

Interfacial Interactions in Polyurethane Elastomer-poly(vinyl chloride) Blends

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An influence of chemical structure of hard segment in poly(urethane-urea)s (PUU) on intermolecular interactions in PUU / poly(vinyl chloride) (PVC) composite systems, as well as their morphology and mechanical properties has been studied. A formation of intra- and intermolecular interaction in the PUU / LiCl and PUU / PVC systems was determined by FTIR. Structural asymmetry and weakening intermolecular interactions in PUU promotes an increasing energy of interfacial H-bonds in PUU / PVC blends. Obtained nanocomposite materials have enhanced tensile properties.

Keywords: Polymer blend, Poly(urethane-urea), Poly(vinyl chloride), Interfacial interaction.

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1. INTRODUCTION

Extensive studies of interfacial interactions and features of a formation of nanoheterogeneous structure in polymer/polymer systems are conducted during last years to obtain the composites with novel functional characteristics. It is well-known fact that bonding at the interface determines the structure of interfacial region, supramolecular structure and mechanical properties of the composites. Relatively high polarity of polyurethane (PU) and PVC macromolecules allows to obtain the mixed-type materials with valuable properties. The chemical structure of soft and hard segments of polyurethane block copolymers has a great impact on phase separation processes, compatibility with chlorinated polymer and properties of PU/PVC composites [1-3]. Previous experiments show that strong hydrogen bonding (H-bonding) network between polar ester, urethane and urea groups in interfacial region of PUU, and chlorine-containing units of PVC provides a formation of nanoheterogeneous structure of the blends containing up to 30-40 wt % of PVC and improves the tensile properties of the final composites.

Generally, soft segments of elastomers consist of ether fragments (PPG or PTMG) are immiscible with PVC macromolecules [3]. However, their immiscibility could be overcome by introducing in PU structure highly polar urethane-urea segments using either 4,4'-methylene-bis(aniline) or water as chain extender [4].

The aim of the present work was studying an effect of the chemical structure of poly(urethane-urea)s hard segments on interactions between PUU and PVC or low-molecular model compound, such as lithium chloride. The supramolecular structure and tensile properties of PUU / PVC blends have been studied as well.

2. MATERIALS

Poly(propylene glycol) (PPG) ($M_n = 1000$) and poly(tetramethylene glycol) (PTMG) ($M_w = 1000$) were used as received. Toluene-2,4-diisocyanate (2,4-TDI) or mixture of isomers 2,4- and 2,6-toluene diisocyanates (2,4-TDI/2,6-TDI = 65/35 w/w) were purified by distillation under reduced pressure according to standard procedure. As chain extenders was used toluene 2,4-diamine (TDA). PUU used in this work were prepared via conventional two-step "prepolyurethane method" and were summarized in Table 1.

Table 1 – Compositional characteristics of PUU

Sample	Ether	TDI	Hard segments content, [%]	$[\eta]$, [cm ³ /g]
PUU-1	PPG	2,4-TDI/ 2,6-TDI	32	0.073
PUU-2	PPG	2,4-TDI	32	0.085
PUU-3	PTMG	2,4-TDI	32	0.062

Lithium chloride, LiCl, (analytical grade, Aldrich Chemicals) was dried at temperature of 550 °C to constant weight, milled and stored in dry atmosphere. Poly(vinyl chloride) (PVC) ($M_w = 8.0 \times 10^4$) with chlorine content of 56.3 wt. % was taken for preparation of the polymer composites.

Pure poly(urethane-urea)s as well as PUU / LiCl and PUU / PVC composite film samples were prepared by casting technique on a Teflon substrate from DMF solutions. Obtained films were dried at 323 K in an oven to a constant weight.

Chemical structure parameters and a compatibility of the components in the polymer systems were evaluated via FTIR analysis using Bruker Tensor® 37 FTIR spectrometer in the spectral region of 400-4000 cm⁻¹.

In order to characterize nano-scale heterogeneity of PUU / PVC samples the morphology studies of the composites prepared

were performed by JEOL JSM 6060 LA Scanning Electron Microscope.

3. RESULTS AND DISCUSSION

It is well known that the most important factors, that have a great influence on phase

Structure of polyurethane block copolymers, are both chemical structure and structural symmetry of the hard segments [5]. An effect of urea units on phase separation and domain structure of PUU is related to differences in polarity of hard and soft segments as well as hydrogen bonding between C = O of urea and NH groups of hard segments. In the case of structural asymmetry of hard segments a formation of domain structure will be hindered significantly due to disordering of the structure. Hard segments based on 2,4-TDI have an amorphous structure due to asymmetry in the structure of diisocyanate fragments, where as 2,6-TDI based hard segments with defined structural symmetry are able to form close-packed crystalline structures [6]. The main feature of elastomers based on asymmetric diisocyanate is substantial quantity of mixed hard/soft segments phase as a result of hydrogen bonding between NH of hard segments and ether fragments of soft segments. In a contrast, an increasing of symmetric 2,6-TDI content in 2,4-TDI / 2,6-TDI blend improves segregation processes in hard segments of PUU.

Hydrogen bonding (H-bonding) in PUU and PUU-based polymer blends was studied by FTIR spectroscopy. A level of participation of urethane-urea groups in H-bonding has been evaluated by changes in NH stretching vibration bands at 3200-3500 cm^{-1} . A degree of H-bonding of C = O groups was determined by changes in *amide I* band. As an internal standard a deformation vibration band of $-\text{CH}_3$ groups at 1370-1375 cm^{-1} was used. A segregation ratio (α) of C = O groups of urea ($\text{C}=\text{O}_{\text{urea-b}}$), which participate in H-bonding, was calculated as a ratio between integrated absorbance of $\text{C}=\text{O}_{\text{urea-b}}$ band and full integrated absorbance of all carbonyls of the system. Different parameters, that were found and calculated from FTIR spectra, such as

maxima of stretching (ν) and deformation (δ) vibration bands, optical density (D_i), α and integrated absorption of H-bonded NH groups (A_{NH}) were summarized in Table 2.

An influence of symmetry of isocyanate fragments on segregation ratio of hard segments was evaluated by comparative analysis of FTIR spectra of polymers. In Figure 1 were shown FTIR spectra of pure PUU-1 and PUU-2 elastomers and their composites with LiCl and PVC. PUU-1 based on 2,4-TDI / 2,6-TDI is characterized by stretching vibration bands of C = O at ~ 1640 (H-bonded C = O of urea – $\text{C}=\text{O}_{\text{urea-b}}$), 1690 cm^{-1} (H-bonded C = O of urethane – $\text{C}=\text{O}_{\text{ureth-b}}$), stretching vibration band at 1730 cm^{-1} (non-associated C = O of urethane – $\text{C}=\text{O}_{\text{ureth-f}}$) and by intensive stretching vibration band of H-bonded NH (NH_b) at 3288 cm^{-1} and $\alpha = 33\%$, where as PUU-2 (based on asymmetric 2,4-TDI) have NH_b band positioned at 3294 cm^{-1} , $\alpha = 10\%$ and increased D_{1730} . Additionally, the intensities of C = C stretching vibration bands of aromatic ring is also depend on isomerism of TDI component. It is well known that conjugation of NH with π -electrons of benzene ring is affected by proton donating properties of NH groups, their position and sterical hindrance [7].

Here, it was observed that optical density of C = C band centered at 1600 cm^{-1} (D_{1600}) of PUU-2 is by 56 % more than that of the PUU-1 polymer due to improved conjugation effect. Earlier [5] it was demonstrated that introducing halogen containing substances of different nature (LiCl or PVC) into PUU having 4,4'-methylenedianiline and 2,4-TDI / 2,6-TDI based hard segments induces partial destruction of hard domains because of formation of H-bonding network between Cl and NH groups of urethane-urea segments. Comparative analysis of FTIR spectra of PUU-1 and PUU-2 elastomers containing 5 wt % of LiCl shown some differences in the spectral region of above 3000 cm^{-1} . For PUU-1 / LiCl it was observed partial destruction of

Table 2 – FTIR spectral parameters of PUUs and PUU-containing blends

Sample	C = O _{urea-b}			C = O _{ureth-f}	Amide II		NH _b		Aryl
	ν [cm^{-1}]	D_i [a.u.]	α [%]	D_{1730} [a.u.]	δ [cm^{-1}]	D_i [a.u.]	ν [cm^{-1}]	A_{NH}	D_{1600} [a.u.]
PUU-1	1639	2.04	33.0	1.27	1539	2.03	3288	9.5	0.51
PUU-1/LiCl	1641	0.83	13.4	-	1543	2.79	3289	11.5	0.85
PUU-1/30 PVC	1639	1.44	26.0	1.34	1539	2.20	3289	7.8	0.60
PUU-1/70PVC	1640	1.18	15.0	2.87	1538	2.60	3289	7.6	0.80
PUU-2	1638	0.54	10.0	1.43	1538	2.33	3294	7.8	0.80
PUU-2/LiCl	-	-	-	-	1543	3.38	3278	12.3	1.63
PUU-2/30PVC	-	-	-	1.62	1537	2.91	3302	7.8	1.17
PUU-2/70PVC	1639	-	-	1.79	1537	2.91	3307	7.5	1.22
PUU-3	1641	2.26	35.0	2.07	1545	3.32	3292	8.2	1.19
PUU-3/LiCl	-	-	-	-	1547	4.67	3285	18.5	2.45
PUU-3/30PVC	-	-	-	2.18	1542	4.67	3291	8.2	1.86
PUU-3/70PVC	1643	0.50	7.0	2.20	1539	4.08	3297	6.6	1.76

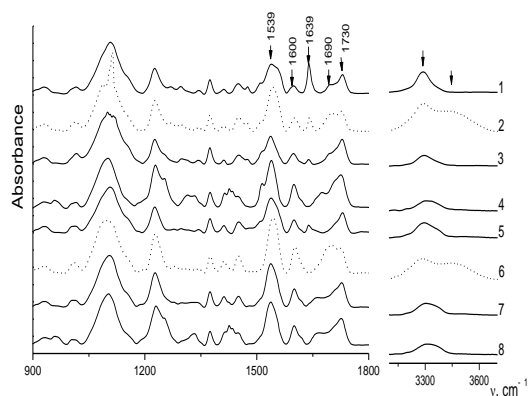


Fig. 1 – FTIR spectra of PUU-1 (1), PUU-1/LiCl (2), PUU-1/30PVC (3), PUU-1/70PVC (4), PUU-2 (5), PUU-2/LiCl (6), PUU-2/30PVC (7) and PUU-2/70PVC (8)

domain structure and decreasing α by 59 % as well as increasing A_{NH} by 21 % and $D_{NH(3289)}$ by 5 % without changes in peak position. For PUU-2/LiCl composition was found destruction of domain structure and increasing the A_{NH} value by 57 % with low-frequency shift of NH band by 16 cm^{-1} . Shift of *amide II* to high-frequency region by 5 cm^{-1} and increasing D_{1543} by 45 % was identified as well. It is known that in H-complexes strengthening H-bonding decreases a frequency of NH stretching vibrations and increases a frequency of deformation vibrations [8]. Clearly, that similar changes for PUU-2 / LiCl system is evidenced of complexation and a formation of strong intermolecular $NH^+ \cdots Cl^-$ bonds, whereas an appearance of new band of “free” NH groups (NH_b) at 3450 cm^{-1} is observed due to destruction of intramolecular $NH^+ \cdots O=C$ bonds in PUU-2. These data are evidenced of formation of dense H-bonds network in PUU-2 / LiCl compared to PUU-1/LiCl system.

Theoretical calculations of the potential of internal rotations as a function of the angle of rotation around $C_{aryl}-N$ bond for both urethane groups of 2,4-TDI shown that rotation vibrations of urethane groups in position 4 less hindered [9]. So, presence of methyl group in 2,4-TDI fragments shifts electron density in benzene ring to *ortho*- and *para*-position and increases proton-donating ability of NH groups in position 4. To the other hand, loosely dense packing of asymmetric hard segments in corresponding domains is caused by high availability of H-bonding between urethane-urea fragments and Cl^- anions of LiCl. Thus, a level of conjugation of NH with π -electrons of benzene ring is higher for PUU-2 / LiCl (D_{1600} values for PUU-2 / LiCl and PUU-1 / LiCl increased by 85 and 66 %, respectively). Redistribution of the bands intensities in the region of *amide I* is due to formation of complexes between Li^+ cations and oxygen of carbonyls and ether groups.

Introducing PVC in PUU elastomers induces some changes in FTIR spectra of the polymer blends. Comparative evaluation of α , A_{NH} , and

integrated intensities of *amide II* and $C=C_{aryl}$ bands is allowed to conclude a formation in PUU / PVC weaker H-bonds network compared to PUU / LiCl compositions. For the PUU-1 / PVC blends containing 30 and 70 % of PVC the α value decreased by 21.0 and 54.3 %, respectively, and A_{NH} decreased by 17.9 and 20 %, respectively, where as for the PUU-2 based compositions H-bonds with $C=O$ of urea groups are destructed and the new band of “free” $C=O$ at 1665 cm^{-1} appears. In spite of destruction of intermolecular H-bonds in PUU-2 / 30PVC the A_{NH} is in a level of pure PUU-2 (7.8), but for PUU-2/70PVC blend A_{NH} decreased by 3.8 %. On the base of aforementioned results it could be concluded that in PUU-2/PVC composite H-bonding network is stronger compared to PUU-1 / PVC systems. The structure of isocyanate fragments in hard segments of the elastomer playing important role in interface interactions in polymer/polymer systems as well.

Replacement of flexible PPG fragments (PUU-2) onto PTMG (PUU-3), which is partially mixed with PVC at interface [3], leads to initiation of phase separation processes between hard and soft segments of the polymer (see Fig. 2).

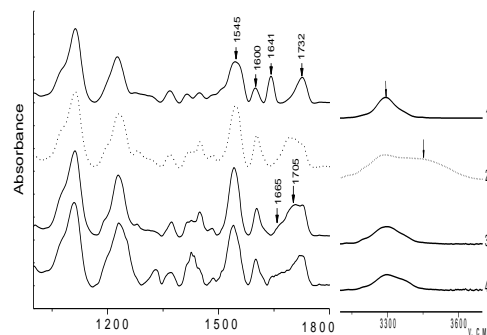


Fig. 2 – FTIR spectra of PUU-3 (1), PUU-3/LiCl (2), PUU-3/30PVC (3) and PUU-3/70PVC (4)

The content of $C=O_{urea-b}$ groups increased by 35 %, A_{NH} value increased to 8,2, and NH_b band slightly shifts to low-frequency region to 3292 cm^{-1} as a result of slight increasing a density of intramolecular H-bonds network. As it was observed the influence of the introduction of LiCl and PVC on domain structure and intramolecular H-bonds network of PUU-3 and PUU-2 is very similar. However, some differences in FTIR spectra of PUU-3 containing composites, namely a position of characteristic bands, were also identified. Shifts of NH_b band to low frequencies ($\Delta\nu = 7 \text{ cm}^{-1}$) and *amide II* band to high frequency region ($\Delta\nu = 2 \text{ cm}^{-1}$) for PUU-3/LiCl composition in comparison with PUU-2/LiCl is probably due to decreasing density of H-bonds network. Introducing 30 % of PVC into PUU-3 do not change a position of NH_b band, where as an increasing wavenumber of the band by 5 cm^{-1} is observed when PVC content reached to 70 %. For PUU-2/30PVC and PUU-2/70PVC

the NH_b band shifts to high frequencies by 8 and 13 cm^{-1} , respectively. Increasing D_i of *amide II* band as a result of conjugation between NH and benzene ring (D_{1600} value for PUU-3/LiCl and PUU-3/30PVC growth by 105 and 56 %, correspondingly) should be also noted.

A number of $\text{C}=\text{O}_{\text{ureth-b}}$ groups in PUU-3 based blend (compared with pure PUU-2) increased by 25 % and a new band at 1705 cm^{-1} appears as a result of enhancing compatibility between PTMG segments and PVC. For PUU-2/30PVC in comparison with pure PUU-2 a quantity of $\text{C}=\text{O}_{\text{ureth-b}}$ groups increased only by 4 %. It is clear, a structure and polarity of soft segments of elastomer have an impact on interface interactions and, therefore, in PUU-3/30PVC system the two types of H-bonds such as $\text{NH}^+\cdots\text{Cl}^-$ and $\text{C}=\text{O}\cdots\text{H}^+$ are identified.

Thus, from FTIR analysis it should be concluded that chemical structure of soft and hard segments of PUU as well as cohesion energy of hard domains have an impact on proton donating ability of NH groups during formation of H-bonds network between PUU and Cl-containing constituent.

Morphology studies (Figure 3) of the composites by SEM show a formation of nanoheterogeneous structure with averaged size of PVC phase of 20-40 nm dispersed in elastomer matrices due to strong interface H-bonds in PUU-2/30PVC and PUU-3/30PVC.

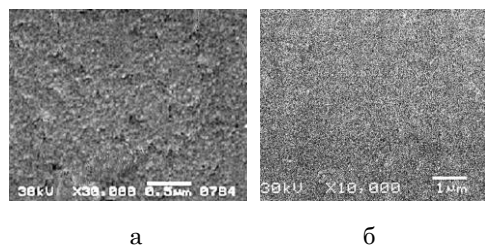


Fig. 3 – SEM images of PUU-2/30PVC (a) and PUU-3/30PVC (b)

Mechanical properties of PUU are governed by chemical structure and phase separation between hard and soft segments of the polymers. An

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absence of structural asymmetry and increasing cohesion energy of hard segments increase their segregation level, tensile strength at break (σ_b) and modulus E_{100} values and reduce elongation at break values as well. As it was observed in Figure 4, deviation of experimental σ_b values from theoretical ones correlates with FTIR spectral data, which describe interface interaction energy in binary systems.

Enhanced compatibility between PVC and PUU-2 and PUU-3 elastomers based on hard segment of asymmetric structure leads to increasing σ_b values in full concentration range. Maximum of strengthening (experimental σ_b values exceed the theoretical ones by 30-35 %) was observed for PUU-2 and PUU-3 based composites containing 30-50 wt. % of PVC.

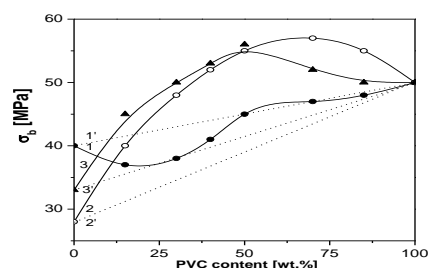


Fig. 4 – Tensile strength at break (σ_b) versus concentration dependences for PUU-1 (1), PUU-2 (2) and PUU-3 (3)

Thus, conducted research shown that chemical structure of poly(urethane-urea) and cohesion energy of hard segment domains have a great impact on the intermolecular interactions between PUU macromolecules and chlorine constituent of LiCl and PVC. Asymmetry of hard segments and weak intradomain H-bonds in PUU are favored by improving interface interaction energy between PUU and PVC. Strong H-bonds network in the polymer/polymer systems promotes a formation of nanoheterogeneous structure and improves the tensile properties of the composites.