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MULTIBLOCK COPOLY(URETHANE-AMIDE-IMIDE)S WITH THE PROPERTIES OF THERMOPLASTIC ELASTOMERS

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Abstract. Multiblock (segmented) copoly(urethane-amide-imide)s containing flexible segments of polypropylene glycol (PPG) and rigid segments of bis(urethane-amide-imide) in repeating units were obtained and investigated. Copolymers were prepared of PPG terminated by 2,4-toluyilene diisocyanate (M_n=2300), 4-chloroformylphthalic anhydride and aromatic diamines. Thermal properties of copolymers were analyzed by TGA and DSC methods. The mechanical properties of copolymer films were measured by tensile test and DMA method. It is shown that copolymers have elastomer properties. The chemical structures of copolymers capable of processing by injection molding were determined and the mechanical properties of the obtained moldings were estimated. A conclusion was drawn that the studied copolymers have the properties of thermoplastic elastomers (thermoelastoplasts).

Keywords: polyurethanes, polyamide-imides, multiblock (segmented) copolymers, thermal stability, glass transition temperature, mechanical properties, films, injection molding, thermoplastic elastomers

1. Introduction

Multiblock (segmented) copoly(urethane-amide-imide)s **(PUAI)** were first synthesized in the 1960s with the purpose of using such polymers as membranes for the pervaporation separation of aromatic hydrocarbons from the mixtures of aromatic and aliphatic hydrocarbons [1]. Attention was drawn to the thermodynamic incompatibility of phases formed by soft (flexible) aliphatic polyester segments and rigid aromatic segments that are parts of copolymer chains. However, the dynamic mechanical properties of these copolymers were not measured, that is copolymers were not characterized as elastomers. At present, interest in multiblock (segmented) PUAI has reappeared due to interest to thermoelastoplasts, which are characterized by increased strength and higher operating temperatures compared with thermoplastic polyurethanes.

Polyurethanes are among the commercial elastomers and are used in many technical fields. For instance, materials with various mechanical properties from very soft foams to resilient elastomers and wear-resistant coatings are obtained on their basis [2]. However, in the general case, mechanical properties of polyurethanes begin to degrade noticeably at temperatures higher than 80°C, and thermal destruction starts at 200°C [3]. A promising way for improving polyurethane elastomer heat resistance and strength is their chemical modification, which consists of introducing the fragments of heterocyclic high-temperature

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resistant polymers into structures of repeating units of polymer chains. Attention to this method of polyurethane modification is paid, for example, in [4-8]. In particular, thermoelastoplastic multiblock poly(ether/ester-imide)s and poly(urethane-imide)s have been successfully studied in recent years by authors' research group [9-15].

Poly(amide-imide)s have become of industrial importance due to a combination of manufacturability and high performance characteristics. Thermoplastic poly(amide-imide)s are processed by extrusion and injection molding methods and have excellent thermal and mechanical properties [16]. Therefore, it seems expedient to modify thermoplastic poly(amide-imides) chemically in order to give these polymers highly elastic properties while maintaining the same processing methods.

Therefore, on the one hand, PUAI should be considered as products of the chemical modification of polyurethanes, which have significantly increased molecular mass and length of hard segments. On the other hand, they are products of thermoplastic poly(amide-imide)s modification. The radicals of aliphatic polyesters are introduced in the structure of their repeating units.

In this article, thermal and mechanical properties of PUAI are investigated in static and dynamic test modes. In PUAI chemical structure, there is the same flexible segment (polypropylene glycol residue) but hard aromatic segments (bis(urethane)amide-imide residues) are varying. It is shown that the studied polymers have elastomers properties and are processed by injection molding into thick-walled products. A priori, it was assumed that the variations of PUAI properties are determined by an interaction of the rigid aromatic phase and the soft aliphatic phasewith the proviso that the phases are thermodynamically incompatible. In each case, the choice of the initial aromatic diamine was proved to be crucial for the polymer properties.

2. Experimental

The following reagents were used in polymer preparation: Poly(propylene glycol), tolylene 2,4-diisocyanate terminated (Mn 2300) (**2300TDI**), 4-Chloroformylphthalic anhydride (**CFPA**), T_m=66-68°C, *m*-Phenylenediamine (**MPD**) T_m=64-66°C, *p*-Phenylenediamine (**PPD**) T_m=145-147°C, 4,4'-Oxydianiline (**ODA**), T_m=188-192°C, 4,4′-(1,3-Phenylenedioxy)dianiline (**TPE-R**) T_m=116°C, 1,4-Bis(4-aminophenoxy)benzene (**TPE-Q**), T_m=173-177°C, 4,4'-Bis(4-aminophenoxy)biphenyl (**BAPB**), T_m=197-200°C, Bis[4-(4-aminophenoxy)phenyl]sulfone (**BAPS**), T_m=194-197°C, Polypropylene oxide (**PO**). *N*-Methyl-2-pyrrolidone (**MP**) was used as a solvent. All of these substances were purchased and have an analytical degree of purity. **2300TDI** was used such as bought in Aldrich.

The following is an example of the preparation of **PUAI** based on **TPE-R**, designated as (CFPA-2300TDI-CFPA)(**TPE-R**). 13.39g (5.82 mmol) **2300TDI** and 2.45g (11.64 mmol) **CFPA** were placed in a two-necked round-bottom flask equipped with an argon inlet-outlet and an overhead stirrer. With constant stirring, contents of the flask were heated according to the following regime: 1 h at 75°C, 1 h at 110°C, 30 min at 160°C and 30 min at 180°C. The reaction mixture was allowed to cool down to room temperature and 13 ml of **MP** was added into the flask, then contents of the flask were cooled down to -10°C. In the cooled mixture (with vigorous stirring), a solution 1.7 g **TPE-R** in 14 ml **MP** was added through an addition funnel. After that, to bring the concentration of the resulting solution to 30%, 13 ml of **MP** were added into the flask for 5 min. The obtained solution was stirred for 30 min at -10°C and for18 h at room temperature. Then, 0.8 ml **PO** was added into the flask in order to neutralize the hydrochloric acid formed during the reaction, by forming chloropropyl alcohol.

IR (film), cm^{-1}: 3485, 3309 (N-H); 2972, 2932, 2868 (C-H); 1780, 1722 (C=O, imide cycle); 1682 (C=O, amid); 1276 (N-C-O); 1089 (C-O-C); 1014, 727 (imide cycle).

^{1}H NMR (DMSO-d_6, 400 MHz) δ = 10.65, 9.77, 8.53, 8.44, 8.32, 8.09, 7.86, 7.50, 7.45, 7.36, 7.29, 7.23, 7.10, 6.87, 6.81, 6.72, 6.61, 4.87, 3.41, 3.31, 2.04, 1.20, 1.03
^{13}C NMR (DMSO-d_6, 100 MHz) δ = 166.9, 163.9, 159.2, 158.3, 156.4, 153.5, 152.4, 140.7, 138. 4, 137.7, 136.9, 135.9, 135.4, 134.8, 134.3, 132.3, 131.2, 130.7, 130.2, 129.6, 127.6, 124.0, 122.7, 120.1, 119.5, 115.7, 114.4, 112.7, 110.1, 108.1, 75.1, 72.9, 18.4, 17.7

All other copolymers were prepared in a similar way. The molecular masses M_w of copolymers averaged between 130000 – 150000.

IR spectra were recorded on a Vertex 70V FT-IR (Bruker, Germany) spectrometer complected with ATR attachment. ^{1}H and ^{13}C NMR spectra were recorded on Avance 400 spectrometer (Bruker, Germany), DMSO was used as solvent. The τ_5 and τ_{10} temperature indices of the polymer thermal stability were determined by thermal gravimetric analysis (TGA) using the TG 209 F1 instrument (NETZSCH, Germany), in argon atmosphere in the temperature range of 30-800°C, with a heating rate 10°C/min. Glass transition temperatures T_g were determined by differential scanning calorimetry (DSC) on the DSC 204 F1 instrument (NETZSCH, Germany) in argon atmosphere, with a heating rate 10°C/min. Dynamic mechanical analyses (DMA) was performed using the DMA 242 C instrument (NETZSCH, Germany) with frequency 1 Hz, strain amplitude 0.1% and a heating rate of 5°C/min. The stretch curves of film and molding samples were recorded using the universal testing system Instron 5940 (Instron, USA) with strain rate 50 mm/min. The samples of polymer moldings were prepared by injection molding on the technological complex DSM Xplore (Xplore instruments, The Netherlands). To determine the molecular mass, the liquid chromatograph "Agilent Technologies 1260 Infinity" was used.

3. Results and discussion

In the presented article, **PUAI** were prepared according to the two-step reaction scheme known in the literature [15]. The preparation of PUAI is based on two chemical reactions. The first –: cyclic anhydrides interact with isocyanates, forming cyclic imides with the elimination of carbon dioxide. The second – amides are formed with the elimination of hydrogen chloride during the acylation of amines with acid chlorides. Accordingly, in the first stage, Poly(propylene glycol), **2300TDI** reacted with (**CFPA**) taken in a double molar excess to form the macro monomer **CFPA-2300TDI-CFPA** which had terminal chloride groups. Then, in the second stage, a chosen aromatic diamine was acylated with macro monomer **CFPA-2300TDI-CFPA** to form a desired polymer. Hydrogen chloride released during the formation of amide bonds was neutralized with **PO**. The **PUAI** preparation was carried out in the one pot manner in MP solution without isolation of the intermediate formed **CFPA-2300TDI-CFPA** product.

The **PUAIs** studied were prepared on the base of 7 aromatic diamines, i. e. only diamines were varied in the reaction scheme. Fig. 1 presents the **PUAI** synthesis scheme (Fig. 1) with the chemical structure of chosen diamines.

As a result, a series of copolymers differing by diamine radicals R was prepared: (CFPA-2300TDI-CFPA)(**MPD**), (CFPA-2300TDI-CFPA)(**PPD**), (CFPA-2300TDI-CFPA)(**ODA**), (CFPA-2300TDI-CFPA)(**TPE-R**), (CFPA-2300TDI-CFPA)(**TPE-Q**), (CFPA-2300TDI-CFPA)(**BAPB**), and (CFPA-2300TDI-CFPA)(**BAPS**).

These polymers have a structure of multiblock (segmented) copolymer, which consists of soft aliphatic segments and hard aromatic segments. Aliphatic soft segment length is determined by using a TDI 2300. Aromatic hard segment includes amide-imide group, urethane group, diamine radical R, urethane group, and amide-imide group, so its length is limited by the choice of diamine. Diamine radicals contain from one to four benzene nuclei and also there is the isomerism of the position of benzene rings.

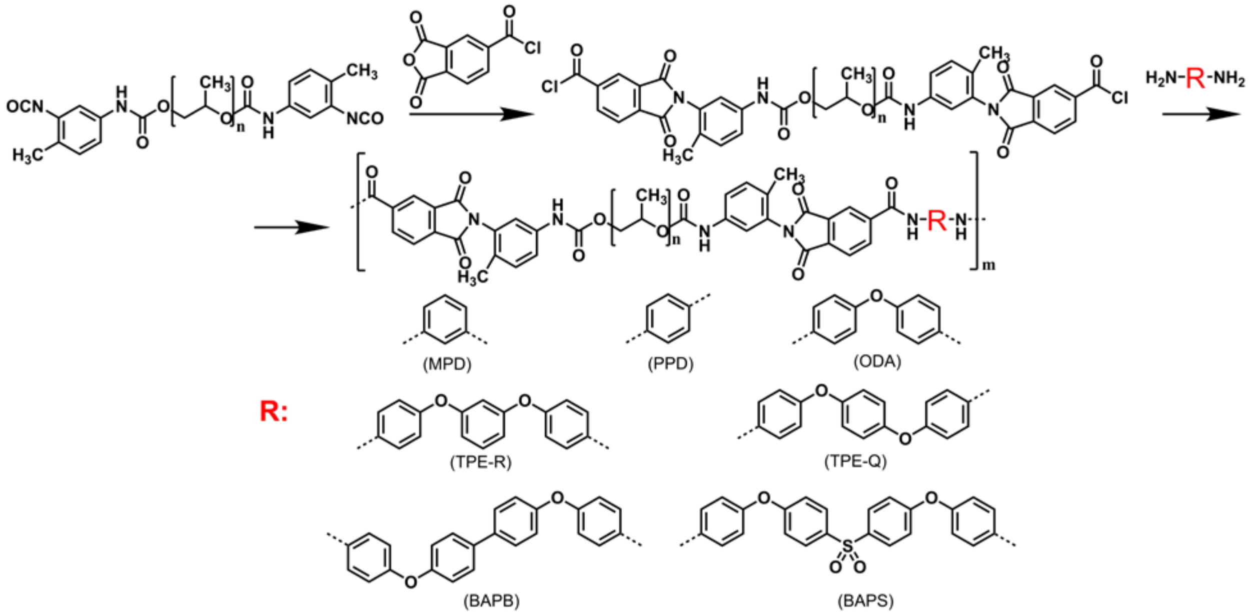


Fig. 1. Synthesis of the (CFPA-2300TDI-CFPA)(R)

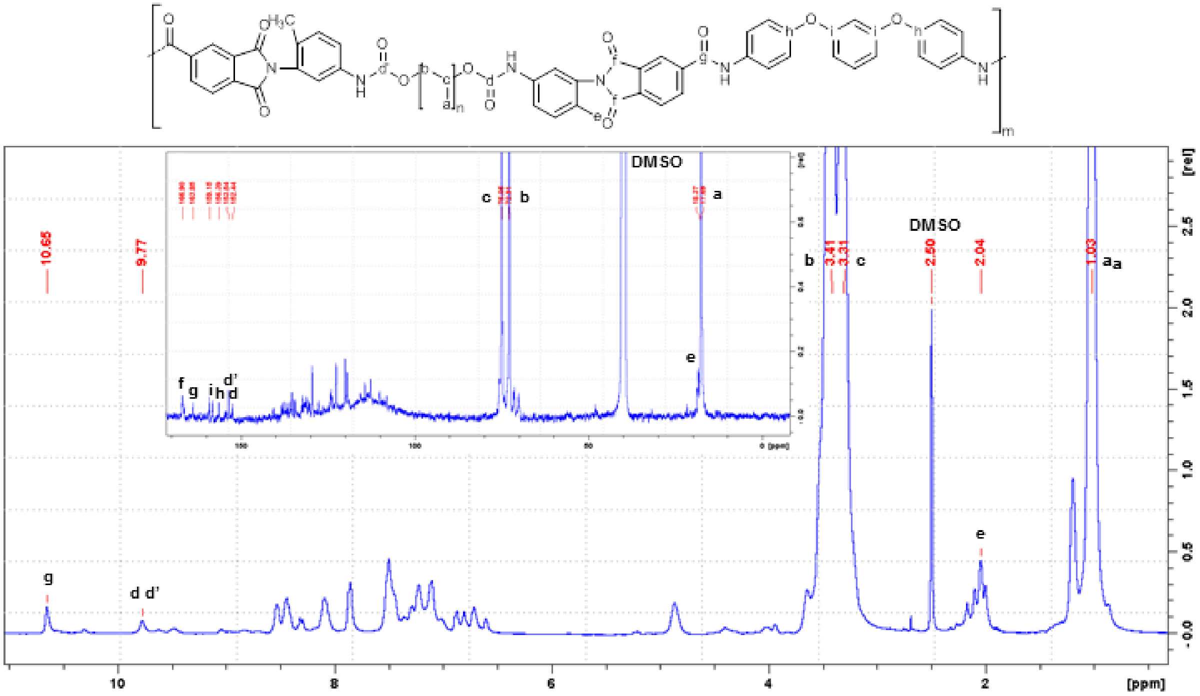


Fig. 2. 1H and 13C NMR spectra of (CFPA-2300TDI-CFPA)(**TPE-R**)

The representative ^{1}H-, ^{13}C NMR and IR spectra of (CFPA-2300TDI-CFPA)(**TPE-R**) were shown in Fig.2-3. ^{1}H NMR method allows analyzing the macromolecular structure by a good discrimination of the different imino protons belonging to either urethane or amide groups. As is clearly shown in the spectrum recorded for polymer (CFPA-2300TDI-CFPA)(**TPE-R**) (Fig. 2), amide NH protons were responsible for a single peak appeared at 10.65 ppm, whereas urethane NH protons led to a peak at 9.77 ppm that is very characteristic for urethane groups within polyurethane macromolecular architectures. In ^{13}C NMR spectrum, the region between 150 and 175 ppm showed four very characteristic peaks appeared at 153.5, 152.4, 163.9, and 166.9 ppm corresponding to urethane groups, amide groups, and imide groups, respectively. Other peaks appeared in this area correspond to (C-O-C)-carbon atoms of amide fragment. Signals at 3.41, 3.31 and 1.03 ppm in ^{1}H NMR spectrum and at 75.1, 72.9 and 17.7 ppm in ^{13}C NMR spectrum corresponds to H- and C-atoms of polypropylene glycol soft segment. Hereby, qualitative interpretation of the NMR spectra fully confirmed the regularity of the proposed macromolecular architecture.

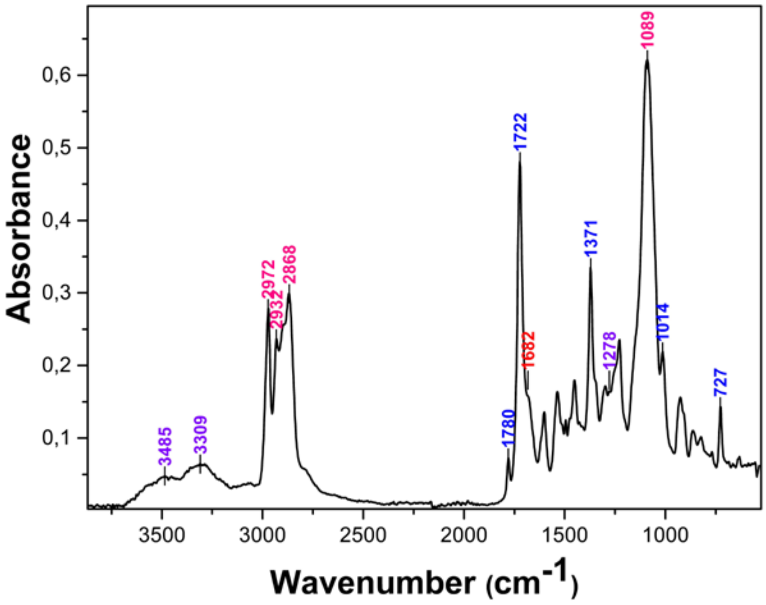


Fig. 3. FT-IR spectra of (CFPA-2300TDI-CFPA)(**TPE-R**)

In IR-spectrum (Fig. 3), a band with an absorption maximum of 1722 cm-1 corresponds to C=O valence vibrations in imide cycles and urethane groups in the indicated spectrum. The arm at 1682 cm^{-1} refers to the C=O vibrations in amide groups. Absorptions at 1780, 727 cm^{-1} which are respectively responsible for the symmetric C=O oscillations and out-of-plane vibrations of imide cycles prove their presence in the polymer under investigation. Wide absorption bands in the 3300-3500 cm^{-1}area characterize N-H groups. The presence of absorption maximum at 1276 cm^{-1} (N-C-O group) confirms the presence of urethane bridges. The group of bands from 2850 to 3000 cm^{-1} refers to the C-H valence vibrations of the aliphatic segment, which the absorption at 1089 cm^{-1}also applies to, relating to ether groups.

As indicated previously, all the studied PUAIs were prepared in the solutions in MP. Strong elastic PUAIs films were formed by watering method. PUAI film tensile tests were carried out. The values of tensile strength, elongation at break, and the modulus of elasticity of polymers are given in Table 1.

Table 1. Mechanical properties of polymer films

Polymer	Tensile test		
	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (MPa)
MPD	1.43±0.2	116±20	1.42±0.2
PPD	0.91±0.1	81±12	2.72±0.6
ODA	1.37±0.2	60±9	8.39±2.6
TPE-R	0.52±0.1	141±20	0.77±0.2
TPE-Q	0.43±0.1	28±8	5.58±1.7
BAPB	1.63±0.4	144±50	1.80±0.2
BAPS	3.21±0.7	340±86	1.16±0.1

In all series of polymers tested, there was no clear dependence of the polymer mechanical properties on the number of benzene rings in the structure of the initial diamine. Nevertheless, it should be noted that in the case of bridged diamines, the highest values of elongation at break (340%) and tensile strength (3.21 MPa) were obtained for (CFPA-2300TDI-CFPA) polymer (**BAPS**), which has oxygen and sulfone bridge groups in the hard segment. There is also an effect of isomerism of the position of benzene rings in the hard segments in the case of **MPD** and **PPD** polymers. A polymer based on the **MPD** diamine is characterized by greater elongation at break and tensile strength values and a lower value of the modulus of elasticity compared to a **PPD** based polymer. This effect may be due to the fact that in the case of **MPD** the meta-position of the amino groups in the diamine structure causes a larger set of macromolecular conformations in **PUAI** as compared to the case of **PPD** with the para position of the amino groups.

Thermal stability of polymers is determined by the processes of their thermal decomposition. **PUAI** thermal stability was evaluated by means of thermal gravimetric analysis (TGA) method. The temperatures corresponding to 5% and 10% mass loss ($\tau_{5,}$ τ_{10}) of the samples at heating were considered as indices of thermal stability. The values of $\tau_{5,}$ τ_{10} and mass residua at 800°C are given in Table 2.

TGA curves are shown in Fig. 4. Vertical section of the curve in the region around 400°C should be associated with the thermal degradation of aliphatic soft segments of the polymers. The sloping portion in the region from 450°C to 800°C can be associated with thermal degradation of aromatic hard segments of polymers. It is indicated that, in general, **PUAI** thermal stability is weakly dependent on the diamine structure, apparently thermal destruction processes begin with chemical bonds in the polyether radical. However, it can be noted that two polymers are significantly distinguished from the other polymer studied. The (CFPA-2300TDI-CFPA)(**MPD**) copolymer has the highest thermal stability (τ_5=312°C, τ_{10}=344°C), and the (CFPA-2300TDI-CFPA)(**TPE-R**) copolymer has the lowest thermal stability (τ_5=272°C, τ_{10}=298°C). It is reasonable to assume that the phase interactions (interpenetration of the phases) formed by the soft and hard segments are manifested with different intensity in the considered cases.

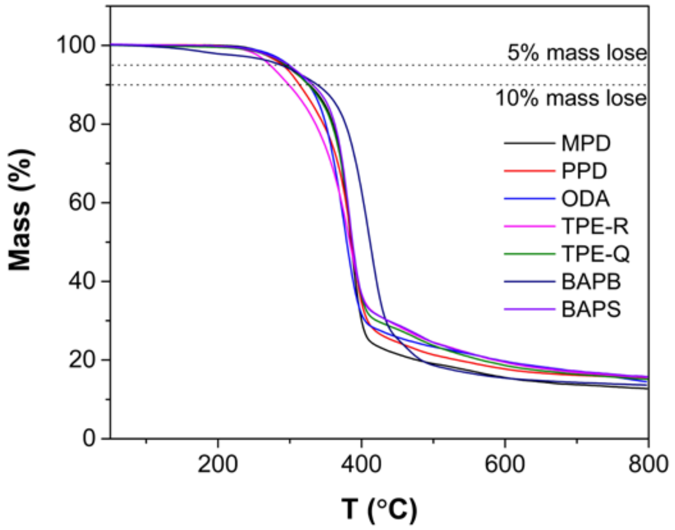
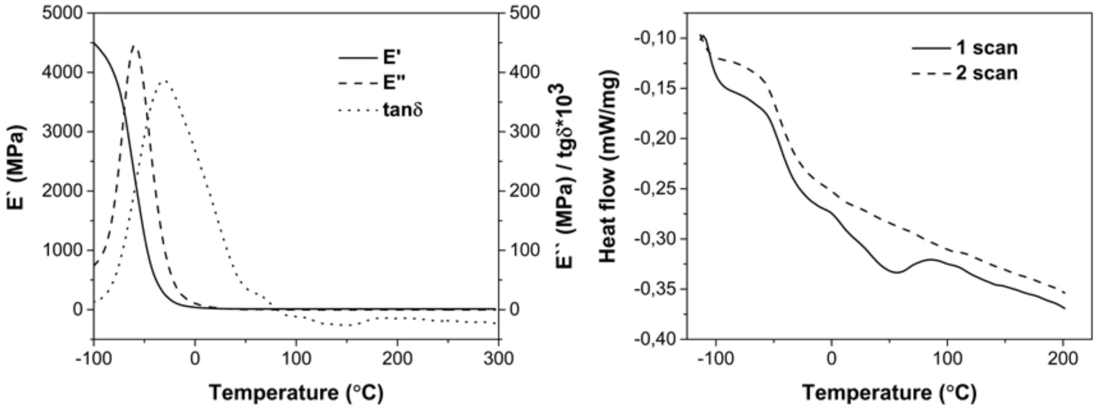


Fig. 4. TGA curves for copolymers

The mechanical properties of the **PUAI** films in the dynamic test mode were measured by means of dynamic mechanical analysis (DMA) method. The temperature dependences curves of the storage modulus (E'), the loss modulus (E") and the angle of mechanical losses (tgδ) were recorded. Typical DMA curves for **PUAI** on the **TPE-R** base are shown in Fig. 5a.

First, attention is drawn to the fact that the maxima on the E', E" and tgδ on temperature dependences are observed in the negative centigrade temperature range. Secondly, these curves have areas corresponding to the practical independence of the values of modulus from temperature, the so-called plateaus of rubber elasticity. It should be noted that the observed effects are typical for multiblock (segmented) copolymers. As it can be seen from Fig. 5a, the plateau of rubber elasticity extends to 280°C, i.e. the sample is in highly elastic state at temperatures, at which polyurethanes are almost completely destructed. Besides, it is reasonable to assume that the significant difference in the values of the maxima on the E" and tgδ temperature dependence curves is a consequence of the interaction between the soft and hard phases. In the case of the polymer (CFPA-2300TDI-CFPA)(**TPE-R**), the thermogram (Fig. 5b) on the first scan indicates the melting of the crystalline phase in the region around 60°C, and in the second scan no traces of recrystallization were detected. That means, in our opinion, that DSC method revealed the processes of melting of the microcrystalline phase formed by the aliphatic polyesters segments.



(*a*) (*b*)

Fig. 5. DMA (*a)* and DSC (*b*) curves for polymer (CFPA-2300TDI-CFPA)(**TPE-R**)

The glass transition temperature (T_g) copolymers was determined using two methods: DSC (Fig. 5b) and DMA (Fig. 5a). In the case of DMA, it should be noted that the T_g values were determined as the temperature of maximum on the temperature dependence of tg δ, as well as of E". Experimental values of T_g of the investigated **PUAI** are presented in Table. 2.

Among the studied polymers (Table 2), a special place is occupied by **MPD** based polymer, which is characterized by the lowest T_g value. In other cases, both according to DSC and DMA data, T_g values decrease with the increase of number of benzene rings in the hard aromatic segments. In addition, in **MPD - PPD** cases, the effects of isomerism of the position of the amide bonds connected to the benzene rings is found, and in **TPE-R - TPE-Q** cases, the effects of isomerism of bridging oxygen atoms connecting the benzene rings take place. These effects are due to the chemical structure of the initial diamines. So, the T_g of **MPD** based sample is significantly lower than **PPD** based analogues (-65.3°C vs. -49.3°C, according to DSC data). In contrast, the T_g of the meta-(aminophenoxy) derivative **TPE-R** is slightly higher than that of the case of the para-(aminophenoxy)derivative **TPE-Q** (-43.9°C vs. -47.1°C, according to DSC data and -30°C vs. -36°C according to the MTA data). It should be assumed that in the cases investigated by us the effect of segmental motion defreezing in the aliphatic polyester chains, which are part of the domains that form the soft phase, appears at temperatures exceeding T_g. The presented data allow suggesting that conformational transitions in hard segments are among the factors affecting segmental motions in the chains that form the soft phase.

Table 2. Thermal properties of copolymers

Polymer	DSC			DMA		TGA		
	T_g (°C)	T_m (°C)	ΔH (J/g)	T_g (°C) by E”	T_g (°C) by tg δ	τ_5 (°C)	τ_{10} (°C)	mass residua (%)
MPD	-65.3	63	13.65	-81	-56	312	344	12.57
PPD	-49.3	-	-	-69	-45	290	313	15.49
ODA	-50.1	50.9	7.99	-75	-51	300	326	14.44
TPE-R	-43.9	56.4	10.2	-59	-30	272	298	15.37
TPE-Q	-47.1	56.9	6.73	-72	-36	295	326	15.14
BAPB	-44.6	45.8	6.33	-65	-41	297	326	10.75
BAPS	-44.6	41.5	5.58	-68	-37	295	330	12.18

The first-scan DSC curves (for example, Fig. 5b) indicate the presence of first-order phase transitions in the investigated copolymers. Table2 shows the experimental values of Tm (the melting temperature) and ΔH (the melting enthalpy) of the copolymers. It is reasonable to assume partial crystallization of soft segments. Attention is drawn to the fact that the values of ΔH in the cases of MPD and TPE-R based copolymer are appreciably higher in comparison with other copolymers. As mentioned above, copolymers of MPD based and TPE-R based contain in their structure benzene rings with substituents in the meta-position, which cause greater freedom of segmental movements in the hard phase. The observed effects confirm the assumption that conformational transitions in the hard segments are among the factors affecting segmental motions in the segments forming the soft phase.

It turned out that the prepared polymers can be processed by the equipment used for thermoplastics processing. Thick-walled products in the form of shoulder blades were made from the prepared polymers by pressure casting method. These moldings were exposed to the tensile test. Typical stress-strain curves are shown in Fig. 6, and the test results are shown in Table 3.

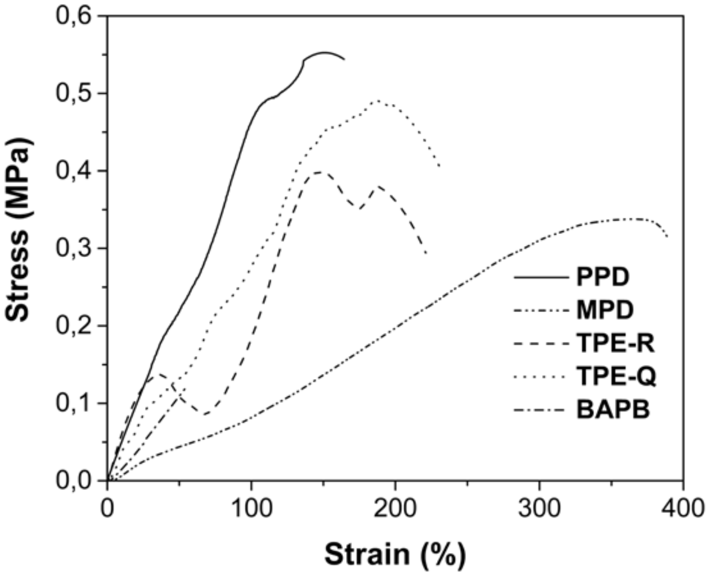


Fig. 6. Stress-Strain curves for polymer molding

Table 3. Mechanical properties of polymer moldings

Polymer	Tensile strength (MPa)	Elongation at break (%)	Initial modulus (MPa)
MPD	0.11±0.03	385±39	0.35±0.1
PPD	0.65±0,2	163±20	0.44±0,3
TPE-R	0.66±0,2	176±27	0.40±0,2
TPE-Q	0.58±0,2	205±32	0.54±0,2
BAPB	0.28±0,1	53±18	0.42±0,1

Results of tensile tests of the moldings indicate that the elongation at break increased in comparison with the film samples in the case of **MPD, PPD, TPE-R** and **TPE-Q** based copolymers. All studied moldings had lower modulus of elasticity as compared with the film samples. The tensile strength of **MPD, PPD** and **BAPB** based copolymers decreased significantly, and tensile strength of **TPE-R** based and **TPE-Q**-based polymers slightly increased within the accuracy. The observed effects can be explained by the domain restructuring during the processing of polymers in the viscous-flow state.

Among the studied moldings, the most interesting is a **MPD** based sample, because it has the maximum elongation at break (385%), while the initial polymer has high thermal stability (τ_5 = 312°C) and the lowest glass transition temperature (T_g = -65.3°C by DSC and T_g = -56°C by tgδ).

4. Conclusion

Multiblock (segmented) copoly(urethane-amide-imide)s containing flexible segments of polypropylene glycol (PPG) and rigid segments of bis(urethane-amide-imide) in repeating units were synthesized and analyzed by ^{1}H-, ^{13}C NMR and IR spectroscopy. Thermal and mechanical properties of synthesized copolymers were studied by TGA, DSC, DMA and tensile tests.

Glass transition temperature (T_g) of all obtained copolymers lies in the negative temperature range on the Celsius scale and, depending on the polymer structure, varies from -65°C to -44°C (by DSC). Copolymers have relatively high thermal stability, τ_5~300°C (by TGA) and are characterized by the presence of a plateau of rubber elasticity in wide temperature range under conditions of dynamic tests.

The investigated multiblock (segmental) copoly(urethane-amide-imide)s have thermoelastoplastic properties and can be processed by conventional equipment for thermoplastics processing, for example by pressure casting method. The moldings, which were made from copolymers, are characterized by tensile elongation values of the order of hundreds of percent.

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