EFFECT OF PHYSICAL CROSS-LINKS ON STRUCTURE AND PROPERTIES OF MICROHETEROGENEOUS IONOMER-CONTAINING POLYMER BLENDS

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Abstract

The structure-property relationships of thermoplastic IPNs (TIPNs) based on fluorine-containing polyurethaneurea (PUUF) and K^+-ion-containing styrene-acrylic acid copolymer (S-co-AA(K^+)) have been investigated by using FTIR, TMA DSC and TGA methods. Convergence of glass transition temperature (T_g) values of PUUF and S-co-AA(K^+) components in the TIPNs studied, as compared to the individual polymers and corresponding PUU/S-co-AA(K^+) compositions, 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. Improvement of end-use properties, i.e. thermal stability has been found for the PUUF/S-co-AA(K^+) TIPNs and explained by formation of additional network of intermolecular ionic bonds between the functional groups of PUUF and S-co-AA(K^+).

1 Introduction

In the present work structure-property relationships for novel thermoplastic IPNs based on fluorine-containing polyurethaneurea (PUUF) and K^+-ionomer of poly(styrene-co-acrylic acid) (S-co-AA(K^+)) were studied and effect of inter- and intramolecular physical cross-links of the components on microphase structure and properties of the blends were discussed. The functionalization of both the components of the TIPNs studied was previously fulfilled for improvement of their compatibility in the compositions [1-3]. The functionalization of the S-co-AA was carried out by partial neutralization of carboxylic groups by KOH leading to formation of K^+-ionomer S-co-AA(K^+).

Functionalization of PUU was fulfilled by using fluorine-containing diamine as chain extender at PUUF synthesis.

2 Experimental

2.1 Materials

The polyurethaneurea (PUU) was synthesized using prepolymer technique from toluene diisocyanate (TDI, mixture of 2,4- and 2,6-isomers, molar ratio 65/35), polyoxypropylene glycol (POPG, $M_w \sim 1500$) and diamine (DA), molar ratio of reagents was 2/1/1. The fluorine-containing PUU (PUUF) was synthesized by the same way but the fluorine-containing DA (4,4′-bis(p-aminophenyl) ether of tetrafluorohydroquinone) was used.
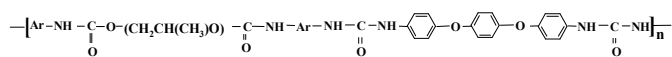
S-co-AA was synthesized by bulk radical copolymerization of S and AA (initiator: benzoyl peroxide), molar ratio of S and AA was ~ 80/20. S-co-AA(K^+) was prepared by partial neutralization of S-co-AA using KOH, the degree of neutralization was ~ 0.6.

Films of individual polymers as well as PUU/S-co-AA(K^+) or PUUF/S-co-AA(K^+) compositions with different component content were prepared by casting from 20%-solutions in DMF onto Teflon plates and subsequent evacuation to constant weight.
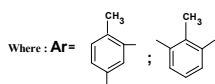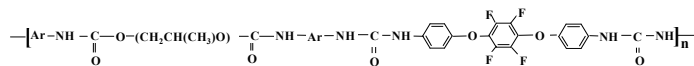
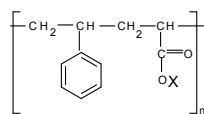The structural formulas of individual PUU, PUUF and S-co-AA(K^+) are shown below:

PUU:

PUUF:

Where: **Ar=**

S-*co*-AA(K$^+$):

Where: X = H ; K

2.2 Methods

FTIR spectra were recorded on a Bruker Tensor 27 DTGS spectrometer between 4000 and 450 cm^{-1} using the Attenuated Total Reflection (ATR) mode. For each spectrum, 32 consecutive scans with a resolution of 4 cm^{-1} were averaged. The degree of OCN-conversion was calculated from the intensity of the OCN stretching absorption band at 2272 cm^{-1}.

The thermal-mechanical curves were obtained using "TMA TMS2" (Perkin Elmer). Samples, with masses 40 g, were heated at 5 ^{o}C·min^{-1} from 20 to 200 ^{o}C. The quartz probe with diameter of 1 mm was used.

Differential scanning calorimetry (DSC) investigations were performed on a Perkin Elmer "Pyris 6 DSC Calorimeter". The calorimeter was calibrated in energy and temperature with Indium standard, under nitrogen atmosphere and with a heating rate equal to 20 K min^{-1}. The sample mass was ~ 10-15 mg. Samples were first heated from 293 K to 463 K with a rate of 20 K min^{-1}, and subsequently cooled to 173 K. A second heating scan was performed under the same heating conditions. All DSC curves are baseline subtracted and normalized to 1 mg of sample. 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).

Thermogravimetric analysis (TGA) was performed in inert atmosphere (nitrogen/argon =1/1) using the "Thermobalance SETARAM TG 92". Sample pellets, with masses of 20 mg, were put in aluminium crucibles, and then heated at 2 K·min^{-1} from 20 to 800 ^{o}C.

The density (ρ, average value over five measurements) of the samples was determined using Archimedes's method at room temperature. The theoretical values of density (ρ_{theor}) were calculated by using additive law.

3 Results and discussion

Typical FTIR spectra of the individual components and TIPNs studied are presented in Figure 1. It can be seen that the spectrum of the composite differs of the spectra of both the individual components.
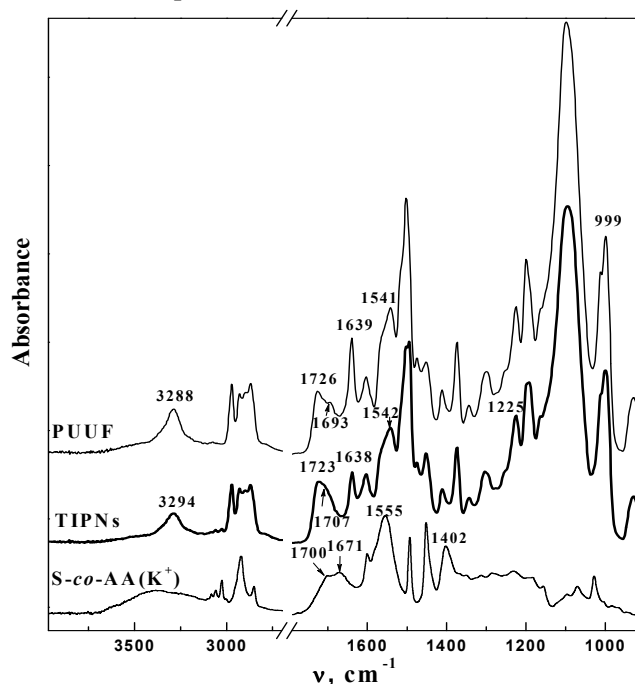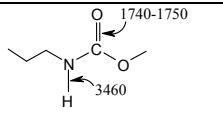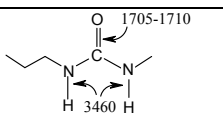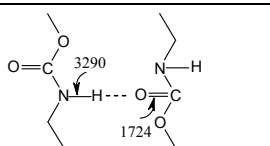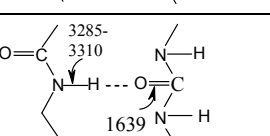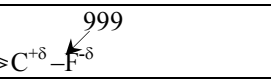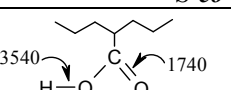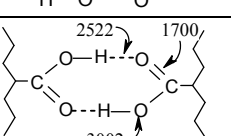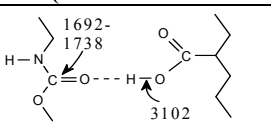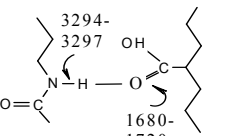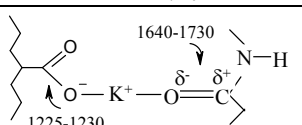

Fig. 1. FTIR spectra of individual PUUF and S-*co*-AA(K$^+$) (indicated in the plot), as well as TIPNs based on PUUF/S-*co*-AA(K$^+$)=80/20(wt.%).

FTIR studies of the individual components and PUUF/S-*co*-AA(K$^+$) composites reveal the mutual effect of components on the formation of a network of intermolecular physical bonds between urea and urethane groups of the PUUF and COOH and COOK groups of the S-*co*-AA(K$^+$), respectively. It can be seen that the spectrum of the composite differs of the spectra of both the individual components. This difference is especially pronounced in spec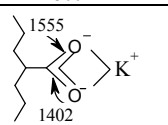tral regions, where the stretching vibrations of C=O, NH, COOK and OH functional groups make themselves evident. Exactly these groups may be involved in formation of physical bonds of various types (cf. Table 1.).

Table 1. Structure of functional groups and main physical bonds formed in individual components and PUUF/S-*co*-AA(K$^+$) TIPNs

Structure of functional groups and physical bonds (absorption bands, ν, cm^{-1})	Characterization
PUUF	
O 1740-1750, N, H, 3460	Free urethane group
O 1705-1710, N, N, H 3460 H	Free urea group
O=C 3290, N—H---O=C, 1724	Self-associated urethane groups
O=C 3285-3310, N—H---O=C, 1639 N—H	Self-associated urea groups
999, ⋙C$^{+\delta}$—F$^{-\delta}$	F$^{-\delta}$-containing dipole
S-*co*-AA(K$^+$)	
3540, C, 1740, H—O, O	Free carboxylic group
2522, 1700, O—H---O=C, O---H—O, 3002	Dimer of self-associated carboxylic groups
1555, O$^-$, K$^+$, O, 1402	Bidental ligand
PUUF/S-*co*-AA(K$^+$) **(main intermolecular physical bonds)**	
1692-1738, H—N, C=O---H—O, O, 3102	C=O of urethane group H-bonded with OH of COOH group
3294-3297, OH, N—H---O=C, O=C, 1680-1720	NH of urethane or urea groups H-bonded with COOH group
1640-1730, O, N—H, O$^-$—K$^+$—O=C δ$^-$ δ$^+$, 1225-1230	Bonded carboxylate groups

Figures 2 show the FTIR-spectra for the PUU/S-*co*-AA(K$^+$) and PUUF/S-*co*-AA(K$^+$) TIPNs.

The first remark concerns the absorption bands of stretching vibrations of C=O groups from polyurethaneureas and S-*co*-AA(K$^+$) components which are essentially overlapped. Nevertheless, for the TIPNs with 10 wt. % of S-*co*-AA(K$^+$) in PUU or PUUF components we observe a significant decrease of intensity and high-frequency shift of the absorption bands ν(C=O$_{as-urea}$) at 1642 cm^{-1} and 1640 cm^{-1} [4-7]. Thus, the number of the urea C=O
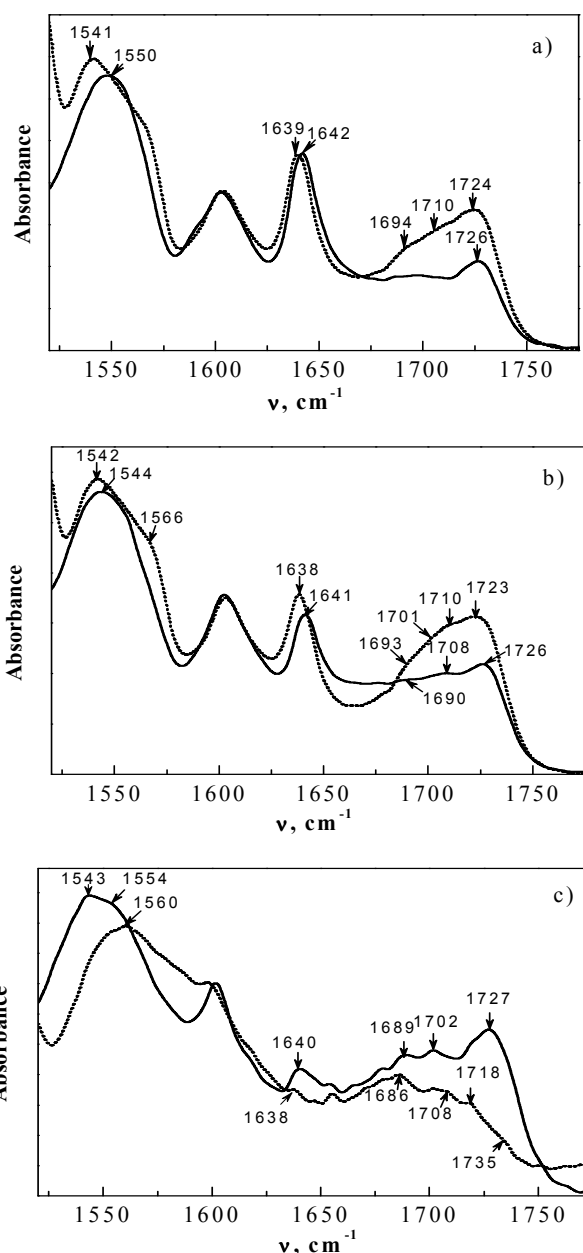

Fig. 2. FTIR spectra of PUU/S-*co*-AA(K$^+$) (solid line) and PUUF/S-*co*-AA(K$^+$) (dot line) TIPNs with different content of S-*co*-AA(K$^+$) (wt. %): (a) 10, (b) 20 and (c) 50.

groups decreases. However, in the PUUF-system the intensity of the absorption band $\nu(C=O_{urea})$ at 1710 cm^{-1} increases, while the opposite behavior occurs for the PUU system.

Increasing the S-*co*-AA(K$^+$) in both series up to 20 and 50 wt. %, leads to amplify the latter observations for PUU systems, while for PUUF system, the previous variations observed for the $\nu(C=O_{urea})$ band at 1710 cm^{-1} are inverted. Thus for composition greater than 20 % a reduction of the number of the urea C=O groups forming hydrogen bonds occurs for both PUU and PUUF systems. It is also found that the number of C=O$_{as}$ groups (area of the bands at 1690-1750 cm^{-1}) is higher in the PUUF-systems. Always for PUUF/S-*co*-AA(K$^+$) a simultaneous redistribution of intensities of the maxima of a complex absorption band $\nu(C=O_{as\text{-}COO}^-)$ and a low-frequency shift of the maximum of this band to 1682 cm^{-1} occurs. This is an evidence for the formation of hydrogen bonds between C=O$_{as\text{-}COO}^-$ and proton-donor groups (NH, OH) [6]. In other words, a significant destruction of the ionic network (bonds between COO$^-$ and K$^+$) takes place as confirmed by a significant increase of intensity of the absorption band $\nu(OH_{free})$ (free hydroxyl groups) at 3540 cm^{-1}.

Comparison of the frequency positions of the absorption bands for $\nu(NH_{as})$ and $\nu(NH_{free})$ and for both series leads to the following conclusions:
1) The low-frequency shift of the absorption bands $\nu(NH_{free})$ observed for PUUF-containing samples is evidence of formation (by NH groups) of shorter and stronger H-bonds than that of the PUU-containing compositions.
2) It was found that introducing 10 wt. % of S-*co*-AA(K$^+$) to PUUF-matrix decreases the concentration of the H-bonds compared to the individual PUUF, whereas increasing of S-*co*-AA(K$^+$) content up to 20 - 50 wt. % leads to growing of concentration of the H-bonds. The appearing of the absorption band of $\nu(NH_{free})$ at ~3460 cm^{-1} in the FTIR-spectrum of PUUF/S-*co*-AA(K$^+$)=50/50 wt. % evidenced of the presence of some free NH groups.
3) On the contrary (compared to PUUF-containing samples), introduction of 10 wt. % S-*co*-AA(K$^+$) to the PUU-matrix results to some increasing of H-bonds content, but follow increasing of S-*co*-AA(K$^+$) content up to 20 - 50 wt. % reduces the H-bonds content. Moreover, it is necessary to note that an absence of the absorption band at ~3460 cm^{-1} for the all samples means that all NH-groups participate in H-bondings.

4) The expansion of the absorption band of $\nu(NH_{as})$ at increasing of S-*co*-AA(K$^+$) content in the samples of both series evidences of existence of different H-bonds types (different length, nature and strength) [7].

Summarizing, one can conclude that the introduction into a polyurethaneurea matrix of 10 wt. %, 20 or 50 wt. % of S-*co*-AA(K$^+$) causes significant restructuring of whole network in both PUU/S-*co*-AA(K$^+$) and PUUF/S-*co*-AA(K$^+$) TIPNs but the PUUF-based system seems more affected.

First we propose to analyze is the density. Such measurements performed on PUU/S-*co*-AA(K) and PUUF/S-*co*-AA(K) are displayed on Figure 3. For each system the value for the density measured for the blend is greater than the value expected by the use of the additive law and they exhibit a maximum for the same S-*co*-AA(K$^+$) content (i.e. ≈ 50 %). At high S-*co*-AA(K$^+$) content (> 80 %) the
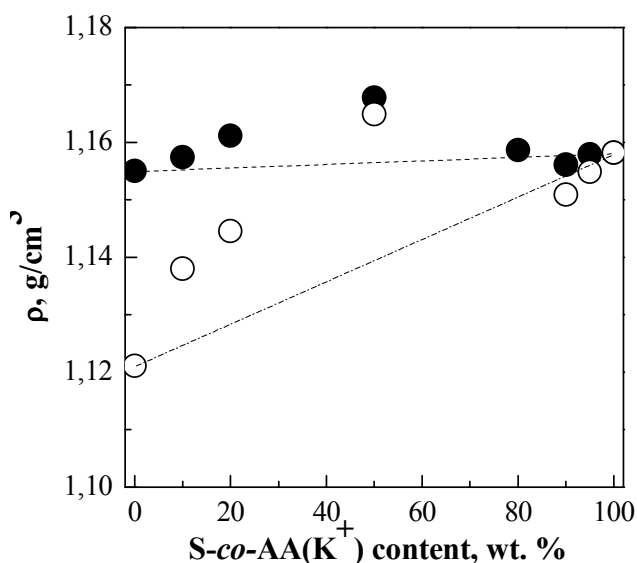
Fig. 3. Concentration dependence of density (ρ) for (○) PUU/S-*co*-AA(K$^+$) and (●) PUUF/S-*co*-AA(K$^+$) TIPNs. Dot and dash lines correspond to additive values.

two systems have quasi-similar density values. Finally for composition lower than 50 % of S-*co*-AA(K$^+$), the variations of density are greater for the PUU/S-*co*-AA(K$^+$) but it density for a given composition remains lower than the one obtained for the PUUF/S-*co*-AA(K$^+$). The evolutions of the density observed for these TIPNs confirm the FTIR data. The fluorine leads to create a material with a higher density but this effect vanishes when S-*co*-AA(K$^+$)) are added in great quantity.

The thermal-mechanical curves for the S-co-AA(K) and some samples of both series are given in

Figure 4. Analysis of these curves allows estimating an influence of an addition of polyurethane component on the behavior of the S-co-AA(K$^+$) matrix. First of all it should be noted that the character of thermal-mechanical curve for individual S-*co*-AA(K$^+$) with 2 transitions evidences its heterogeneous structure, perhaps, caused by existence of some ionic aggregations. We suppose that the first transition (Tg$_1$) at 92.5°C is explained by transition of the part of S-*co*-AA(K$^+$) chains without ionic groups from solid to viscoelastic state and the second transitions (Tg$_2$) at 113°C is explained by the glass transition of the ioncontaining S-*co*-AA(K$^+$) chains may be accompanied by destruction of ionic aggregates.
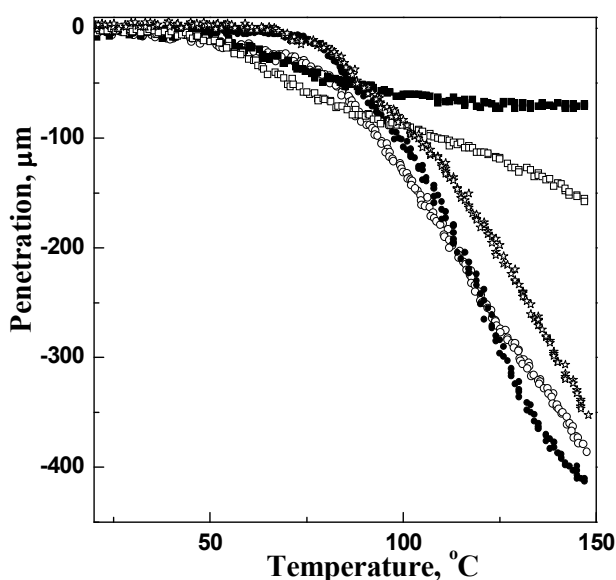

Fig. 4. Thermal mechanical curves of (☆) individual S-*co*-AA(K$^+$), as well as TIPNs based on (○, □) PUU/S-*co*-AA(K$^+$) or (●, ■) PUUF/S-*co*-AA(K$^+$) with content of S-*co*-AA(K$^+$) (○, ●) 95 and (□,■) 50 wt. %.

It can be seen from Figure 4 that changes in content and chemical structure of the polyurethane component influence significantly on the character of thermal-mechanical curves of TIPNs studied. For example, introducing just 5 % of PUU or PUUF to S-*co*-AA(K$^+$) matrix decreases the *Tg$_1$* of S-*co*-AA(K$^+$) from 92.5°C to 80.9 (for PUU-based sample) and 79.4 °C (for PUUF-based sample), correspondingly. One can note the stronger influence of PUU-F than PUU on the behavior of S-*co*-AA(K$^+$) matrix that surely evidences the better compatibility of the latter with F-containing polyurethane in the TIPNs. Increasing of PUU or PUUF content up to 50 wt.% deepens the differences in thermal-mechanical properties of TIPNs samples,

but in both cases we can observe 2 transitions. For the sample PUU/S-*co*-AA(K$^+$)=50/50 *Tg$_1$*=47.2°C and *Tg$_2$*=120.1°C, whereas for the sample PUUF/S-*co*-AA(K$^+$)=50/50 *Tg$_1$*=52.6°C and *Tg$_2$*=107.0°C. We consider that in both samples the lower *Tg$_1$* corresponds to the glass transition of so-called mixed phase formed by both components, but rich in polyurethane component, while the higher Tg$_2$ corresponds to the glass transition of the microphase consisting almost of the S-*co*-AA(K$^+$) component. Obviously, the sample PUUF/S-*co*-AA(K$^+$)=50/50 is characterized by better compatibility of the components than the PUU/S-*co*-AA(K$^+$) sample of the same composition. We suppose that this is connected with a higher density of the network of physical bonds (ionic, ion-dipole, hydrogen, etc.) in the fluorine-containing polyurethane.

DSC investigations were carried out and glass-transition temperatures, *Tg*, of individual components and the components in TIPNs prepared were determined (cf. Table 2). It was found that changes of the chemical structure of the polyurethaneurea component and its content in the TIPNs essentially influences on a character of the DSC thermograms of the systems studied and cause the changes in T$_g$ values. As it can be seen from data presented in Table 2 the TIPNs on the basis of PUUF/S-*co*-AA(K$^+$) containing 10 % of PUUF are characterized by rather strong effect of the polyurethaneurea component on the polystyrene matrix: the *T$_g$* reduces on ~13 K, whereas for PUU/S-*co*-AA(K$^+$) sample with the same composition only on ~10 K, that, certainly, testifies to a greater compatibility of the components in the former system.

Table 2. Glass transition temperature (DSC data) for individual components and TIPNs studied

Content of S-*co*-AA(K$^+$) in TIPNs, wt.%	T_g, °C	
	PUU / S-*co*-AA(K$^+$)	PUUF / S-*co*-AA(K$^+$)
100	130.8	130.8
90	- / 120.3	- / 118.0
50	-48.7 / 125.8	-41.1 / 112.0
20	-40.8 / -	-43.8 / -
10	-48.1 / -	-39.3 / -
0	-29.9	-34.9

The thermal stability has been also checked. This was performed by means of thermogravimetry measurements. Figures 5 shows the TGA and DTG curves obtained for individual PUU, PUUF and for S-*co*-AA(K$^+$). The curve for pure S-*co*-AA(K$^+$) shows a first mass loss of 10 % between 100° C and 250 °C. This is due to the evaporation of solvent. The main degradation is observed at T ~ 383 °C and some residues (≈ 10 %) are obtained at high temperature. The individual PUU and PUUF are stable up to ≈ 200 °C but as shown with more details on the derivative curves, the fluorine leads to decrease the amount transformed at 300 °C and shift to higher temperature the complete degradation of the polymer.
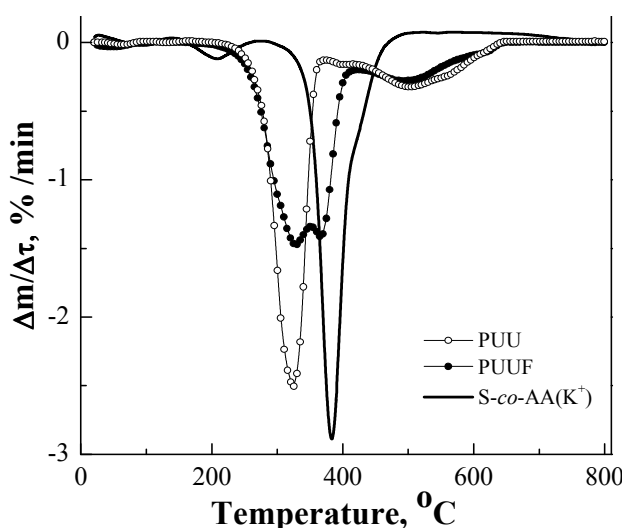

Fig. 5. Differential Thermal Gravimetry (DTG) curves for individual polymers studied (indicated in the plot).

We have reported on Figure 6 the variations obtained and we may say that these systems exhibit common feature. Two peaks are observed for composition greater than 10 % of S-*co*-AA(K$^+$) and it is easy to recognize the degradation of the PUU or PUUF part as the first degradation peak, while the second peak corresponds to the degradation of the S-*co*-AA(K$^+$). In fact the small variations of temperature measured here come more from the fact that the peaks overlap rather than a composition variations. A second point must be pointed out, when S-*co*-AA(K$^+$) is introduced, the thermal stability of PUU and PUUF seems to be reduced.

This is well evidenced by analyzing the beginning of the degradation process. First methods consist to determine the temperature of degradation for a given mass loss. First, from an arbitrary way, we choose 50 % of mass loss. The results are shown in Fig. 7. One more time we find that S-*co*-AA(K$^+$)
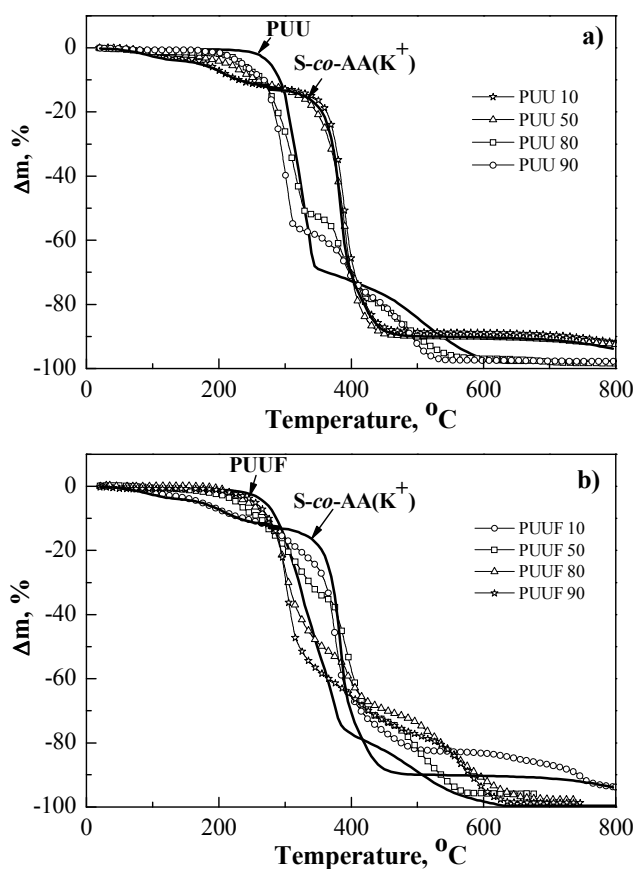

Fig. 6. Thermogravimetry curves for individual polymers (indicated in the plot) and (a) PUU/S-*co*-AA(K$^+$) and (b) PUUF/S-*co*-AA(K$^+$) TIPNs with different component content.
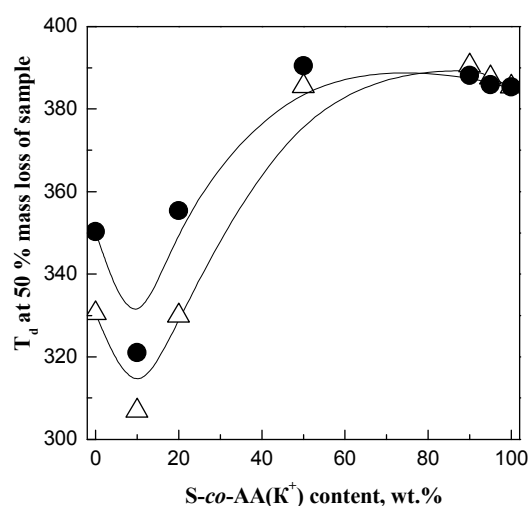

Fig. 7. Concentration dependence of destruction temperature (T$_d$) at 50% mass loss of (△) PUU/S-*co*-AA(K$^+$) and (●) PUUF/S-*co*-AA(K$^+$) TIPNs studied.

decreases the thermal stability of PUU and PUUF but PUUF-based samples remains better than PUU. Thus from these data we conclude that S-*co*-AA(K$^+$) decrease the thermal stability but kept the PUUF/S-*co*-AA(K$^+$) samples more stable.

On the basis of the studies performed it is possible to conclude that the functionalization of the components of polyurethaneurea-polystyrene compositions (TIPNs) allows changing the compatibility of components, phase structure (transitions temperature) and thermal-physical properties of final materials. We consider that such significant changes in a microphase structure of the given compositions are occurred due to reformation of several networks of physical bonds between components and inside the microphases enriched in one of components. The compositions investigated are promising from a practical point of view as they have good film forming properties, high physical-mechanical characteristics and can be also used as biopolymeric materials.

References

[1]. Koning C., Duin V.M., Pagnoulle C. "Strategies for compatibilization of polymer blends." *Prog. Polym. Sci.,* Vol. 23, pp. 707-757, 1998.

[2]. Utracki L.A. Polymer "*Alloys and Blends. Thermodynamics and Rheology*." Munich: Hanser Publ., 1989.

[3]. Hara M., Eisenberg A. "Miscibility enhancement via ion-dipole interactions. I. The polystyrene ionomer/poly(alkylene oxide) systems." *Macromolecules*., Vol. 17, pp. 1335-1340, 1984.

[4]. Sung C.S.P., Schneider N.S. "Infra-red studies of hydrogen bonding in toluene diisocyanate based polyurethanes." *Macromolecules*., Vol. 8, №1, pp. 68-73, 1975.

[5]. Lee J. Y., Painter P.C., Coleman M.M. "Hydrogen bonding in polymer blends. III. Blends involving polymers containing methacrylic acid and ether groups." *Macromolecules*., Vol. 21, pp. 346-354, 1988.

[6]. Gupta N, Srivastava A.K. "Ionomer IPNs formed by transition metal coordination of styrene-based polymers." *Eur. Polym. J.* Vol. 32, pp. 635-638, 1996.

[7]. Shekera O.V., Borodin A.E., Chranovskiy V.O. "Fluorine-containing segmented polyurethaneureas." *Ukr.Chem.J.* Vol. 67, pp. 50-53, 2001. (in Ukrainian).