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NOVEL POLYMER BLENDS BASED ON POLY(ETHER-URETHANE) IONOMER AND ION–CONTAINING STYRENE COPOLYMER

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The structure-property relationships of thermoplastic polymer blends based on poly(ether-urethane) ionomer (PEUI) and ion-containing styrene-acrylic acid copolymer (S-*co*-AA(K)) have been investigated by using DMTA, DSC and TGA, as well as tensile tests. Convergence of the glass transition temperature (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 improving 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. Character of $E'=f(T)$ and $E''=f(T)$ dependencies confirms the increase of the effective density of physical networks in the compositions studied compared to individual PEUI and S-*co*-AA(K). Improvement of end-use properties, i.e. thermal stability and tensile properties has been found for the PEUI/S-*co*-AA(K) compositions with lower content of S-*co*-AA(K) (i.e. <10 mass%) and explained by formation of additional network of intermolecular ionic bonds between the functional groups of PEUI and S-*co*-AA(K).

Keywords: *compatibility, phase structure, poly(ether-urethane) ionomer, styrene-acrylic acid copolymer*

Introduction

Investigations in the field of structure-property characterization of polymer alloys and blends based on immiscible physically crosslinked polymers have received considerable attention during the last years [1–3]. 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, in which the physical bonds play the role of effective crosslink sites. It is well known that polymer blends of this TIPNs type exhibit lower degree of phase separation of the components and improved physical-chemical properties (flexibility, tensile strengths and impact factors, chemical resistance, etc.) compared to traditional polymer blends [1–5].

The aim of the present work is to contribute to the investigation of structure-property relationships of novel 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 differential scanning calorimetry (DSC), thermogravimetric analysis (TG) and dynamic mechanical thermal analysis (DMTA) and also to check the effect of ionic bonding of the components in the blends on their tensile properties.

Experimental

Materials

K^+–containing styrene-acrylic acid copolymer, S-*co*-AA(K), was synthesized by bulk radical styrene/acrylic acid copolymerization (component ratio S/AA=55/45 mass%), followed by partial neutralization of carboxylic groups by potassium hydroxide, the degree of neutralization being ~60 mass%.

PEUI was prepared by sulfonation of macrodiisocyanate (MDI) synthesized from diethylene glycol, polyoxypropylene glycol (MM~1052) and toluene diisocyanate (TDI, mixture of 2,4- and 2,6-isomers with a ratio of 65/35) with H_2SO_4, followed by complete neutralization of sulfuric groups with triethylamine.

Novel PEUI/S-*co*-AA(K) and PEUI/S-*co*-AA films of several compositions were prepared from aqueous emulsion of the components using a solution technique.

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Methods

DSC was carried out using PerkinElmer Pyris 6 DSC under nitrogen flux with a programmed heating rate of 20°C min^{-1}. The equipment was calibrated with indium (T_m=156.6°C and ΔH_f = 6.8 cal g^{-1}) as standard. The sample mass was 8–10 mg. All DSC curves were baseline subtracted and normalised to 1 mg of sample. The second heating scan (from –100 to 240°C) was taken for data analysis. The temperature dependence of the heat capacity C_p was determined and the midpoint of the endothermic jump of the function C_p=*f*(*T*) was taken as the glass transition temperature (T_g).

TG was performed using the Q-1500D Derivatograph system developed by F. Paulik, J. Paulik and L. Erdey (MOM, Budapest, Hungary). TG traces were registered in the temperature range from 25 to 800°C at a heating rate of 10°C min^{-1} in air by evacuating the volatile products. The sample mass was 50 mg.

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 rate of 4°C min^{-1}.

Tensile tests were performed on dumbbell shaped specimens at ambient temperature at an extension rate of 10 mm min^{-1} using an Instron-1122 type universal testing machine. Specimen dimensions were 5.0·0.65·0.3 cm.

Results and discussion

T_g values of the PEUI/S-*co*-AA(K) blends obtained by DSC are summarized in Table 1. It can be clearly seen that, in comparison to individual PEUI, the compositions studied exhibit some increasing of T_g values of PEUI-matrix at incorporation into the matrix and further increasing of the S-*co*-AA(K) content up to 20 mass%. Obviously, this is a result of improvement of compatibility between the components of the blends due to incorporation of the S-*co*-AA(K) component (or part of it) into the PEUI-matrix, and formation of mixed microphases enriched in both components [1–3].

Further increasing of the content of the S-*co*-AA(K) component up to 50 mass% in Table 1 results into decreasing of the T_g values of the PEUI-rich phase by ≈2.4°C (in comparison to the blend with 20 mass% of S-*co*-AA(K)). However, it can be seen that the T_g values of the S-*co*-AA(K) component are lower, as compared to the T_g value of 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 T_g value of the component. Therefore, we can assume that, even in blends with content of the S-*co*-AA(K) component higher than 20 mass%, 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 components. This point will be further discussed below on the basis the DMTA results.

DMTA measurements (cf. Fig. 1) confirm the above DSC data. The 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 mass% is observed compared to individual PEUI. However, further increase of the S-*co*-AA(K) content up to 40 mass% results into decreasing of the T_g values of the PEUI-rich phase of the blend (compared to the blend with 20 mass% of S-*co*-AA(K)). As mentioned above, we suppose that the two components have higher compatibility in the compositions where the content of S-*co*-AA(K) is less than ~20 mass%. Analysis of the temperature dependence of storage modulus *E*' and loss modulus *E*'' (cf. Fig. 1) has shown that the PEUI/S-*co*-AA(K) compo-

Table 1 T_g values (DSC and DMTA data) for the individual polymers and for the PEUI/S-*co*-AA(K) compositions studied in dependence on the component content

PEUI/S-*co*-AA(K)/ mass%	T_g/°C (DSC data)		T_g/°C (DMTA data)
	PEUI rich phase	S-*co*-AA(K) rich phase	PEUI rich phase
PEUI	–18.6	–	–12.1
95/5	–12.6	–	–10.1
90/10	–13.7	–	–7.9
80/20	–13.6	162	–4.3
70/30	–15.0	161	–5.1
60/40	–15.8	160	–5.9
50/50	–16.0	158	–
S-*co*-AA(K)	–	167	176.5

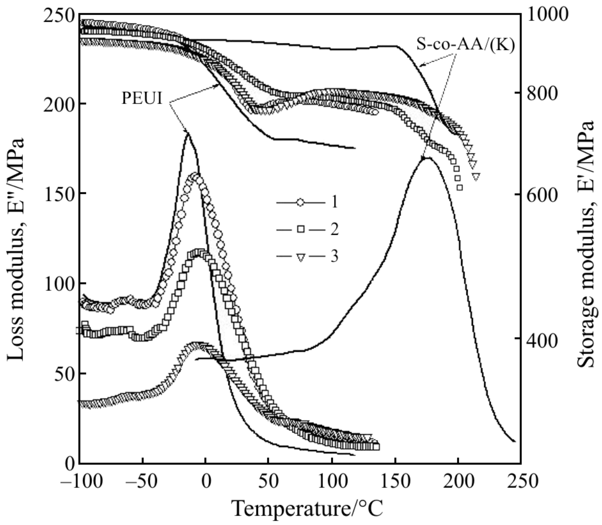

Fig. 1 Typical temperature dependence of storage (*E*') and loss (*E*'') modulus for individual PEUI and S-*co*-AA(K) (indicated in the plot), as well as for the PEUI/S-*co*-AA(K) compositions with different content of PEUI (mass%): 1 – PEUI 90, 2 – PEUI 70, 3 – PEUI 60

sitions studied are characterized by increased effective density of physical networks compared to individual PEUI. The significant decreasing of the height of the *E*'' peaks and the increasing of the *E*' values at temperatures lower than T_g of the PEUI component provide evidence for that conclusion. Obviously, this is a result of the formation of new physical networks formed by ion-dipole and ion-ion interactions between ionic groups of the components. We suppose that in PEUI/S-*co*-AA(K) compositions with high S-*co*-AA(K) content (higher than about 20 mass%) intensification of microphase separation of the components is observed, obviously due to predominance of intra-molecular physical (hydrogen, ion-dipole, ion-ion, etc.) bonding, as compared to inter-molecular bonding [1–4].

Thermal-oxidative decomposition of individual PEUI and S-*co*-AA(K), as well as of PEUI/S-*co*-AA(K) blends with S-co-AA(K) content of 10, 30 and 50 mass% has been investigated by TG and the corresponding decomposition temperature (T_{di}) and mass loss (W_i) data are summarized in Table 2. The thermal decomposition of different polyurethanes has been investigated in detail in [6, 7] and the decomposition of polystyrenes, as well as of styrene copolymers, in [8–10]. Based on that literature, we supposed that the decomposition of individual PEUI consists of at least four stages, whereas that of individual St-*co*-AA of at least five stages (cf. Table 2). S-*co*-AA(K) is characterized by higher thermal stability, as compared to PEUI, since T_{dmax} of the main decomposition stage of S-*co*-AA(K) is higher by 75°C compared to the corresponding T_{dmax} of PEUI (cf. Table 2), whereas the loss mass W of S-*co*-AA(K) is lower by 13% compared to the corresponding value of PEUI.

One can observe that the thermal-oxidative decomposition of the PEUI/S-*co*-AA(K) (cf. Fig. 2) compositions studied exhibit complicated character, especially that of the blend with 50% of S-*co*-AA(K). Analysis of the TG data reported in Table 2 evidences that introducing of 10% of S-*co*-AA(K) into the PEUI matrix leads to improving of the thermal stability of the matrix of the blend. Indeed, one can see increasing of all T_{dmax} values and decreasing of the corresponding loss mass, W, values. It may be assumed that the improvement of the thermal stability of the composition, as compared to individual PEUI, is due to intermolecular physical (hydrogen, ion-dipole, ion-ion, etc.) attraction between the PEUI and S-*co*-AA(K) components. As a result of that attraction, more energy is required to overcome the intermolecular physical forces. It is known [6] that, if the mixing scale of polyblend is poor, the decomposition of each component occurs independently from that of the other. Con-

Table 2 TG/DTG parameters for individual PEUI and S-*co*-AA(K), as well as for the PEUI/S-*co*-AA(K) blends studied

$T^{a)}_{dmax}$(°C)/ W(Δmass%)^{b}	PEUI	S-*co*-AA(K)	PEUI/S-*co*-AA(K)/mass%		
			90/10	70/30	50/50
T_{d1max}/W_1	315/26	305/20	320/31	255/9	255/10
T_{d2max}/W_2	**350/69**$^{c)}$	**425/56**	**370/66**	315/31	320/30
T_{d3max}/W_3	455/84	590/66	495/83	**350/56**	**340/42**
T_{d4max}/W_4	530/91	665/71	545/87	490/78	390/63
T_{d5max}/W_5		720/74	660/88	540/79	420/67
T_{d6max}/W_6				665/84	490/74
T_{d7max}/W_7					720/84
Char residue value$^{a)}$ (mass%)	0.3	10.6	12.0	12.0	16.1

$^{a)}$Decompositon temperature, T_d, corresponds to the temperature position of the decomposition peaks in Differential Thermal Gravimetry (DTG) curves; $^{b)}$mass loss, W, is determined from Thermogravimetry (TG) curves; $^{c)}$The values which are marked by 'bold' correspond to the main decomposition stage

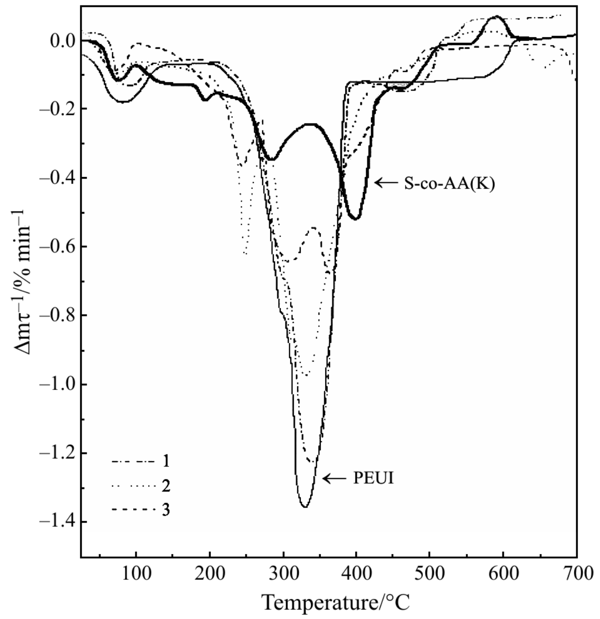

Fig. 2 DTG curves for individual PEUI and S-*co*-AA(K) (indicated in the plot), as well as for PEUI/S-*co*-AA(K) blends of the different component content (mass%): 1 – 90/10; 2 – 70/30; and 3 – 50/50

versely, when the mixing of the two polymers reaches the molecular scale, a co-pyrolysis takes place with partial interactions. Note that co-pyrolysis with partial interactions is observed in the DTG curve (cf. Fig. 2) for the composition with 10% of S-*co*-AA(K). Increasing of the S-*co*-AA(K) component up to 30% and, especially, up to 50% results into disappearing of some of the decomposition stages and appearing of new ones, which are similar to decomposition stages of S-*co*-AA(K) (cf. Table 2). In general, the thermal stability of the blends studied remains higher compared to PEUI and lower compared to S-*co*-AA(K). However, it can be seen that the char residue values of all the blends studied are higher compared to the neat PEUI and S-*co*-AA(K) components.

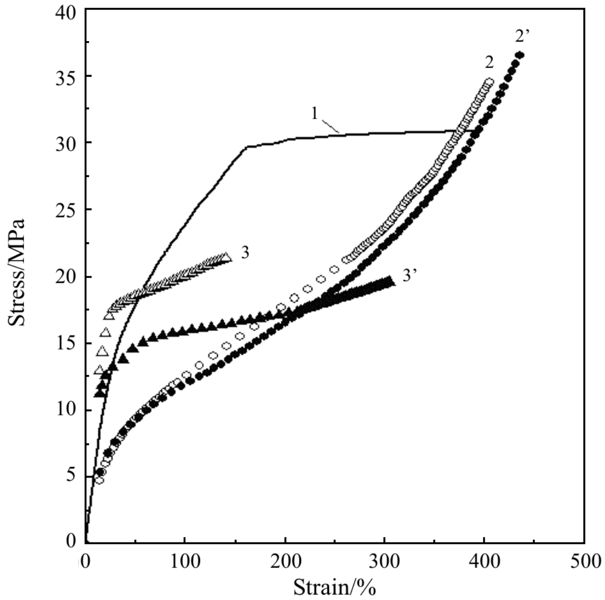

Fig. 3 Stress-strain curves for 1 – individual PEUI, and for 2, 3 – PEUI/S-*co*-AA and (2', 3') PEUI/S-*co*-AA(K) blends with composition (mass%): (2, 2') 90/10 and (3, 3') 50/50

The stress-strain curves of the PEUI/S-*co*-AA(K) compositions with S-*co*-AA(K) content of 10 and 50% are shown in Fig. 3. 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 blends (S-*co*-AA is in acid form) have also been obtained and studied (cf. Fig. 3). It can be clearly seen that the PEUI/S-*co*-AA(K) composition with lower content of S-*co*-AA(K) (i.e. 10 mass%) 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 mass%). For both types of the blends, increasing of the styrene copolymer content leads to worse values of σ_b and ε_b, whereas the presence of ions K^+ in the carboxylic groups of the styrene copolymer results into improving these tensile properties, even at high content of the brittle styrene copolymer. It can be supposed that for the blends studied the formation of additional network of intermolecular ionic bonds between the functional groups of the components is the reason of improvement of their end-use properties [11].

Conclusions

The structure-property relationships of thermoplastic polymer blends based on poly(ether-urethane) ionomer (PEUI) and ion-containing styrene-acrylic acid copolymer (S-*co*-AA(K)) have been investigated by using various thermal analysis methods. 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 improving 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. The degree of incompatibility is determined, to a large extent, by inter- and intramolecular hydrogen bonds and ionic interactions between the functional groups of the components. Analysis of the temperature dependencies of E' and E'' modulus confirms the increase of the effective density of physical networks in the compositions studied compared to individual PEUI and S-*co*-AA(K). Improvement of end-use properties, i.e. thermal stability and tensile properties has been found for the blends studied.

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