

Miscibility of the polyurethane elastomer with poly(vinyl chloride)

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An influence of interfacial interactions on the morphology, thermal stability and mechanical properties of the polymer blends derived from oligoethers based poly(urethane-urea)s (PUU) elastomers and poly(vinyl chloride) (PVC) were studied. The polymer blends were produced via solution-cast technique using N,N-dimethylformamide as a solvent. In accordance with DSC studies the polymer-polymer compositions with strong interfacial interactions and a size of dispersed PVC phase of 30–50 nm which uniformly distributed in elastomeric matrix are characterized by single phase transition temperature. Otherwise, for the compositions with weaker interfacial interactions were identified two glass transition temperatures and a size of dispersed PVC phase increases up to 2 μm. TGA thermograms demonstrate the enhanced thermal stability of the blends in comparison with neat PUU and thermal degradation process proceeds in three stages. The comparative analysis of experimental composition-dependent tensile strength at break curves with theoretical (additive) ones has shown an impact of interfacial interactions on physical-mechanical properties of the compositions. Finally, the tensile strength values determined for nanoheterogeneous composition with PVC content of 30 wt% grows by 30 %.

Keywords: polymer blend, poly(urethane-urea)s, poly(vinyl chloride), nanocomposite, thermal stability.

Introduction.

Polyurethane elastomers (PU) that consist of immiscible hard and soft segments are well-known as versatile polymers because of variety of their compositions and unique properties, such as biocompatibility, frictional resistance, softness and low-temperature properties. PU polymers find industrial application as a component of polymer blends. A special interest attracts the recipes based on PU and poly(vinyl chloride) (PVC) because of possibilities of regulation of interfacial adhesion and structure of the components as well as physical-mechanical properties of polymer materials in accordance to requirements. Miscibility between the components of aforementioned polymer-polymer blends is controlled by specific interfacial interactions between α -hydrogen of PVC and carbonyl group of another polymer. Binary blends are characterized by enhanced hydrolysis resistance, long-term exploitation ability and lower cost compared with commercial polyurethane based thermoplastic elastomers. The PU/PVC blend systems are typically used in several applications such as coatings, artificial leather, adhesives and materials for medical uses.

The chemical structure of soft and hard segments of polyurethane block copolymers has a great impact on phase separation processes, compatibility with chlorinated polymers and mechanical properties of the composites [1–6]. Poly(ether-urethane)s synthesized from

poly(oxypropylene glycol) (PPG) are immiscible with PVC and its blends are characterized by poor mechanical properties in all compositional range. Poly(tetramethylene glycol) (PTMG) segments of PUU are partially compatible with PVC resulting in increased glass transition temperature of corresponding flexible segments. However, poor miscibility could be overcome by introducing highly polar urethane-urea hard segments into PUU structure. It was found a great impact of a structure of both diisocyanate and a chain extender of urethane-urea hard segments on the interfacial interactions of PUU with PVC [7]. Structural asymmetry of hard segments and weak intradomain H-bonding in PUU improves interface interaction energy between PUU and PVC components. Nanoparticulate PVC phase (content 30–40 wt%) playing a role of physical cross-links in elastomeric matrix improves the tensile properties of the final composites. Otherwise, increasing thermoplastic PVC content in the polymer blends reduces an interfacial adhesion and mechanical properties of composites moderately.

Extensive studies of interfacial interactions and features of a formation of nanoheterogeneous structure in PU/PVC systems are conducted during last years to achieve novel functional characteristics for polymer-polymer nanocomposites. Previous experiments show that strong H-bonding network [7] between polar urethane and

Table 1. Compositional characteristics of PUU

Sample	Oligoether	Chain extender	Viscosity $[\eta]$, [m ³ /kg]	Density, 10 ³ kg/m ³
PUU-1	PTMG	DMDA	0,085	1,120
PUU-2	PPG	TDA	0,062	1,105
PUU-3	PTMG	HMDA	0,125	1,097

urea groups of PUU and PVC provide a formation of nanoheterogeneous structure of the composites containing up to 30–40 wt% of PVC.

The aim of the present work was to study an effect of chemical structure of PUU on morphology, thermal stability and mechanical properties of the polymer-polymer composites containing 30 wt% of PVC.

Experimental.

Materials.

PPG ($M_n = 1000$) and PTMG ($M_w = 1000$) were used as received. Toluene-2,4-diisocyanate (2,4-TDI) was purified by distillation under reduced pressure according to standard procedure. 4,4'-methylenedianiline (DMDA), toluene-2,4-diamine (TDA) and hexamethylenediamine (HMDA) as chain extenders were used. PUU used in the studies were produced via conventional two-step prepolymer approach in N,N-dimethylformamide (DMF) solution. Compositional characteristics of PUU were summarized in Table 1. Poly(vinyl chloride) ($M_w = 8.0 \cdot 10^4$) with chlorine content of 56.3 wt.% was selected for preparation of the polymer composites. Pure poly(urethaneurea)s as well as PUU/PVC composite film samples were prepared by casting of DMF solutions on a Teflon substrate. Obtained films were dried at 50 °C in oven to a constant weight.

Characterization.

The glass transition temperatures (T_g) of the samples were measured using a differential scanning calorimeter DSC-2M in the temperature range from -100 to 200 °C at a heating rate of 2 °C/min. The morphology studies of the composites were performed by JEOL JSM 6060 LA Scanning Electron Microscope. Thermogravimetric analysis was performed on a TG 50 Mettler Toledo analyzer oper-

Table 2. DSC characteristics of PUU-1 and PUU/PVC blends

Sample	T_{g1} , °C	T_{g2} , °C	T_{g3} , °C	T_{g4} , °C
PUU-1	-54	117	-	-
PUU-1/PVC	-30	-	78	41
PUU-2/PVC	1	-	-	-
PUU-3/PVC	-4	-	83	-

ating in dynamic mode at heating rate of 20 °C/min. Mechanical properties were measured with a tensile tester at room temperature. The intrinsic viscosity $[\eta]$, was measured at 25 °C in DMF.

Results and discussion.

It is known that the chemical structure of soft and hard segments PU has a great effect on phase separation and domain structure of polyurethane block copolymers. An effect of urea units on 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 could be hindered significantly due to disordering of the structure.

The miscibility of PUU with PVC (content 30 wt%) was investigated by DSC (table 2). Phase separation between soft and hard segments of pure PUU-1 leads to appearance of glass transition temperature of amorphous oligoether phase with $T_{g1} = -54$ °C, T_{g2} of the hard domains at 117 °C and an endothermic peak of melting process at the temperature of 190 °C. PVC component has glass transition temperature (T_{g3}) at about 70 °C. The PUU-1/PVC blend is characterized by higher T_{g1} , T_{g3} and appearance of glass transition of mixed phase (T_{g4}) at 41 °C. It means that polymer-polymer system became a partially compatible. The T_{g3} value is attributed to combined glass transition of domain structure of PUU-1 and PVC phase. As we suppose a growing T_{g3} is due to restriction of segmental mobility of PVC polymer chains as a result of their intermolecular interactions with hard segments of the elastomer at interface. Enhancing mutual diffusion of macromolecules of

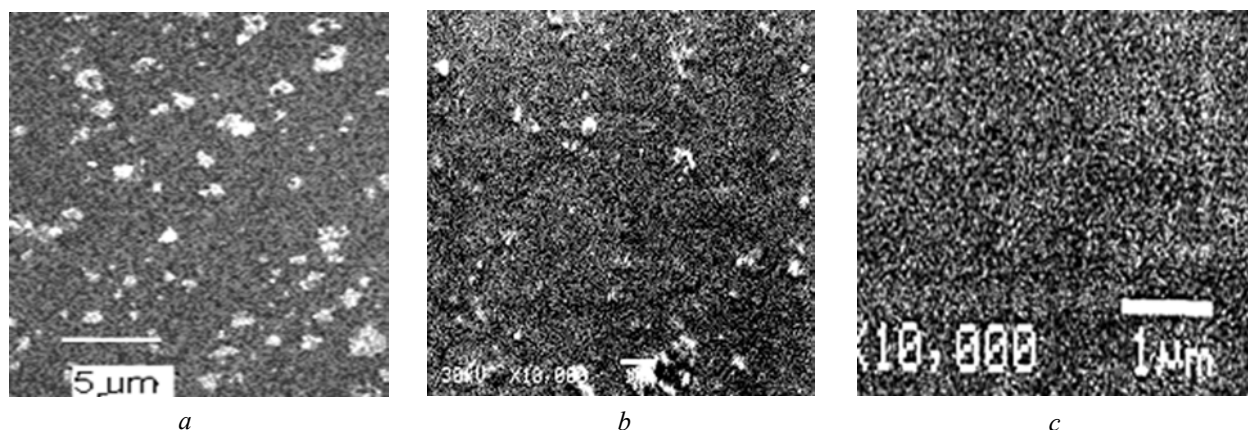


Fig. 1. SEM images of PUU-3/PVC (a), PUU-1/PVC (b) and PUU-2/PVC samples (c)

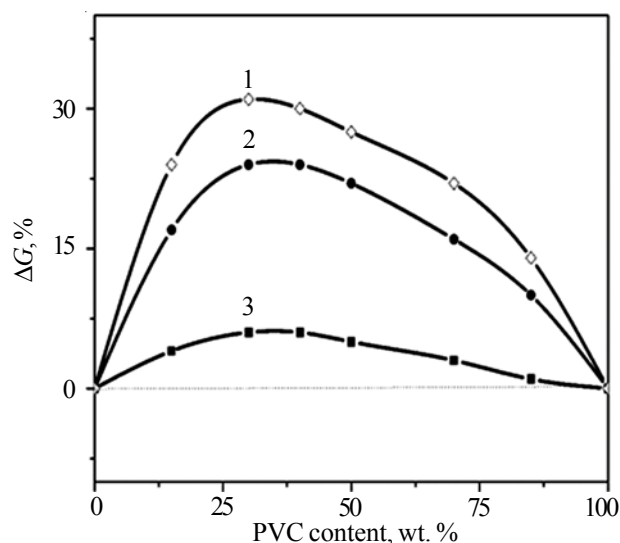


Fig. 2. Deviation of experimental tensile strength at break from theoretical ones for PUU-2/PVC (1), PUU-1/PVC (2) and PUU-3/PVC (3) compositions

both polymers because of its interactions improves interface adhesion of compositions studied. The PUU-2/PVC blend is characterized by a presence of a single glass transition temperature, which indicates onto enhanced compatibility between polymers. Stronger interfacial interactions in PUU-2/PVC compared to PUU-1/PVC composites was confirmed by FTIR spectroscopy analysis [7]. The PUU-3/PVC blend has two glass-transition temperatures due to typical biphasic structure of the compositions.

These conclusions were confirmed by the scanning electron microscopy analysis. The effect of interfacial interactions on a size of PVC phase dispersed within elastomeric matrix is shown in Fig. 1.

SEM image of heterogeneous PUU-3/PVC composition demonstrates an average particle size of dispersed PVC phase as much as 1–2 μm (Fig. 1a). Enhanced compatibility between PUU-1 and PVC reduces averaged size of PVC particles to 150 nm (Fig. 1b). Stronger interfacial interactions in PUU-2/PVC blend (Fig. 1c) increase contact surface area and decrease a size of PVC particles to nanoscale (30–50 nm) and as a result the nanocomposite forms. Nanoparticulate PVC phase playing a role of physical cross-links and maximal strengthening effect was achieved for PUU-2/PVC blends (Fig. 2). For PUU-1/PVC and PUU-2/PVC composites a difference between experimental tensile strength at break values from theoretical ones ($\Delta \sigma$) reaches 24–30%. Weaker H-bonding network in PUU-3/PVC system promotes a formation of biphasic structure.

Conventional polyurethanes are known to exhibit small resistance to heat, whereas thermal stability of PU/PVC blends demonstrates contradictory results. Typically PVC/PU blends have lower thermal stability than neat elastomer [8]. The reason of better thermal stability of some PVC/PU blends can be explained by analysis of specific

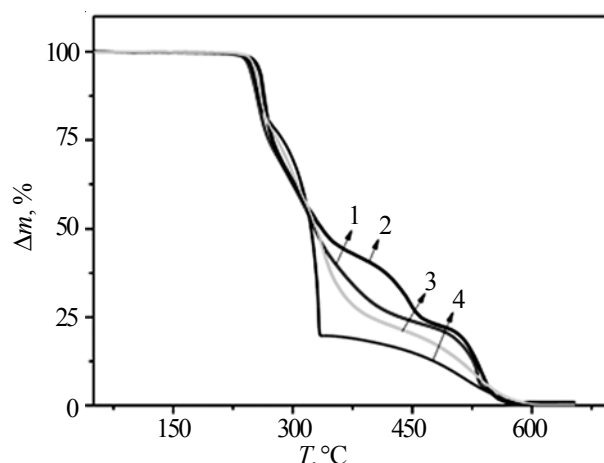


Fig. 3. TGA curves of PUU-1 (1), PUU-1/PVC (2), PUU-2/PVC (3) and PUU-3/PVC (4)

interactions between the C=O groups of the urethane segments and α -H of chlorinated polymer or dipole-dipole C=O...C1–C interactions [9, 10]. Thermal stability of PVC is also enhanced because of favorable interactions of PVC macrochains and PU hard segments of the elastomer [11].

Thermal stability was evaluated by TGA data. The TGA curves of PUU-1 and the polymer blends are shown in Fig. 3. The decomposition curves of PUU-1 and polymer blends show a typical three-step weight loss. First step of the PUU-1 weight loss in the range of 232–283 $^{\circ}\text{C}$ is related to decomposition of urethane groups. In the second step (283–446 $^{\circ}\text{C}$) a degradation of urea groups of the elastomer at high decomposition rate occurs. The third step at the temperatures of 446–577 $^{\circ}\text{C}$ relates to degradation of ether segments of the elastomer. The initial decomposition temperature (T_{in}), the temperatures of the weight loss percentage $T_{\Delta m5\%}$ (temperature of the 5% weight loss), $T_{\Delta m10\%}$, $T_{\Delta m20\%}$, $T_{\Delta m30\%}$, $T_{\Delta m50\%}$ and activation energy (E_a) determined by Friedman method [12] are given in Table 3. A two stage degradation pattern is seen in the case of PVC [11]. The first stage begins at 180 $^{\circ}\text{C}$ and ends at 375 $^{\circ}\text{C}$ with a weight loss of 59,8%/. The second stage of degradation proceeds at 375–490 $^{\circ}\text{C}$ with weight loss of 89,5%. The temperature of 5% weight loss for PVC polymer reaches 220 $^{\circ}\text{C}$. It has been found that the initial decomposition temperature, the temperatures of the weight

Table 3. Thermogravimetric characteristics of PUU-1 and PUU/PVC blends

Sample	T_{in} , $^{\circ}\text{C}$	$T_{\Delta m5\%}$, $^{\circ}\text{C}$	$T_{\Delta m10\%}$, $^{\circ}\text{C}$	$T_{\Delta m20\%}$, $^{\circ}\text{C}$	$T_{\Delta m30\%}$, $^{\circ}\text{C}$	$T_{\Delta m50\%}$, $^{\circ}\text{C}$	E_a , kJ/mol
PUU-1	232	246	252	262	281	327	229
PUU-1/PVC	246	257	262	269	284	336	303
PUU-2/PVC	241	252	257	269	299	323	300
PUU-3/PVC	239	249	255	268	270	329	239

loss percentage and activation energy for PUU-1/PVC blend is higher than those of the pure elastomer. It should be noted that PUU-3/PVC sample has lower thermal stability. The higher thermal stability of PUU-1/PVC and PUU-2/PVC blends in comparison with PUU-3/PVC composition can be explained by stronger interfacial interactions between NH groups of the hard segments of elastomer

and chlorine groups of PVC.

Thus, the studies conducted demonstrate that increasing of interface interaction energy between PUU and PVC components of polymer blends provides a formation of nanoheterogeneous structure, improves the tensile properties and thermal stability of the final composites.

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Сумісність поліуретанових еластомерів з полівінілхлоридом

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Досліджено вплив міжфазних взаємодій на морфологію, термічну стійкість і механічні властивості сумішей поліуретаносечовинних еластомерів (ПУМ) на основі олігоетерів і полівінілхлориду (ПВХ). Суміші полімерів отримували з розчину диметилформаміду. Згідно з даними ДСК, полімер–полімерні системи з сильними міжфазними взаємодіями і розмірами частинок дисперсної фази ПВХ в еластомерній матриці близько 30–50 нм характеризуються одним релаксаційним переходом, тоді як при слабших взаємодіях на межі поділу фаз бінарні системи характеризуються двома релаксаційними переходами температури склування і розмір дисперсної фази збільшується до 2 мкм. Дослідження методом ТГА показало, що полімерні суміші у порівнянні з ПУМ мають підвищену термостабільність і термодеструкція відбувається у три стадії. Порівняльний аналіз експериментальних і теоретичних (адитивних) залежностей міцності при розриві від складу композицій демонструє істотний вплив міжфазних взаємодій на механічні характеристики композитів і міцність наногетерогенної системи підвищується на 30 % за 30 %-вого вмісту ПВХ.

Ключеві слова: полімерна суміш, поліуретансечовина, полівінілхлорид, нанокompозит, термостійкість.

Совместимость полиуретановых эластомеров с поливинилхлоридом

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Исследовано влияние межфазных взаимодействий на морфологию, термическую стойкость и механические свойства смесей полиуретанмочевинных эластомеров (ПУМ) на основе простых олигоэфиров и поливинилхлорида (ПВХ). Смеси полимеров получали из раствора диметилформамида. Согласно данным ДСК, полимер–полимерные системы с сильными межфазными взаимодействиями и размером частиц дисперсной фазы ПВХ в эластомерной матрице около 30–50 нм характеризуются одним релаксационным переходом, тогда как при более слабых взаимодействиях на межфазной границе бинарные системы характеризуются двумя релаксационными переходами температуры стеклования и размер дисперсной фазы увеличивается до 2 мкм. Исследование методом ТГА показало, что полимерные смеси по сравнению с ПУМ имеют повышенную термостабильность и термодеструкция протекает в три стадии. Сравнительный анализ экспериментальных и теоретических (аддитивных) зависимостей прочности на разрыв от состава композиций демонстрирует существенное влияние межфазных взаимодействий на механические характеристики композитов, и прочность наногетерогенной системы повышается на 30 % при 30 %-ном содержании ПВХ.

Ключевые слова: полимерная смесь, полиуретанмочевина, поливинилхлорид, нанокompозит, термостойкость.