systems, in which at least one component is chemically crosslinked (as a rule, by covalent bonds) to avoid the incipient phase separation.<sup>3,4</sup>

In thermoplastic IPNs (TIPNs), as opposed to classical or true IPNs, the components are

crosslinked by means of physical bonds (like ionic and hydrogen bonds) and/or microcrystallites playing the role of effective crosslinking sites. Their components (block copolymer, semicrystalline polymers, and polymers with ionic groups $^{4,5}$ ) are able to form physical networks, and are characterized by a mutual penetration of phases. Thus, TIPNs are intermediate between mixtures of linear polymers and true IPNs; they behave like chemically crosslinked polymers at relatively low temperatures and as thermoplastics at high temperatures. TIPNs are prepared either by mechanical mixing of components, in the melt state or in common solvent (mechanically blended TIPNs), or by a matrix polymerization technique (chemically blended TIPNs).

Correspondence to: P. Pissis.

Contract grant sponsor: INTAS; contract grant number: 93-3379-Ext.

Journal of Applied Polymer Science, Vol. 73, 385-397 (1999)

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This work deals with the investigation of the structure-property relationships in mechanically blended TIPNs of a crystallizable polyurethane (CPU) and a styrene/acrylic acid copolymer (S/ AA). These mixtures will be called thermoplastic apparent IPNs, t-AIPNs, because S/AA was used in the acid form and not in the salt form. (At a next stage TIPNs will be prepared from CPU and ionomers of S/AA.) Due to the good mechanical properties of polyurethanes, IPNs of polyurethane with different kinds of polymers have been widely studied by a variety of experimental techniques and used as industrial materials.<sup>7-15</sup> In this work several compositions of the t-AIPNs were prepared from a common solvent and investigated by means of wide-angle and small-angle X-ray scattering (WAXS and SAXS), dynamical mechanical analysis (DMA), dielectric relaxation spectroscopy (DRS), thermally stimulated depolarization currents (TSDC) measurements, and several physicochemical and physicomechanical characterization measurements. In a previous publication the morphology of some of these compositions was studied by means of WAXS, SAXS, and differential scanning calorimetry, DSC.<sup>16</sup>

# **EXPERIMENTAL**

#### **Materials**

The crystallizable polyurethane (CPU) was prepared by the reaction (3 h at 75°C) of toluene diisocyanate, TDI (mixture of 2,4- and 2,6-isomers, molar ratio 65/35) with oligomeric butylene adipate glycol, BAG (molar mass 2000) in 70% solution of ethyl acetate (molar proportion of reagents 1.01/1.00, catalyst: tin dibutyl laurate, 0.2 wt %).

The styrene–acrylic acid copolymer (S/AA) was obtained by a bulk radical copolymerization (6 h at 70°C) of styrene and acrylic acid (molar ratio 75/25, initiator: benzoyl peroxide, 0.3 wt %) in nitrogen flux. Composition homogeneity was ensured by arresting the reaction at the transformation degree about 70%. The reaction product was dissolved in methanol, precipitated by water, filtered, and vacuum dried. The molar ratio of comonomers in S/AA was, approximately, 72/28 (estimated from carboxyl groups content by base titration).

Molar masses determined by means of a Du-Pont Liquid Chromatograph were as follows:  $M_w$ = 115,000,  $M_n$  = 43,000,  $M_w/M_n$  = 2.68, for CPU, and  $M_w$  = 127,000,  $M_n$  = 55,000,  $M_w/M_n$  =2.31 for S/AA. The general formula of the components is as follows:

S/AA - poly(styrene-co-acrulic acid):



CPU is physically crosslinked by means of strong bonds (hydrogen bonds and microcrystallites acting as effective crosslinking sites). S/AA may be considered as a linear thermoplastic polymer (acid form), although significant physical crosslinking is expected to occur by means of hydrogen bonding.

Films, 0.2–0.5 mm thick, of t-AIPNs of several compositions were prepared by casting from 20% solutions in dioxane onto Teflon plates and subsequent evacuation to constant weight.

#### Methods

Wide-angle and small-angle X-ray scattering (WAXS and SAXS) curves were recorded by X-ray diffractometers DRON-4-07 and KRM-1, respectively (Cu-K<sub> $\alpha$ </sub> radiation monochromatized by an Ni filter). The mean size of the crystallites  $\langle D \rangle$  was calculated by the Scherer equation from the WAXS data:<sup>17</sup>

$$D = \frac{\lambda}{\beta \cos \Theta} \tag{1}$$

where  $\lambda$  is the X-ray wavelength ( $\lambda = 1.54$ ),  $\beta$  is the breath in radians, and  $\Theta$  is the Bragg angle.

The crystal lattice spacing  $\langle d \rangle$  (i.e., the distance between reflecting planes) was calculated by the Bragg equation from the WAXS data:^{17}

$$d = \frac{n\lambda}{2\,\sin\,\Theta} \tag{2}$$

where *n* is the image order (n = 1 for polymers).

The degree of crystallinity  $\langle X \rangle$  was calculated from the WAXS data by the equation:<sup>17</sup>

$$X = \left[\frac{Q_{\rm cr}}{(Q_{\rm cr} + Q_{\rm am})}\right] \times 100\%$$
(3)

where  $Q_{\rm cr}$  is the area under the crystalline maxima and  $Q_{\rm am}$  is the area under the amorphous halo.

The mean distance between centers of nearest crystallites  $\langle L \rangle$  (the periodicity) was calculated by the Bragg equation from the SAXS data:<sup>17</sup>

$$L = \frac{n\lambda}{2\,\sin\Theta_{\rm max}} \tag{4}$$

where  $\Theta_{\rm max}$  is the angle position of diffusive maximum.

Dynamical mechanical analysis (DMA) measurements were obtained on a viscoelastometer (in the tensile test mode), with temperature scans from -100 to 140°C at a frequency of 100 Hz. The heating rate was 1°/min, the samples had dimensions of approximately  $0.5 \times 6.0 \times 0.02$  cm. The storage modulus (*E*') and the loss modulus (*E*'') were calculated from measurements of the complex modulus (*E*) and plotted versus temperature.

The deformation and strength characteristics were measured on a TIRATEST-2151 testing machine at a crosshead speed of 50 mm/min. For water uptake measurements dry samples (24 h in vacuum at 35°C) were immersed in water for 24 h at 20  $\pm$  1°C. They were then removed from water, blotted dry, and weighed. The water uptake W was expressed as the weight of the water absorbed by the sample divided by the dry weight.

The thermally stimulated depolarization currents (TSDC) method consists of measuring the thermally activated release of stored dielectric polarisation.<sup>18</sup> It allows a quick characterization of the dielectric relaxation processes in the temperature domain (from -190 to 30°C in our measurements). The method is as follows. The sample is polarized by a DC electric field and then cooled down to a sufficiently low temperature (in our case, liquid nitrogen temperature) to freeze in the polarization. The field is then switched off and the sample is warmed up at a constant rate while the depolarization current, as the dipoles relax, is measured. Thus, for each polarization mechanism an inherent current peak can be detected. The theory, the apparatus, and the procedures used to determine the parameters characterizing the dielectric behavior of a sample have been described



**Figure 1** Experimental (points) and additive (solid lines) WAXS curves for t-AIPNs of the following CPU/ (S/AA) compositions: 0/100 (1); 10/90 (2); 20/80 (3); 65/35 (4); 80/20 (5); 90/10 (6); 100/0 (7). Beginning from the second curve from the bottom, each next curve was shifted upwards by five digits.

elsewhere.<sup>18</sup> For TSDC measurements samples of 13-mm diameter with evaporated Ag electrodes on both surfaces clamped between brass electrodes were used.

Dielectric relaxation spectroscopy (DRS) measurements were carried out in the frequency range  $10^{-2}$ – $10^{6}$  Hz by means of a frequency response analyzer (Schlumberger SI 1260) supplemented by a buffer amplifier of variable gain (Chelsea Dielectric Interface) and of an LCR meter (HP 4284A) combined with the TO-19 type thermostatic oven and the SE-70 dielectric cell (Ando). The samples, 30 mm in diameter, with evaporated Ag electrodes on both surfaces, were clamped between Au-coated brass electrodes. Two-terminal complex admittance measurements were performed.<sup>19</sup>

## **RESULTS AND DISCUSSION**

#### X-ray Scattering

The WAXS curve of pure S/AA (Fig. 1, curve 1) is typical for an amorphous polymer with a broad amorphous halo around  $2\Theta = 19.2^{\circ}$ , most proba-

Composition, wt %		Degree of Crystallinity, X (%)		
CPU : S/AA	Size of Crystallites, $D$ (Å)	Experimental	Additive	Crystal Lattice Spacing (Å)
0 : 100	0	0	0	_
5:95	61	3	3	4.20
10 : 90	64	4	5	4.11
20 : 80	62	8	10	4.07
35:65	69	12	17	4.07
50 : 50	63	27	25	4.07
65:35	70	39	32	4.15
80 : 20	68	40	39	4.07
90:10	64	47	44	4.07
95:5	65	49	47	4.07
100 : 0	69	49	49	4.11

Table I The Crystalline Structure Parameters of the t-AIPNs

bly due to local spatial correlations between phenyl rings of styrene sequences.<sup>16</sup> The WAXS curve of pure CPU (Fig. 1, curve 7) is typical for a semicrystalline polymer with several sharp diffraction peaks superposed on a broad amorphous halo. The position of the diffraction peaks (at  $2\Theta$ = 17.6, 21.2, and 24.2°), the degree of crystallinity, derived from eq. (3),  $\langle X \rangle$  = 0.49 (Table I), and the mean size of microcrystals, derived from eq. (1),  $\langle D \rangle$  = 69 Å (Table I), match rather closely those of an individual semicrystalline BAG-2000.<sup>16</sup>

The diffraction maximum at  $2\Theta = 25$  min on the SAXS curve of pure CPU (Fig. 2, curve 1) is attributed to microcrystallites of BAG. The mean distance of their centers, determined by eq. (4), is  $\langle L \rangle = 210$  Å. Both the low overall intensity and the smooth shape of the SAXS curve for pure S/AA (Fig. 2, curve 7) indicate the absence of large-scale heterogeneities.

As a general remark, the experimental WAXS curves for all t-AIPNs in Figure 1 approximately match the corresponding additive curves, indicating the existence of regions with the structure of individual components for all compositions. It follows that both crystallizability of BAG in CPU and the mean size of BAG microcrystallites  $\langle D \rangle$ are little affected by S/AA.<sup>16</sup> In fact,  $\langle D \rangle$  in Table I, as well as the crystal lattice spacing  $\langle d \rangle$ , do not particularly change with composition, whereas the experimental and the theoretical (on the base of additivity) values of the degree of crystallinity  $\langle X \rangle$  are rather close to each other (further comments on that point will, however, follow). These results suggest weak affinity between CPU and S/AA, in agreement with DSC results.<sup>16</sup> They are confirmed by the results of SAXS in Figure 2: the

microheterogeneity of CPU is preserved in the t-AIPNs and the angular position of SAXS maximum [i.e., the mean distance between centers of nearest crystallites  $\langle L \rangle$ , derived from eq. (4)], does not particularly change with compositions.<sup>16</sup>

Closer inspection of Figures 1 and 2, and of Table I, however, force us to slightly modify the



**Figure 2** Experimental (solid lines) and additive (dot lines) SAXS curves for t-AIPNs of the following CPU/(S/AA) compositions: 100/0 (1); 80/20 (2); 65/35 (3); 20/80 (4); 10/90 (5); 5/95 (6); 0/100 (7).



Figure 3 Temperature dependence of storage modulus (E') for t-AIPNs of the following CPU/(S/AA) compositions: 100/0 (CPU); 90/10 (1); 80/20 (2); 65/35 (3); 50/50 (4); 20/80 (5); 10/90 (6); 7/93 (7); 5/95 (8); 0/100 (S/AA).

picture presented above. The deviation between the additive and the experimental WAXS curves in Figure 1 indicates partial miscibility of CPU and S/AA. This is probably caused by the formation of H-bonds between the functional groups of the components. DSC measurements on the same samples lead to the conclusion that a mixed microphase of fixed composition [CPU/(S/AA) = 90/10] coexists with essentially pure microphase of S/AA at all nominal compositions.<sup>16</sup> In addition to the SAXS maximum at  $2\Theta = 25$  min, we observe in Figure 2 an increase of SAXS intensity in the range of approximately  $2\Theta = 20$  min for t-AIPNs with CPU content up to 20 wt % (curves 6, 5, and 4). This result indicates an increase of structural heterogeneity in these systems.

Comparison of the experimental degree of crystallinity  $\langle X \rangle$  with the theoretical (additive) one in Table I shows that  $\langle X \rangle_{exp}$  is less than  $\langle X \rangle_{add}$  when the amorphous S/AA component prevails (S/AA > 50 wt %). For S/AA < 50 wt %  $\langle X \rangle_{exp}$  is larger than  $\langle X \rangle_{add}$ . This means that the formation of CPU crystallites in the t-AIPNs is made easier when CPU is the continuous phase, and is made more difficult when CPU is the dispersed phase.

#### **Dynamical Mechanical Analysis (DMA)**

The mechanical spectra of pure CPU in Figures 3 and 4 are typical for biphase semicrystalline polymers.<sup>20,21</sup> Two transition regions are observed,

corresponding to the glass transition of the amorphous phase ( $\alpha$  transition, at about  $-25^{\circ}$ C) and of the crystalline phase ( $\alpha_c$  transition, in the region from -5 to  $+20^{\circ}$ C). (In another terminology these relaxations in semicrystalline polymers have been called  $\beta$  and  $\alpha$ , respectively<sup>21</sup>). Compared to the calorimetric glass transition of the amorphous phase,  $T_g = -39^{\circ}$ C,<sup>16</sup> the dynamic glass transition temperature here is shifted to higher temperatures, mainly due to the higher frequency of DMA measurements (100 Hz). We will further comment on that point later. In the region of temperatures above 50°C melting of CPU begins, in agreement with the results of DSC measurements.<sup>16</sup>

The mechanical spectra of S/AA show the dynamic glass transition at  $80^{\circ}C^{20}$  and a further structure [a shoulder in the E''(T) plot] at about 70°C, which is indicative of limited heterogeneity. The heterogeneity is assumed to be caused by microsegregation of acrylic acid component due to the formation of H-bonds between —COOH groups,<sup>22</sup> in agreement with the results of IR measurements.<sup>23</sup>



**Figure 4** Temperature dependence of the loss modulus (*E''*) for t-AIPNs of the following CPU/(S/AA) compositions: **a**—100/0 (CPU); 90/10 (1); 80/20 (2); 65/35 (3); 50/50 (4); **b**—20/80 (5); 10/90 (6); 7/93 (7); 5/95 (8); 0/100 (S/AA).

As a general remark, the viscoelastic properties of the t-AIPNs with CPU content 50% or more (Figs. 3 and 4, curves 1-4) are determined by CPU, whereas those of t-AIPNs with less than 50% CPU (Figs. 3, and 4, curves 5-8) are determined by S/AA. This result was expected on the basis of phase continuity deduced from X-ray data. Closer inspection of the spectra shows a significant influence of small content of CPU on the viscoelastic properties of S/AA. The shoulder on E''(T) for pure S/AA at about 70°C (Fig. 4) takes the form of a peak for CPU contents of 5, 7, and 10% (Fig. 4, curves 6–8), which changes position and height, depending on CPU content. The morphological counterpart of these changes is the increased SAXS intensity in the range of approximately  $2\Theta = 20$  min for t-APINs with CPU content up to 20% (Fig. 2, curves 4-6). We consider they are caused by the formation of the networks of intra- and intermolecular H-bonding, which results in formation of a double-phase continuity. The intermolecular H-bonding promotes the improvement of the compatibility of the components in the t-AIPNs. However, the degree of segregation of the CPU and the S/AA microphases simultaneously increases, as AA and BAG move out of the S/AA and the CPU phases, respectively, because their functional groups take part in intermolecular H-bonding. Intramolecular H-bonding promotes a deepening of the microphase separation of the t-AIPNs components.

On further increasing the CPU content to 20% (Figs. 3 and 4 curve 5) two peaks appear in the E''(T) spectra, at about 10 and 80°C, respectively. In addition, the peak on the low-temperature side of the 80°C peak for the samples with 5, 7, and 10% CPU (Fig. 4, curves 8–6) becomes again a shoulder (at about 65°C). The later suggests that the microphase structure of the S/AA component returns to the initial level of heterogeneity. The E''(T) peak at about 80°C due to the dynamic glass transition of the S/AA-rich component does not change position with CPU content (Figs. 3 and 4, curves 5-8), indicating that the glass transition of this component is independent of CPU content. This point could not be studied by DSC, due to melting events of CPU dominating in this temperature region. In agreement with the WAXS results, these results indicate weak affinity between CPU and S/AA.<sup>12</sup> The strong E''(T) peak at about 10°C for the sample with 20% CPU (Fig. 4, curve 5) is difficult, at this stage, to bring into connection with any specific morphological characteristic on the base of X-ray scattering and DSC.<sup>16</sup> It may be indicative of extensive interfacial layers of t-AIPNs at this composition. As pointed out by Mai and Johari, additional relaxations may appear in IPNs due to different types of local regions of mobility.<sup>7</sup>

The increase of CPU content to 50% (Figs. 3 and 4, curve 4) leads to phase inversion, as indicated by the E''(T) peak of the dynamic glass transition of the CPU-rich phase at about  $-25^{\circ}$ C. For samples with more than 50% CPU (Figs. 3 and 4, curves 1-3) there are significant changes in the viscoelastic behavior compared to pure CPU. The dynamic glass transition temperature of the CPU-rich phase shifts to lower (curve 1) and then to higher temperatures (curve 2). This behavior resemples that of polyurethane in polyurethanepolystyrene IPNs,<sup>8</sup> and in poly(urethane-epoxy)/ allyl novolac resin IPNs.<sup>12</sup> The shift to lower temperatures may be due to increased free volume with S/AA addition.<sup>8</sup> This point will be studied in more detail by TSDC. For the sample with 35% S/AA the glass transition peak of the amorphous phase degenerates into a shoulder (curve 3). For the t-AIPNs with 10, 20, and 35% S/AA a E''(T)peak appears in the temperature region -15 to 10°C. This is close to the region of the  $\alpha_c$  transition in the crystalline CPU regions. It cannot be attributed, however, to an increase of the degree of CPU crystallinity, in agreement with the results in Table I. Rather, the peak should be due to the existence of extensive interfacial layers, consistent with the picture of a mixed microphase of fixed composition [CPU/(S/AA) = 90/10] concluded from DSC measurements.<sup>16</sup> This point will be further studied by TSDC and DRS.

The main DMA relaxations of CPU and S/AA in some blends present peaks in E'', which are higher than in pure polymers [see, e.g., curves 1 and 2 in Fig. 4(a)]. Obviously, the formation of H-bonds between COOH-groups of the S/AA component and urethane and ester groups of the CPU component leads to an increase of microsegregation of amorphous and crystalline parts the CPU component, as it is known that the amorphous part of semicrystalline CPU predominantly takes part in H-bond formation. Finally, the crystallites moves partly out of the CPU amorphous phase near the glass transition temperature of the CPU component. As it is shown below, this fact leads to changes in the t-AIPNs microphase structure and in their physicomechanical properties, particularly to increase the density and to decrease the water uptake and the elasticity modulus on addition of small amounts of S/AA to CPU (Figs. 5 and 6).



**Figure 5** Experimental (points) and additive (dot lines) concentration dependence of density,  $\rho(1)$ , and of water uptake, W(2), of the t-AIPNs.

In conclusion, DMA shows that the t-AIPNs can be considered as multiphase systems, having at least two amorphous and one crystalline phases and regions on mixed compositions. Their mechanical properties are determined by the heterogeneity of the individual components, as well as by the heterogeneity caused by the thermodynamic incompatibility of these components. The degree of incompatibility is determined, to a large extent, by the ratio of intra- and intermolecular H-bonds between the functional groups of CPU and S/AA. For t-AIPNs with CPU content up to 10%, CPU–S/AA interactions mainly take place, whereas at higher CPU contents CPU–CPU and S/AA–S/AA interactions begin to dominate.

#### **Physicomechanical Characterization**

The density  $\rho$  in Figure 5 changes nonadditevely with the composition. The composition regions of lower and higher values than the additive ones coincide with the regions of a lower and higher degree of crystallinity than the additive ones in Table I. The water uptake W in Figure 5 shows the opposite behavior, with maxima and minima, with respect to the additive values, at low and high CPU contents, respectively. This behavior is expected on the basis of increased sorption of water for samples with higher values of free volume.<sup>24</sup> We have commented on that point in previously, in connection with the high values of E''in some blends in Figure 4.

The mechanical properties of the t-AIPNs, elasticity modulus E, and tensile strength  $\sigma$ , change nonadditevely with composition (Fig. 6). The extrema are observed in the regions of small

Table IIPhysicomechanical Properties of thet-AIPNs

Composition (wt %)		
CPU : S/AA		Elongation at Break, $\sigma_r$ (%)
0 : 100	*	1
5:95	*	1
10:90	*	1
20 : 80	*	1
35:65	*	1
50 : 50	10.9	12
65:35	14.3	89
80:20	14.4	210
90:10	15.8	1040
95:5	14.5	1000
100 : 0	13.5	1010

\* The samples having a brittle character fracture.

contents (10-15%) of CPU or S/AA in the t-AIPNs, i.e., in the regions where phase mixing effects are observed in X-ray scattering and DMA measurements (compare to this point our comments in the previous section). For example, for t-AIPNs with 5–10% S/AA the tensile strength is by about 20% higher than for pure CPU. From the point of view of technological applications we see here, in principle, the possibility of obtaining composites with the desired properties by changing the composition and the method of preparation. Flow limit and elongation at break of the t-IPNs are listed in Table II.



**Figure 6** Experimental (points) and additive (dot lines) concentration dependence of the elasticity modulus, E (1), and tensile strength,  $\sigma$  (2), of the t-AIPNs.



**Figure 7** TSDC thermogram measured on a CPU sample (full line) and thermal sampling responses in the central region of the peaks (dotted line, details in text).

# Thermally Stimulated Depolarization Currents (TSDC) Measurements

Figure 7 shows a typical TSDC thermogram for pure CPU. Four peaks are observed at -143, -103, -37, and  $-6^{\circ}$ C. Following the results of TSDC studies on polyurethanes,<sup>19,25</sup> and in consistency with those of other relaxation spectroscopy techniques,<sup>20,26</sup> the TSDC peaks are designed as  $\gamma$ ,  $\beta$ ,  $\alpha$ , and MWS (Maxwell-Wagner-Sillars) peaks in the order of increasing temperature. By using the thermal sampling (TS) technique the apparent activation energy E and the preexponential factor  $\tau_o$  in the Arrhenius equation,

$$\tau (T) = \tau_o \exp\left(\frac{E}{kT}\right) \tag{5}$$

in the central region of the  $\gamma$ ,  $\beta$ , and  $\alpha$  peaks were determined. In eq. (5),  $\tau$  is the dielectric relaxation time and k is the Boltzmann's constant. The TS technique consists of "sampling" the relaxation process within a narrow temperature range by polarizing at a temperature  $T_p$  and depolarizing at a temperature  $T_d$ , a few degrees lower than  $T_p$ .<sup>18,27</sup> Representative TS responses are shown in Figure 7, the values of E and  $\tau_o$  are listed in Table III. E was calculated by using the expression<sup>27</sup>

$$E = \frac{T_1 T_2}{4738(T_2 - T_1)} \tag{6}$$

where E is in eV and  $T_1$  and  $T_2$  denote the temperatures at which the current drops to half its

Table III Apparent Activation Energy E and Preexponential Factor  $\tau_0$  in the Arrhenius Equation for the Secondary Relaxations in CPU and in S/AA and for the  $\alpha$ -Relaxation in CPU

Relaxation	E (eV)	$\tau_0~(\mathrm{s})$
γ CPU (TSDC)	0.30	$2.5 imes10^{-10}$
$\beta$ CPU (TSDC)	0.46	$3.1 imes10^{-12}$
$\beta$ S/AA (TSDC)	0.32	$1.5 imes10^{-9}$
β S/AA (DRS)	0.40	$2.4 imes10^{-14}$
$\alpha$ CPU (TSDC)	1.40	$1.6 imes10^{-28}$

maximum value on the low-temperature and high-temperature sides, respectively.  $\tau_o$  was then calculated using the following equation<sup>27</sup>

$$\tau_o = \frac{kT_m^2}{bE} \exp\left(-\frac{E}{kT_m}\right) \tag{7}$$

where  $T_m$  is the temperature of current maximum (peak temperature) of the TS response, and *b* is the heating rate.

The  $\gamma$  peak has also been observed in mechanical relaxation spectroscopy on polyurethanes (at about  $-140^{\circ}$ C at  $1 \text{ Hz}^{20,26}$ ). It has been associated with crankshaft motions of the  $(CH_2)_n$  sequences. The TSDC  $\beta$  peak has been assigned to an association of absorbed water molecules with the polar carbonyl groups,<sup>25</sup> similar to the mechanical  $\beta$ peak, which is located at higher temperatures.<sup>8,20,26</sup>

The TSDC  $\alpha$  peak in polyurethanes has been shown to correspond to the main  $(\alpha)$  relaxation at the glass transition of the amorphous soft segment phase.<sup>25</sup> This is confirmed here by the high value of the apparent activation energy E and, correspondingly, the unrealistically small value of  $\tau_o$  in Table III. The peak temperature  $T_m$  of this peak is, in general, a good measure of the calorimetric glass transition  $T_g$  for two reasons, corresponding to similar time and spatial scales, respectively, of the motions measured by the two techniques. First,  $T_g$  can be defined as the temperature at which the dielectric relaxation time reaches 100s,<sup>28</sup> i.e., the range of  $\tau$  values where a TSDC peak reaches its maximum.<sup>18</sup> Second, both DRS and DSC have been shown to measure the same characteristic relaxation time over their common frequency range.<sup>29,30</sup> This is confirmed here by the similar values of  $T_g = -39^{\circ}C^{16}$  and  $T_m = -37^{\circ}$ C (Fig. 7) for CPU.

The MWS peak in polyurethanes has been related to ionic polarization of the Maxwell-Wag-



**Figure 8** TSDC thermogram measured on a S/AA sample (full line) and thermal sampling responses in the central region of the peaks (dotted line, details in text).

ner-Sillars type (interfacial polarization) in the diffuse interphase boundary region between hard and soft segment phase.<sup>25</sup> This peak measures glass transition properties and, more specifically, reflects changes of the morphology at glass transition. In the case of crystallizable polyurethanes, like CPU, additional interphases exist between crystalline and amorphous regions. The MWS peak occurs in the temperature region of the mechanical  $\alpha_c$  relaxation (Fig. 4). It is not clear at this stage as to whether the two processes are linked to each other. It is interesting to note, however, that a TSDC peak in semicrystalline poly(ethylene terephthalate) at temperatures higher than the  $\alpha$  peak (peak  $\alpha_c$ ) has been ascribed to a polar relaxation associated with the crystalline phase.<sup>31</sup>

Figure 8 shows a representative TSDC thermogram of the S/AA copolymer together with a TS response in the central region of the low-temperature peak at -133°C. The activation characteristics, E and  $\tau_{\alpha}$ , of this TS response are listed in Table III. We assign the -133°C TSDC peak to the rotation of the —COOH side group about the C—C bond, which links it to the main chain, i.e., to the  $\beta$  relaxation of the acrylic units. In consistency with this interpretation, the TSDC peak is broad [the same also being true for the  $\gamma$  and  $\beta$ peaks in CPU (Fig. 7)], as expected for secondary relaxations.<sup>20,26</sup> For comparison, dielectric measurements on random copolymers of methyl acrylate and styrene show a  $\beta$  relaxation with E = 0.41 eV,  $\tau_o = 7.4 \times 10^{-16}$  s (unaffected by the introduction of styrene units).<sup>20</sup> Extrapolation of the Arrhenius plot of this relaxation to  $\tau = 100$  s (the characteristic relaxation time for TSDC

peaks) gives  $T_m = -148$ °C, in rough agreement with  $T_m = -133$ °C in Figure 8 (bearing in mind that the rotating groups are different, —COOH in S/AA and —COOCH<sub>3</sub> in the copolymers of methyl acrylate and styrene). The complex TSDC band in the temperature region between -40 and 0°C could not be identified with a dipolar relaxation. This is probably due to conductivity effects and interfacial (MWS) polarization, consistent with the microheterogeneous nature of S/AA concluded from DMA (Fig. 4).

In the following we discuss the modifications in the characteristics of the TSDC peaks of pure CPU and pure S/AA induced by blending. The secondary  $\gamma$  and  $\beta$  relaxations of CPU shift to lower temperatures by addition of 10 wt % S/AA (the  $\gamma$  peak from -143 to -148 °C, and the  $\beta$  peak from -103 to -109°C), and do not practically change position by further addition of S/AA. These changes cannot be explained by simple overlapping with the  $\beta$  peak of S/AA at  $-133^{\circ}$ C. neither the direction nor the magnitude of the shifts. Interestingly, these changes in the properties of CPU occur in the region of compositions where the density is larger than the additive one showing a maximum (Fig. 5) and the degree of crystallinity is larger than the additive one (Table I). The changes are assigned to interactions between CPU and S/AA through intermolecular Hbonding. The limit of changes of about 10 wt % S/AA is in agreement with the conclusion from DSC results,<sup>16</sup> that upon addition of S/AA to CPU a mixed microphase of fixed composition [CPU/(S/ AA) = 90/10] is formed in coexistence with an essentially pure microphase of the excess of S/AA. We also note that DMA showed significant changes in the viscoelastic behavior of the t-IPNs compared to CPU upon addition of small amounts of S/AA (Figs. 3 and 4). Little attention has been paid in the literature to the changes in the secondary relaxations of polyurethanes induced by blending in IPNs. In polyurethanes-polystyrene IPNs the mechanical  $\beta$  relaxation of polyurethanes was found not to change its temperature on blending or to slightly shift to lower temperatures on crystallization of the soft-segment phase.8

The secondary  $\beta$  relaxation of S/AA does not practically change its temperature position on addition of CPU to S/AA. Increasingly, the same was observed also in DMA for the E''(T) peak of the dynamic glass transition of S/AA.

The TSDC  $\alpha$  peak associated with the glass transition of the amorphous CPU phase is located at  $T_m = -36 \pm 2^{\circ}$ C, independent of composition



**Figure 9** Log-log plot of  $\varepsilon'$  versus frequency f at  $T = 22^{\circ}$ C for t-AIPNs of the following CPU/(S/AA) compositions: 100/0 ( $\Box$ ); 90/10 ( $\bigcirc$ ); 80/20 ( $\triangle$ ); 50/50 (\*); 20/80 ( $\blacktriangle$ ); 10/90 ( $\textcircled{\bullet}$ ); 5/95 ( $\bigstar$ ); 0/100 ( $\blacksquare$ ).

at least up to 50 wt % S/AA. [For higher S/AA contents the TSDC  $\alpha$  peak becomes comparable in magnitude to the S/AA space charge polarization peak in the temperature region between -40 and  $0^{\circ}$ C (Fig. 8), and  $T_m$  cannot be determined unequivocally.] The same is also true for the peak temperature  $T_m$  of the MWS peak. For both peaks the normalized magnitude  $I_n$ , defined as the current maximum normalized to the same polarizing field and the same heating rate, decreases more than additively with degreasing CPU content.  $I_n$ is a measure of the number of relaxing units (dipoles, charges) contributing to the TSDC peak. These results show that the glass transition temperature of the amorphous CPU soft-segment phase as determined by TSDC does not change with composition, suggesting poor affinity between CPU and S/AA. Moreover, the independence of  $T_m$  of the MWS peak from composition suggests that the morphology of the t-IPNs with respect to CPU does not change much with composition. These results provide further support for the conclusion drawn from SAXS measurements (Fig. 2) that the microheterogeneity of CPU is preserved in the t-AIPNs.

The three techniques used here and in our previous article<sup>16</sup> to determine the glass transition temperature of CPU in the t-IPNs, DSC, DMA, and TSDC, show, in agreement with each other, negligible effects on  $T_g$  of CPU on addition of S/AA. Small differences should, however, be pointed out:  $T_g$  does not change with composition in TSDC; it shifts slightly (by about 5°C) to lower and then to higher temperatures upon addition of

S/AA in DMA; it is slightly (by about 5°C) lower in CPU than in the t-IPNs in DSC. These apparent discrepancies may be attributed to differences in the spatial scale of local heterogeneity probed by the different techniques,<sup>32</sup> in particular, in complex systems like IPNs.<sup>7-12</sup>

#### **Dielectric Relaxation Spectroscopy (DRS)**

The real and imaginary parts of  $\varepsilon'$  and  $\varepsilon''$  of dielectric permittivity are shown in log–log plots in Figures 9 and 10, respectively, for the pure CPU and S/AA components and for several t-IPNs at room temperature,  $T = 22^{\circ}$ C. At this temperature CPU is in the rubbery stage ( $T_g$  at about  $-40^{\circ}$ C), whereas S/AA is in the glassy state ( $T_g$  at about  $80^{\circ}$ C). This explains the overal higher values af  $\varepsilon'$ and  $\varepsilon''$  for CPU compared to S/AA.

For CPU we observe in Figures 9 and 10 a weak and broad dispersion centered at 10 kHz, whereas the onset to another dispersion is indicated at higher frequencies. Consistent with the results of TSDC measurements and of DRS measurements at variable temperature, the dispersion at 10 kHz should be due to the  $\alpha$  relaxation associated with the glass transition of the amorphous CPU phase, whereas the secondary  $\gamma$  and  $\beta$ relaxations are located at higher frequencies. The  $\alpha$  relaxation is very weak and very broad due to the high degree of crystallinity<sup>21</sup> of CPU (49%, Table I). This was not quantitatively studied further. At frequencies lower than 10–100 Hz we observe high values of both  $\varepsilon'$  and  $\varepsilon''$ . These do not correspond to bulk properties, but are rather due to conductivity effects and space charge polarization.<sup>33</sup>



**Figure 10** Log-log plot of  $\varepsilon''$  versus frequency f at  $T = 22^{\circ}$ C for t-AIPNs of the following CPU/(S/AA) compositions: 100/0 ( $\Box$ ); 90/10 ( $\bigcirc$ ); 80/20 ( $\triangle$ ); 50/50 (\*); 20/80 ( $\blacktriangle$ ); 10/90 ( $\bigcirc$ ); 5/95 ( $\diamondsuit$ ); 0/100 ( $\blacksquare$ ).



**Figure 11** Semilogarithmic plot of  $\varepsilon''$  versus frequency f for the  $\beta$  relaxation in S/AA at several temperatures:  $-10^{\circ}$ C ( $\blacksquare$ );  $-20^{\circ}$ C ( $\bullet$ );  $-30^{\circ}$ C ( $\blacktriangle$ );  $-40^{\circ}$ C ( $\blacktriangledown$ );  $-50^{\circ}$ C ( $\blacklozenge$ );  $-60^{\circ}$ C ( $\boxdot$ ). The lines are HN fittings [eq. (8)] to the experimental data.

For S/AA we observe a relaxation at 100 kHz to 1 MHz, and a weak one centered at about 10 Hz. The high-frequency relaxation should be the secondary  $\beta$  relaxation, giving rise to the TSDC peak at -133°C (Fig. 8). To further clarify this point, the high-frequency relaxation was measured at variable lower temperatures. Figure 11 shows log–log  $\varepsilon''(f)$  plots for this relaxation at temperatures between -10 and -60°C. The two-shape parameter Havriliak-Negami expression<sup>34</sup> was fitted to the data

$$\varepsilon^*(f) - \varepsilon_{\infty} = \frac{\Delta \varepsilon}{\left[1 + \left(\frac{i^f}{f_o}\right)^{1-a}\right]^{\beta}}$$
(8)

In this expression  $\varepsilon^*$  is the complex dielectric permittivity,  $\varepsilon^* = \varepsilon' - i\varepsilon'' f$  the frequency,  $\Delta \varepsilon$  the dielectric strength,  $\varepsilon_{\infty} = \varepsilon'(f)$  at  $f >> f_o$ , a  $(0 \le a < 1)$  and  $\beta (0 < \beta \le 1)$  the shape parameters,  $f_o$  a constant and  $i = \sqrt{-1}$ . The shape parameters a and  $\beta$  depend on temperature. The dispersion is broad, as expected for secondary relaxations,<sup>20,26</sup> and becomes broader with decreasing temperature.

The Arrhenius plot (semilogarithmic plot of the frequency of maximum dielectric losses  $\varepsilon''$ ,  $f_{\rm max}$ , against reciprocal temperature) for the  $\beta$  relaxation of S/AA is shown in Figure 12. The apparent activation energy E is determined to E = 0.40 eV,  $\tau_o$  in the Arrhenius equation to  $2.4 \times 10^{-14}$  s. For comparison, E = 0.32 eV and  $\tau_o = 1.5 \times 10^{-9}$  s from TSDC measurements on the same samples

(Table III), and E = 0.41 eV,  $\tau_o = 7.4 \times 10^{-16} \text{ s}$ from dielectric measurements on random copolymers of methyl acrylate and styrene,<sup>20</sup> suggesting the same mechanism for these relaxations, namely rotation of the —COOH (the —COOCH<sub>3</sub>, respectively) side group about the C—C bond which links it to the main chain.

The weak relaxation in S/AA centered at about 10 Hz (Fig.10) should be the AC counterpart of the complex TSDC band in the temperature region between -40 and  $0^{\circ}$ C (Fig. 8), assigned to conductivity effects and interfacial (MWS) polarization. Support for this interpretation is coming from the DRS results obtained with the t-IPNs. Upon addition of a small amount of CPU to S/AA the relaxation increases significantly in magnitude (and shifts slightly to lower frequencies; Fig. 10). The increase in magnitude is due to the higher electrical conductivity of CPU compared to S/AA, and the increase in heterogeneity with addition of CPU, in agreement with and in support of, the results of SAXS and of DMA. The shift to lower frequencies is related with the inner topology of conducting paths, a point that cannot be further quantitatively studied here. The relaxation is observed for samples with CPU content up to 50 wt %; at higher CPU contents it is masked by DC conductivity.

On the basis of the results in Figures 9 and 10, the t-IPNs can be classified into two groups. Samples with CPU contents up to 20% exhibit the overall behavior of S/AA. The second group contains samples with CPU contents equal to and larger than 50%, the typical overall behavior here being that of CPU. This classification is in agreement with the DMA results (Figs. 3 and 4). We note that significant changes in the overall values of both  $\varepsilon'$ 



**Figure 12** Arrhenius plot for the  $\beta$  relaxation in S/AA.

and  $\varepsilon''$  of S/AA are observed in addition to small amounts of CPU (5%). In the second group of samples  $\varepsilon'$  at high frequencies is lower for CPU than for the t-IPNs, i.e., the t-IPNs show higher  $\varepsilon'$  values than the components, in disagreement with any mixture formula. This result can be understood on the basis of the DMA and the DSA results on the same samples and the conclusions therefrom on the existence of a mixed microphase.

# **CONCLUSIONS**

Structure-property relationships in thermoplastic apparent interpenetrating polymer networks (t-AIPNs), prepared by mechanical mixing in a common solvent of crystallizable polyurethane (CPU) and styrene/acrylic acid random copolymer (S/AA), were investigated by means of wide-angle and small-angle X-ray scattering (WAXS and SAXS), dynamic mechanical analysis (DMA), thermally stimulated depolarization currents (TSDC) techniques, dielectric relaxation spectroscopy (DRS), and density, water uptake, deformation, and strength characteristics measurements. The main results, including those of differential scanning calorimetry (DSC) on the same samples,<sup>16</sup> can be summarized as follows.

- 1. The techniques used for detecting molecular mobility (DSC, DMA, TSDC, DRS) probe, in general, different spatial scales of local heterogeneity—a point to be taken into account in comparing results obtained by different techniques.
- 2. In the semicrystalline CPU (WAXS, SAXS) the mechanical  $\alpha$  and  $\alpha_c$  relaxations (DMA), corresponding to the glass transition of the amorphous and of the crystalline phases, respectively, and the dielectric secondary  $\gamma$  and  $\beta$  relaxations, primary  $\alpha$  relaxation and interfacial Maxwell-Wagner-Sillars (MWS) relaxation (TSDC, DRS) were characterized. In amorphous S/AA, characterized by limited heterogeneity (SAXS, DMA), the primary  $\alpha$  relaxation, as well as the interfacial MWS relaxation (TSDC, DRS) were studied.
- 3. In the t-AIPNs the two components show weak affinity to each other: the crystallisability of CPU is little affected by S/AA (WAXS, DSC), the microheterogeneity of CPU is preserved in the t-AIPNs (SAXS),  $T_g$  of S/AA is unaffected in the t-AIPNs (DMA),  $T_g$  of CPU is little affected by addition of

S/AA (DCS, DMA, TSDC), the  $\beta$  relaxation of S/AA is unaffected in the t-AIPNs (TSDC), the MWS relaxation of CPU is preserved in t-AIPNs (TSDC).

- 4. The t-AIPNs can be classified into two groups: t-AIPNs with CPU content  $\geq 50\%$  showing essentially the behavior of CPU and t-AIPNs with CPU content  $\leq 50\%$  showing essentially the behavior of S/AA (WAXS, DMA, DRS).
- 5. Deviations from additivity in WAXS, density, water uptake, elasticity modulus, and tensile strength measurements indicate interactions between the two components, caused by the formation of H-bonds between the functional groups, and resulting in partial miscibility.
- 6. Significant effects are observed on addition of small amounts of CPU to S/AA: increase of structural heterogeneity of S/AA (SAXS, TSDC), changes in the viscoelsatic properties of S/AA (DMA), significant changes in the values of  $\varepsilon'$  and  $\varepsilon''$  of S/AA (DRS). These results suggest that for t-AIPNs with CPU content up to10% CPU-S/AA interactions mainly take place, whereas at higher CPU contents CPU-CPU and S/AA-S/AA interactions begin to dominate.
- 7. For samples with more than 50% CPU significant changes in the viscoelastic behavior are observed compared to pure CPU (DMA); the secondary  $\gamma$  and  $\beta$  relaxations of CPU shift to lower temperatures compared to pure CPU (TSDC); the  $\varepsilon'$  values at high frequencies are larger than those of pure CPU (DRS). These changes can be explained by the existence of a mixed microphase [with a fixed composition of CPU/(S/AA): 90/ 10, as suggested by DSC<sup>16</sup>].

These results are explained by the formation of the networks of inter- and intramolecular Hbonding, which results in formation of a doublephase continuity. The intermolecular H-bonding between the functional groups of the components promotes the improvement of the compatibility of the components in the t-AIPNs. On the other hand, the degree of segregation of the CPU and the S/AA microphases simultaneously increases, as AA and BAG move out of the S/AA and the CPU phases, respectively, because their functional groups take part in intermolecular H-bonding. Intramolecular H-bonding promotes a deepening of the microphase separation of the t-AIPNs components. This work was supported by the INTAS project 93-3379-Ext.

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