Effect of Specific Interactions on Structure-Property Relationships of Thermoplastic IPNs Based on Polyurethane and Styrene-*co*-Acrylic Acid Ionomers

Olga Grigoryeva,[1] *Olga Slisenko,*[*1] *Alexander Bismarck,*[2] *Lyudmila Sergeeva*[1]

Summary: The structure-property relationships of thermoplastic polymer blends based on poly(ether-urethane) ionomer (PEUI) and K^+-Ion containing styrene-acrylic acid random copolymer (S-*co*-AA(K)) have been investigated by different methods. Convergence of the glass transition temperature values of the PEUI and the S-*co*-AA(K) components in the blends studied and improvement of end-use properties have been found.

Keywords: compatibility; interpenetrating polymer networks; polyurethane

Introduction

The study of polymer blends and alloys represents one of the important fields in polymer science today.[1,2] Polymer materials with desired physical-chemical properties can be prepared simply by blending two or more polymers together instead of synthesis of new polymer. However, most of polymer pairs are generally incompatible, since the entropy of mixing for polymers is very small and enthalpy is generally positive unless favourable interactions are involved between the components. One of the most effective ways to compatibilize two immiscible polymers is through the interactions between ionic groups, which can be chemically incorporated to one or both polymers.[3–6] In some cases, miscibility is reached due to proton transfer from an acidic site of one polymer to a basic site of the other one, leading to ion–ion interactions. In others, the transfer of a metal cation from an ionomer to a polar polymer as a result of ion–dipole interactions has been involved. Among the various polymer pairs compatibilized by use of ionic interactions, polymer blends based on polyurethanes have received special attention due to their potential applications and academic interest.[7–9] Polymer blends of this type can be classified as thermoplastic interpenetrating polymer networks (TIPNs), which are usually formed from two or more physically crosslinked polymers, such as block-copolymers, semicrystalline or ion-containing polymers, where the physical bonds play the role of effective crosslink sites.[10] It is well known that polymer blends of the TIPNs type exhibit lower degree of phase separation of the components and improved physical-chemical properties (flexibility, tensile and impact strengths, chemical resistance etc.) compared to traditional polymer blends.[1,2,10–12]

The objective of the present work is to contribute to the investigation of structure-property relationships of new polymer blends of the TIPNs type based on sulfonated poly(ether-urethane) ionomer (PEUI) and K^+-containing styrene-acrylic acid copolymer (S-*co*-AA(K)) by using different methods, such as DSC, DMTA and tensile testing.

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[1] Institute of Macromolecular Compounds of the National Academy of Sciences of Ukraine, Kharkivske shose 48, 02160 Kyiv, Ukraine
E-mail: olgaslisenko@rambler.ru

[2] Chemical Engineering, Polymer & Composite Engineering Group, Imperial College London, 526/ACEx, Prince Consort Road, South Kensingtouk

Experimental Part

Materials

K^+–containing styrene-acrylic acid random copolymer, S-*co*-AA(K), was synthesized by a bulk radical styrene/acrylic acid copolymerization (component ratio S/AA = 55/45 wt.%), followed by partial neutralization of carboxylic groups by potassium hydroxide, the degree of neutralization being ~0.6. Macrodiisocyanate, MDI, was synthesized from diethylene glycol (DEG), polyoxypropylene glycol (POPG, molar mass ~1000) and toluene diisocyanate (TDI, mixture of 2,4- and 2,6-isomers with a ratio of 65/35), the component molar ratio being DEG/POPG/TDI = 1/2/6. PEUI was then obtained by sulfonation of MDI with H_2SO_4 (~3 mol.%) and complete neutralization of sulfuric groups by thriethylamine, followed by extension by hydrazine hydrate. Chemical structures of the individual PEUI and S-*co*-AA(K) are represented in the Scheme 1 below.

The films of new PEUI/S-*co*-AA(K) and PEUI/S-*co*-AA blends of several compositions were prepared using a solution technique.

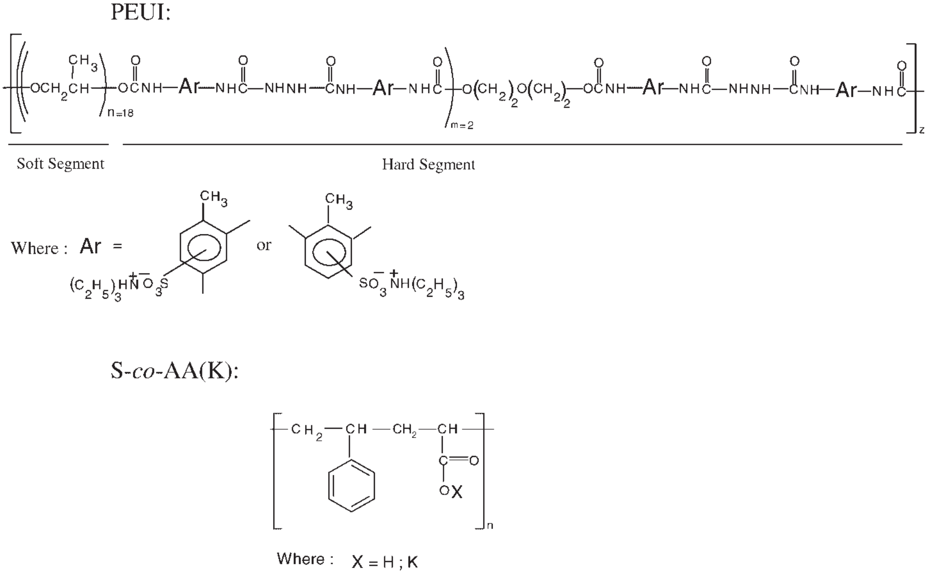
Characterization Techniques

FTIR measurements were carried out using a Bruker Tensor 27 DLATGS 4000–450 cm^{-1} using Attenuated Total Reflection (ATR) mode. For each spectrum 32 consecutive scans with resolution of a 4 cm^{-1} were averaged. Far-infrared spectra (70–470 cm^{-1}) were measured with spectrometer Hitachi far-infrared spectrophotometer (model FIS-21).

Differential Scanning Calorimetry (DSC) was carried out using a Perkin Elmer Pyris 6 DSC under nitrogen flux in the temperature range from −100 to 240 °C with a programmed heating rate of 20 °C/min. Sample weight was 8–12 mg. All DSC curves are baseline subtracted and normalized to 1 mg of sample. The first heating scan was taken for data analysis.

Dynamic Mechanical Thermal Analysis (DMTA) measurements were performed with a Rheometric Scientific Dynamic Mechanical Thermal Analyzer (MK II). The samples were measured in the bending mode at a fixed frequency of 10 Hz from −100 to 200 °C using a heating ramp of 4 °C/min.

Tensile testing was performed on dumbbell shaped specimens at ambient tempera-



Scheme 1.
Chemical structure of individual PEUI and S-*co*-AA(K).

ture at an extension rate of 10 mm/min using an Instron-1122 type universal testing machine.

Results and Discussion

In Figure 1 FTIR-spectra of individual PEUI, S-*co*-AA(K) and PEUI/S-*co*-AA(K) TIPNs the stretching vibrations of free and associated by hydrogen bonds OH, NH, and C=O groups are presented.

The analysis of the PEUI FTIR-spectrum allows us to conclude, that PEUI has the developed network of physical bonds, thus practically all NH-groups participate in the formation of hydrogen bonds of various length and force. This fact is evidenced by the position (a maximum at 3292 cm^{-1}) and form (superposition of bands in the range 3400–3100 cm^{-1}) of the υNH_{ass} band. Wide non-intensive absorption band at 3700–3400 cm^{-1} is obviously caused by the presence of moisture absorbed by the PEUI during formation of ionomeric form. Low-frequency asymmetry of a complex band $\nu C{=}O_{ass}$ (see Figure 1) testifies that urethane groups of PEUI form significant amount of strong H-bonds (self-associates of urethane groups), and the bigger associates, so- called, inter-urethane associates, are formed too. This fact is confirmed by the presence of a new absorption band $\nu C{=}O_{ass}$ at 1726 cm^{-1}. C=O and NH groups also form self-associates that is confirmed by the appearance of new bands attributed to the stretching vibrations of associated C=O groups at 1640–1655 cm^{-1}.

The analysis of a complex absorption band $\nu C{=}O$ (Figure 1) of individual S-*co*-AA(K) has shown a shift of $\nu C{=}\ O_{ass(D)}$ to high-frequency region (up to 1709 cm^{-1}) (in comparison with S-*co*-AA) due to destruction of hydrogen bonds in dimeric COOH-groups. Comparison of the integral intensities of the absorption bands $\nu C{=}O_{ass(D)}$, $\nu C{=}O_{ass}$ and $\nu C{=}O_{free}$ has shown that about 60% of COOH-groups participate in the formation of dimer type associates, ~30% of COOH-groups form the more complex associates (trimer, tetramer, etc.) and ~10% of COOH-groups are free (i.e. do not participate in H-bonding).

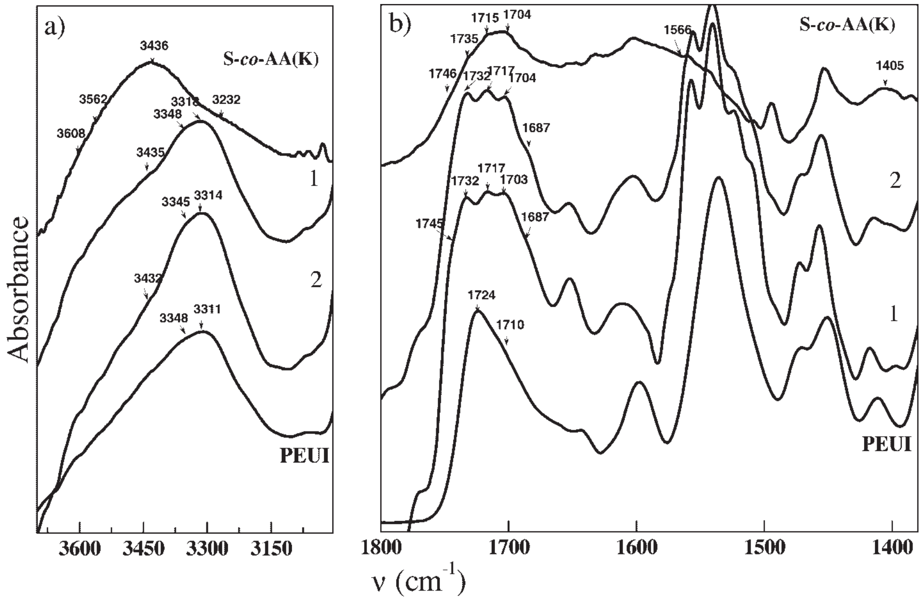


Figure 1.

FTIR spectra of a) NH and OH groups (3700–3000 cm^{-1}), b) C=O and COO^--groups (1800–1350 cm^{-1}) of individual PEUI, S-*co*-AA(K) and PEUI/S-*co*-AA(K) TIPNs with different PEUI content (wt.%): (1) = 90, (2) = 70.

In other words the presence of ionic groups in S-*co*-AA(K) prohibited the formation of dimeric associates. Moreover, a formation of larger associates also occurs by means of longer and weaker hydrogen bonds.[13]

The occurrence of new bands in the spectrum of S-*co*-AA(K) at 1550 and 1568 cm^{-1} attributed to the stretching vibrations of COO^- groups has been observed. Rufino with co-authors have shown[14] that the bands with maximum at ~1550 cm^{-1} and ~1560 cm^{-1} are attributed to the asymmetric stretching vibrations of carboxylate-anion in ionic multiplets and ionic clusters, respectively. The presence of double bands of asymmetric stretching vibrations of COO^- groups at spectrum of S-*co*-AA(K) evidences an existence of at least two types of ionic aggregation of COO^-K^+ groups. This conclusion is confirmed by far IR-spectroscopy data below.

FT-IR study of the PEUI/S-*co*-AA(K) TIPNs has shown a destruction of the networks of hydrogen and ionic bonds, inherent to the individual polymers that was confirmed by redistribution of the intensities and shift of position of the corresponding absorption bands of carbonyl, urethane, urea and ether groups, as well as the ionogenic groups of the blend components. It was found that the new network of intermolecular physical bonds is formed between corresponding ionogenic fragments of both the components.

Far-IR-spectra of PEUI, S-*co*-AA and S-*co*-AA(K) as well as PEUI/S-*co*-AA(K) blends are shown in Figure 2. The dominant feature of S-*co*-AA(K) and PEUI/S-*co*-AA(K) spectra is a presence of a well-defined complex band in the region below 300 cm^{-1}. It is important that in the spectrum of S-*co*-AA component this band was not detected. The maximum of this complex band has a position at about 180 ± 5 cm^{-1}.

As it was recently reported[14] that band is assigned to motion of cations in the

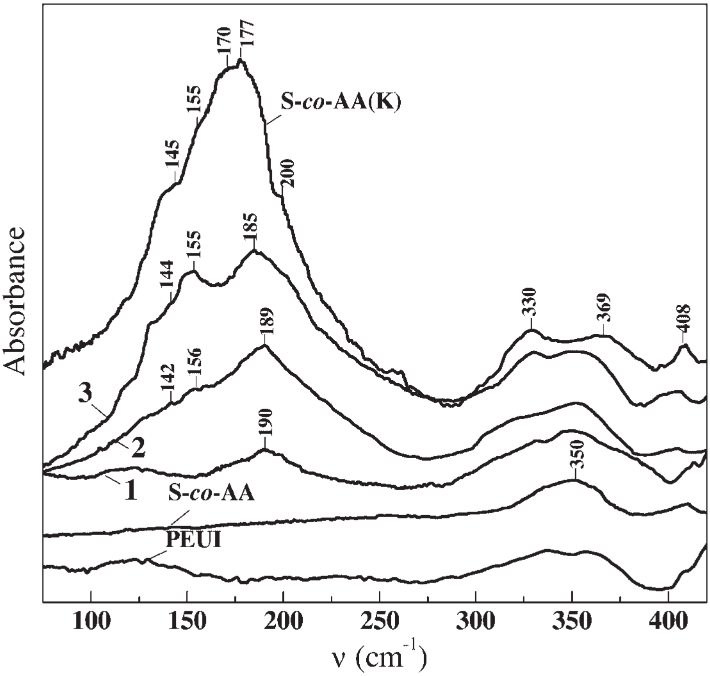


Figure 2.
Far-IR-spectra (70–400 cm^{-1}) of the individual components and PEUI/S-*co*-AA(K) TIPNs with different S-*co*-AA(K) content (wt.%): (1) = 10, (2) = 30, (3) = 50.

electrostatic field of anionic carboxylate groups. The bands at ca 155 cm^{-1} are assigned to the vibrations of aggregates involving many cations and anionic sites together that correspond to formation of high amount of aggregates and/or clusters. The large half-width of the cation-motion bands is most likely due to the superposition of several non-resolved peaks, which arise from the presence of different forms of cation-anion site associations. The cation-motion bands may be assigned to ion pairs and associated structures (multiplets and clusters).

The T_g values for the PEUI/S-*co*-AA(K) TIPNs, as well as for individual PEUI and S-*co*-AA(K) (obtained from DSC data) are shown in Table 1. It can be clearly seen that, in comparison to individual PEUI, the compositions studied exhibit increasing T_g values of PEUI-matrix at incorporation of the S-*co*-AA(K) into the matrix and further increase of its content up to 20 wt.%. Obviously, this is a result of improvement of compatibility between the components of the blend and formation of mixed microphases enriched in both components. Further increasing of the content of the S-*co*-AA(K) component up to 50 wt.% results into decreasing the T_g values of the PEUI-rich phase by ≈2.4 °C (in comparison to the blend with 20% of S-*co*-AA(K)). However, it can be seen that the T_g values of the S-*co*-AA(K) component in the blends are lower, as compared to the T_g value of the individual S-*co*-AA(K). Furthermore, one can see that the higher the content of the S-*co*-AA(K) component in the blend, the lower the its T_g value. Therefore, we can assume that, even in the blends with content of the S-*co*-AA(K) component higher then 20%, some mixed microphases (consisting of both components) have been formed, obviously due to formation of a new strong network of physical bonds (hydrogen, ion-dipole, ion-ion etc.) between the functional groups of the components.

DMTA measurements confirm the above DSC data. The temperature dependence of loss modulus (E'') for the individual PEUI and S-*co*-AA(K), as well as for the PEUI/S-*co*-AA(K) blends studied are shown in Figure 3, the corresponding T_g values are summarized in Table 1. Note, that it was impossible to measure the T_g values of the copolymer component due to softening and breaking of the samples at temperature above T ~ 145 °C.

It can be seen that for the compositions studied some growth of the T_g values of the PEUI matrix at incorporation and further increase of the S-*co*-AA(K) content up to 20 wt.% is observed compared to individual PEUI. However, further increase of the S-*co*-AA(K) content up to 40 wt.% results into decreasing the T_g values by ≈2 °C of the PEUI-rich phase of the blend compared

Table 1.
DSC and DMTA data, as well as density values for the individual polymers and for the PEUI/S-*co*-AA(K) TIPNs studied in dependence on the component content.

PEUI/S-*co*-AA(K), wt.%	T_g, °C (DSC data) of phases rich in:		DMTA data of PEUI rich phase:		Density, g/cm^3	
			T_g	E'[a]		
	PEUI	S-*co*-AA(K)	°C	MPa	ρ_{exp}	ρ_{add}
PEUI	−18.6	–	−12.1	3020	1.152	1.152
95/5	−12.6	–	−10.1	4467	1.162	1.157
90/10	−13.7	–	−7.9	3891	1.168	1.161
80/20	−13.6	162	−4.3	3388	1.176	1.170
70/30	−15.0	161	−5.1	2754	1.177	1.179
60/40	−15.8	160	−5.9	1514	1.165	1.188
50/50	−16.0	158	−6.2	1047	1.166	1.198
S-*co*-AA(K)	–	167	176.5[b]	2041[b]	1.243	1.243

[a] The values of E' are measured at temperature $T = -50$ °C;
[b] The values correspond to the S-*co*-AA(K) component.

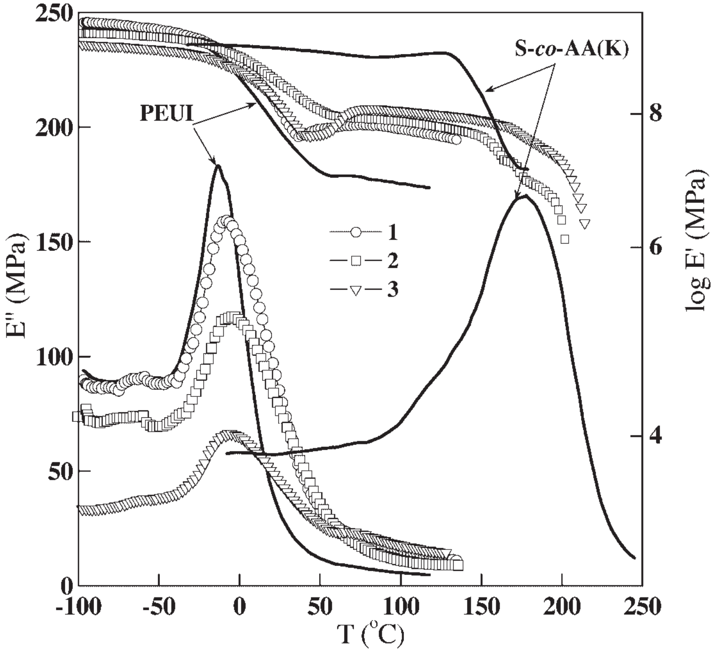


Figure 3.
Storage and loss moduli *versus* temperature for the individual PEUI and S-*co*-AA(K), as well as for the TIPNs with different content of PEUI (wt.%): (1) = 95, (2) = 90, (3) = 80, (4) = 70, (5) = 60.

to the blend with 20% of S-*co*-AA(K). As it was mentioned above, we suppose that the components have higher compatibility in the compositions, where the content of S-*co*-AA(K) is less than ~20%.

Analysis of temperature dependencies of loss modulus E'' (cf. Figure 3), as well as of storage modulus E', has shown that the above mentioned compositions are characterized by increased effective density of physical networks compared to the individual PEUI. Indeed, significant decreasing the height of the E'' peaks (cf. Figure 3) and increasing the E' values (cf. Table 1) at temperatures lower than T_g of the PEUI component (as example, at temperature $T = -50\,^\circ C$) provide evidence for the conclusion. Obviously, this is a result of formation of new physical networks formed by ion-dipole and ion-ion interactions between ionic groups of the components.[10,11] The density data (cf. Table 1) agree well with the above conclusion as the PEUI/S-*co*-AA(K) TIPNs with S-*co*-AA(K) content less than ~20% are characterized by higher experimental value of density (ρ_{exp}) compared to the corresponding additive ones (ρ_{add}). However in PEUI/S-*co*-AA(K) TIPNs with high S-*co*-AA(K) content (≥20 wt.%) intensification of microphase separation of the components occur, obviously due to predominance of intra-molecular physical bonding (hydrogen, ion-dipole, ion-ion etc.).[6,10,11]

The tensile characteristics of the PEUI/S-*co*-AA(K) TIPNs with S-*co*-AA(K) content of 10 and 50% are presented in Table 2. To check the effect of ionic bonding of the components in the blends on their tensile properties, the stress-strain curves for PEUI/S-*co*-AA TIPNs (S-*co*-AA is in acid form) have also been recorded and studied.

It can be clearly seen that the PEUI/S-*co*-AA(K) TIPN with lower content of S-*co*-AA(K) (i.e. 10 wt.%) is characterized by improved tensile properties compared to the PEUI/S-*co*-AA blend of the same component content and also to the blends with higher content of S-*co*-AA(K) or S-*co*-AA (i.e. 50 wt.%). For both types of

Table 2.
Tensile characteristics of PEUI, as well as PEUI/S-*co*-AA and PEUI/S-*co*-AA(K) blends studied.

PEUI content	Tensile strength		Elongation at break ε_b
	at break σ_b	at 300% deformation σ_{300}	
wt.%	MPa	MPa	%
PEUI	30.9	30.7	395
PEUI/S-*co*-AA			
90	34.6	23.5	407
50	21.3	–	142
PEUI/S-*co*-AA(K)			
90	36.5	22.2	435
50	19.6	19.5	305

the blends, increasing the styrene copolymer content leads to lower values of σ_b and ε_b, whereas the presence of ions K^+ of the styrene ion-containing copolymer results into improving tensile properties, even at high content of the brittle styrene copolymer. It can be supposed that for the blends studied the formation of the additional network of intermolecular ionic bonds between the functional groups of the components is the reason of improvement of their end-use properties.

Conclusions

The structure-property relationships for thermoplastic PEUI/S-*co*-AA(K) blends have been investigated by using various methods. It was found that the degree of incompatibility of the components is determined, to a large extent, by inter- and intra- molecular hydrogen bonds and ionic interactions between the functional groups of the components. Convergence of the T_g values of the PEUI and the S-*co*-AA(K) components in the blends studied, as compared to the individual polymers, was found and explained by improved compatibility of the components due to increasing effective density of physical networks formed by ion-dipole and ion-ion interactions of ionic groups of the components. Improvement of the end-use properties has been found for the blends studied.

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