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Influence of soft segments on thermal and mechanical properties of terpoly(ester-ether-ester)s

RAPID COMMUNICATION

Summary — The aim of the work was preparation and investigation of new multiblock terpoly(ester-ether—ester)s (TEEE) containing phthalic acid units as in poly(butylene terephthalate) (PBT) (hard segments) and hydrogenated dimer of dilinoleic acid called as dilinoleic acid sequences (DLA) as hydrophobic ester soft segments, and poly(ethylene glycol) (PEG) as hydrophilic ether soft segments. PEG of different molecular weight (1000 and 4600) was used. Synthesis was performed in a presence of α-tocopherol as non-toxic thermal stabilizer since these materials are targeted for biomedical applications. In this paper, the influence of amount and molecular weight of PEG on thermal and mechanical properties of TEEE is discussed.

Keys words: multiblock terpolymers, thermoplastic elastomers, poly(ethylene glycol), dimer of linoleic acid.

WPŁYW SEGMENTÓW GIĘTKICH NA WŁAŚCIWOŚCI TERMICZNE I MECHANICZNE MULTIBLOKOWYCH TERPOLI(ESTRO-ETERO-ESTRÓW)

Streszczenie — Celem niniejszej pracy było przedstawienie syntezy i badań nowych multiblokowych terpoli(estro-etero-estrów) (TEEE) składających się z kwasowych reszt ftalowych tworzących poli(tereftalan butylenu) (PBT) (segmenty sztywne) i uwodornionego kwasu dilinolowego (DLA) wchodzącego w skład estrowych segmentów giętkich o charakterze hydrofobowym i poli(glikolu etylenowego) (PEG), tworzącego eterowe segmenty giętkie o charakterze hydrofilowym (tabela 1). Zastosowano PEG o różnym ciężarze cząsteczkowym (1000 i 4600). Syntezę prowadzono w obecności α-tekoferolu jako nietoksycznego stabilizatora termicznego ze względu na potencjalne zastosowanie biomedyczne tych polimerów. W pracy przedstawiono wyniki badań wpływu ciężaru cząsteczkowego PEG na właściwości termiczne (tabela 2, rys. 1 i 2) i mechaniczne (rys. 3) TEEE.

Słowa kluczowe: multiblokowe terpolimery, elastomery termoplastyczne, poli(glikol etylenowy), dimer kwasu linolowego.

Thermoplastic elastomers (TPE) are unique class of materials with interesting properties. Though being macroscopically homogeneous, these polymers show phase separation at a microscopic (nanometer) scale. Discreet plastic phases are embedded in the continuous elastomer phase and form physical crosslinks. Hence, TPEs behave like cured rubbers at room temperature and can be processed as plastics at higher temperatures. The development of new biomaterials for specific applications (*e.g.* flexible finger joints) requires different systems, including elastomers (rubbers) with interesting combination of specific physicochemical, mechanical and processing properties [1—3].

Novel materials, namely poly(aliphatic/aromatic-ester)s (PED) of segmented (multiblock) structure (hard/soft segments) were synthesized by El Fray and Slonecki [4] and extensively investigated for biomedical applications [1, 5—7]. PEDs are composed of semicrystalline poly(butylene terephthalate) (PBT) or poly(ethylene terephthalate) (PET) (hard segments) [8] and unsaturated dimer of linoleic acid (DLA) (soft segments). PEDs are synthesized without, often irritant, thermal stabilizers due to excellent oxygen and thermal stability of a component of soft segments (DLA). This feature is especially important if the material is intended for biomedical applications. PED copolymers are biocompatible *in vitro* and *in vivo*, and specially modified with active molecules, they show antibacterial properties [7].

Additionally, their chemical structure can be modified by introducing different monomers being components of soft segments, such as poly(dimethylsiloxane) units [9] or poly(tetramethylene oxide) segments [4, 10],

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contributing specific properties to resulting terpolymers. Poly(ethylene glycol) (PEG) is well known hydrophilic and biocompatible material widely used in biomedical applications [11]. Therefore, novel materials of tailored hydrophilic-hydrophobic properties were prepared by introducing PEG units (molecular weight 1000 or 4600) into PED structure, thus giving PBT/DLA/PEG terpolymers [12].

In this work, we report on the synthesis of new terpoly(ester-ether-ester)s (TEEE) containing PBT, DLA and PEG. The influence of amount and molecular weight of PEG on thermal and mechanical properties was investigated.

EXPERIMENTAL

Materials

The following materials were used in this work:

— dimethyl terephthalate (DMT, ZWCh "Elana", Poland);

— 1,4-butanediol (BD, BASF, Germany);

— poly(ethylene glycol)s with two different molecular weight values, *i.e.* 1000 (PEG_{1000}) and 4600 (PEG_{4600});

— hydrogenated dimer of linoleic acid (DLA, Uniqema/Croda, the Netherlands);

— α-tocopherol (Medana Pharma Terpol Group) used as thermal stabilizer.

Synthesis

The synthesis was performed in two steps. First, an oligomer of butylene terephthalate (PBT), being a component of hard segments, was obtained by transesterification between DMT and BD at elevated temperature in the presence of MgTi catalyst. During the second stage of the reaction PEG_{1000} or PEG_{4600} and hydrogenated DLA, being a component of soft segments, were added with thermal stabilizer (α-tocopherol). The polycondensation was carried out at temp. 250—255 °C under 0.5—0.6 mm Hg of vacuum. The process was considered complete on the basis of the observed power consumption of the stirrer motor when the product of highest melt viscosity was obtained, up to a constant value of power consumption by the reactor stirrer was achieved. The chemical structure of terpolymer is shown by formula (I). In synthesized materials, hard segments content was kept constant (26 wt. %), while DLA and PEG concentrations changed on the feed as presented in Table 1.

T a b l e 1. The compositions and intrinsic viscosity ([η]) of TEEE terpolymers obtained

Number of sample	Composition, wt. %				[η] dl/g
	PBT	DLA	PEG_{1000}	PEG_{4600}	
1	26	74	—	—	0.799
2		59	15	—	0.898
3		37	37	—	0.953
4		15	59	—	1.165
5		—	74	—	1.208
6		59	—	15	1.070
7		37	—	37	1.362
8		15	—	59	1.623
9		—	—	74	1.829

Methods of testing

The intrinsic viscosity ([η]) of TEEEs in phenol-trichloroethylene (50:50) was determined using an Ubbelohde viscometer with capillary k = 0.0112 at temp. 30 °C.

Differential scanning calorimetry (DSC) scans were performed using TA Instruments (DSC Q100) apparatus. The samples were dried before analysis in vacuum at 70 °C, and then kept in a desiccator. DSC analysis was carried out in a triple cycle: first heating, then cooling, and second heating in the range from -120 °C to 30 deg higher than melting temperature of each copolymer. The rate of heating and cooling was 10 deg/min. Glass transition temperature (T_g) was determined from the temperature diagrams as the mid point on the curve inflexion.

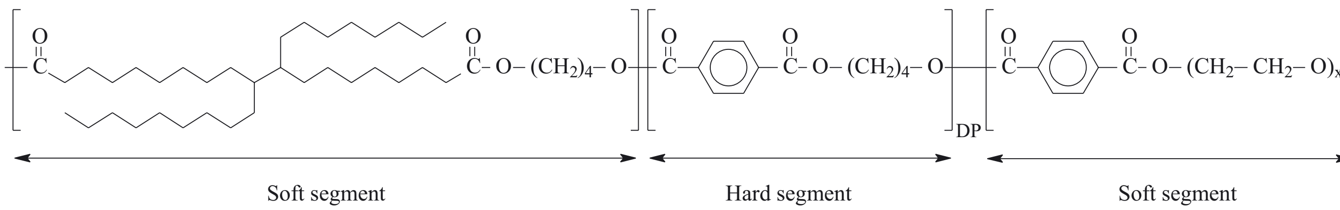
Percentage crystallinity of soft and hard segments (w_{cs} and w_{cn}, respectively) was calculated based on a standard heat of 100 % crystalline PEG (ΔH_1^0 = 219.24 J/g) and PBT (ΔH_2^0 = 144.5 J/g).

The quasi-static tensile data were obtained at room temperature using an Instron 1160 tensile tester equipped with a 500 N load cell employing a crosshead speed of 100 mm/min. The strain was measured using the clamp displacement according to DIN 53 455 standard. The starting clamp distance was 25 mm. The obtained results were averaged for 6 specimens with cross sections of 0.5×4 mm.

RESULTS AND DISCUSSION

TEEE materials were prepared with the use of different concentrations and compositions of soft segments being oligoester and oligoether sequences, respectively. Additionally, oligoethers (PEG) of different molecular weight (M_w = 1000 or 4600) were used. Different M_w of PEG had strong influence on physicochemical behavior of co- and terpolymers. The highest value of [η] was found for sample 9 containing the highest (74 wt. %) concentration of PEG_{4600} (1.829 dl/g). High values of [η] were also found for samples 7 and 8 containing 37 and 59 wt. % of PEG_{4600} (1.362 and 1.623 dl/g, respectively). The lowest value was observed for sample 1 containing only one component of soft segments *i.e.* 74 wt. % of DLA (0.799 dl/g).

According to the main principle of the elastothermoplastic character of multiblock copolymers, at least one of the blocks has to be a soft (low T_g value) material,



(I)

DP — degree of polymerization of hard segments, x = 22, 105

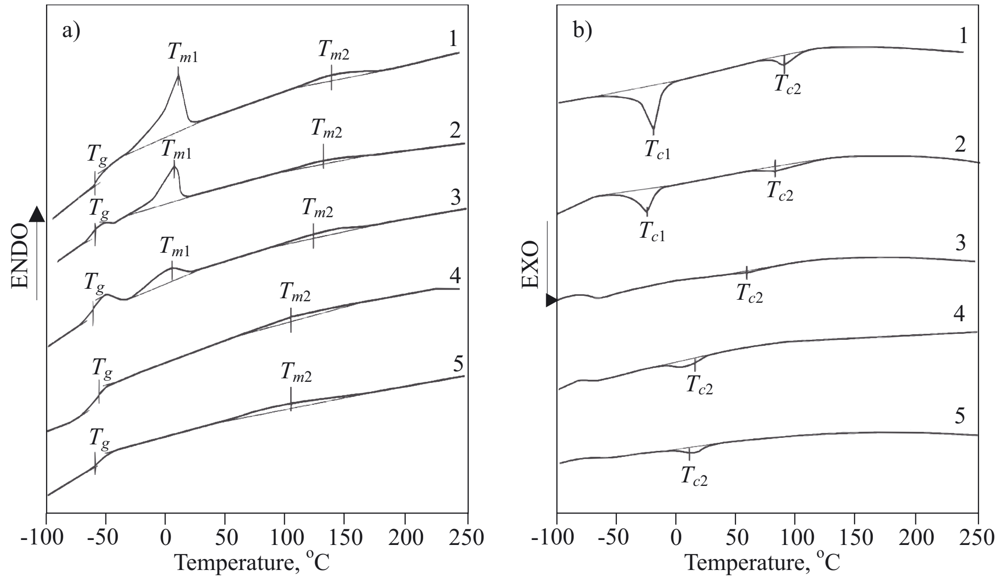


Fig. 1. DSC thermogram during II heating cycle (a) and cooling (b) of multiblock terpolymers with PEG_{1000}; descriptions of curves in agreement with numbers of samples (see Table 1)

T a b l e 2. Thermal properties of TEEE terpolymers

Number of sample	Soft segments						Hard segments					
	T_{g1}, °C	ΔC_p, J/gC	T_{c1}, °C	ΔH_1, J/g	T_{m1}, °C	ΔH_{m1}, J/g	T_{c2}, °C	ΔH_2, J/g	T_{m2}, °C	ΔH_{m2}, J/g	w_{ch}, %	w_{cs}, %
1	-49	0.326	—	—	—	—	11.5	7.641	103	8.492	6	—
2	-55.6	0.530	—	—	—	—	13.4	7.565	102.7	6.072	4	—
3	-62.4	0.484	—	—	3.4	8.381	58.9	5.784	122.3	8.016	5.5	4
4	-59.3	0.504	-32.9	15.55	5.8	24.25	60.2	9.244	125.6	8.738	6	11
5	-59.1	0.442	-20.2	35.76	5.9	36.06	89.9	8.407	137.9	8.899	6.1	16
6	-54.4	0.298	-45.3	14.02	32.7	15.25	30.0	7.261	123.5	5.593	3.8	7
7	-50.7	0.282	-5.7	34.40	34.2	34.79	68.0	6.139	142.9	10.19	7	16
8	-51.3	0.320	8.8	54.69	40.5	59.38	125.9	7.945	174.0	6.091	4.2	27
9	-57.3	0.3234	15.7	61.76	39.6	74.48	153.5	7.621	195.2	6.809	5	34

while the second component must consist of a hard segment characterized by high T_g or T_m values, and the hard and soft segments have to be chosen such that the free energy of mixing is positive [13]. Thus, the mutual incompatibility of the segments induces microphase separation in the solid state. A common tool to determine changes, such as phase segregation, glass transitions, and melting is DSC. This method was used to examine the effect of PEG soft segment content on thermal response in TEEEs.

The melting temperature (T_m), crystallization temperature (T_c) and melting enthalpy of the crystalline phase (ΔH_m) were determined by DSC measurements (corresponding thermograms are shown in Figs. 1 and 2) and are collected in Table 2. For materials containing PEG_{1000} (samples 2—5) we observed low T_g values from about -56 to -62 °C (Fig. 1a and b). We also noticed for samples 3—5 containing growing amounts of oligoether segments a low melting temperature (T_{m1}), and high melting temperature (T_{m2}) which is shifting toward higher values with increasing concentration of PEG_{1000} (Fig. 1a, Table 2). Similar tendency is observed during cooling of the material: the low crystallization temperature (T_{c1}) is detected for sample 4 and 5. Observed distinct peaks (at -20.2 and -32.9 °C) can be ascribed to cold crystallization of these materials (Fig. 1b).

For materials containing PEG_{4600} we observed higher intensity of peaks ascribed to thermal transitions of soft

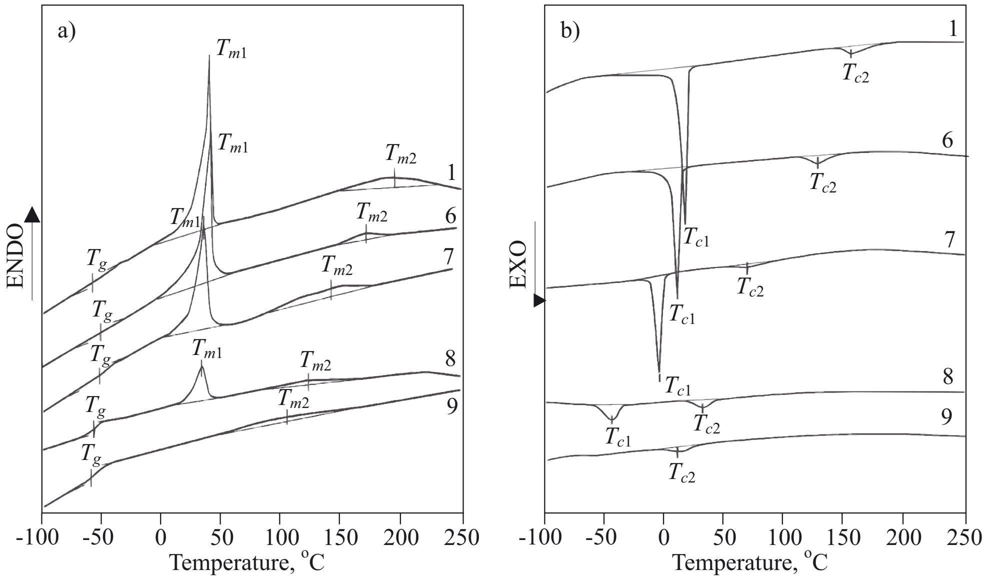


Fig. 2. DSC thermogram during II heating cycle (a) and cooling (b) of multiblock terpolymers with PEG$_{4600}$*; descriptions of curves in agreement with numbers of samples (see Table 1)*

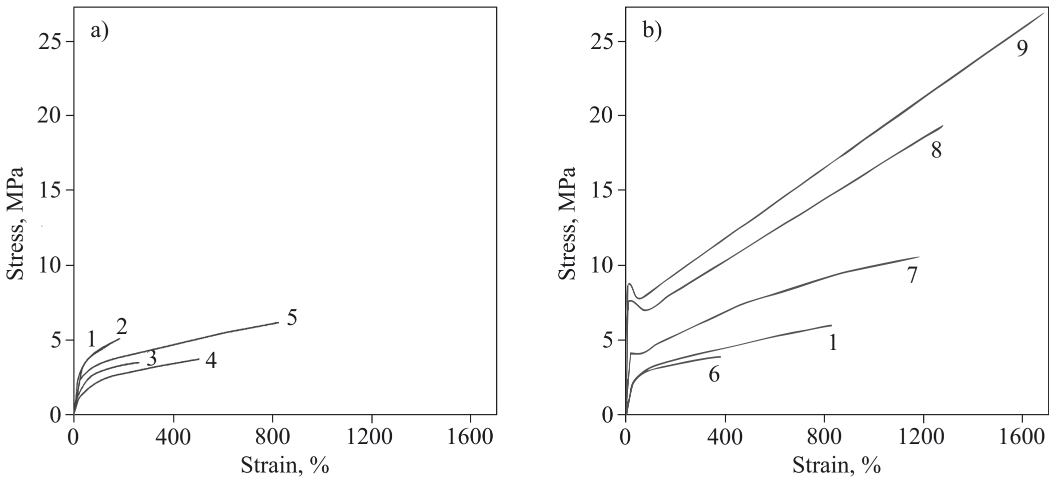


Fig. 3. Stress-strain curves for TEEE obtained with: a) PEG$_{1000}$*, b) PEG*$_{4600}$*; descriptions of curves in agreement with numbers of samples (see Table 1)*

segments T_{m1} and T_{c1} increasing with higher content of PEG$_{4600}$ (Fig. 2a and b). T_{m1} value was found between 32 °C and 39 °C (Fig. 2a). We also observed an increase in ΔH_{m1} value with higher concentration of PEG$_{4600}$. We found a characteristic shift of T_{m2} from 123 °C to 195 °C with increasing concentration of oligoether segments. The T_{c1} temperature ascribed to cold crystallization of soft segments was significantly shifted to low temperature region as compared to PEG$_{1000}$. The crystallization enthalpy (ΔH_{c1}) was much higher for these polymers where PEG$_{4600}$ was used (14.02—61.76 J/g) (Fig. 2b).

DSC investigations of samples obtained without or with small amounts of PEG showed an appearance of two characteristic temperature transitions: a single low-temperature glass transition ascribed to soft segments and a single melting temperature ascribed to hard segments. Moreover, at higher concentration and with higher molecular weight of PEG, formation of crystallizable soft phase was detected, thus confirming multiblock microseparated two-phase structure characteristic for thermoplastic elastomers.

Synthesised TEEE terpolymers showed the strain (ε) versus stress (σ) characteristics typical for thermoplastic elastomers as presented in Fig. 3. Their tensile properties were strongly dependent on the molecular weight of oligoether segments (1000 or 4600) as well as on the concentrations of DLA/PEG, which are components of soft segments. In classical thermoplastic elastomers, rigid hard segments are responsible for mechanical properties and impart a higher toughness to the material. In TPEs mixed soft segments (amorphous and crystallizable ones) as in the TEEE systems, we found that PEG$_{4600}$ showing susceptibility to crystallization, strongly affects tensile properties. We stated that increasing concentration of PEG$_{4600}$, from 15 wt. % to 59 wt. % (samples 6—8), contributes to increase in elongation at break and tensile strength (Fig. 3b). Terpolymers obtained with PEG$_{1000}$ (Fig. 3a) showed low values of tensile strength and elongation at break and the stress-strain curves shapes were typical for elastomers. Materials obtained with PEG$_{4600}$ showed elongation at break well above 1000 % and tensile strength up to 25 MPa, with characteristic strain-stress curves showing distinct yield point (Fig. 3b).

CONCLUSIONS

New TEEE materials were prepared in a two-stage process of transesterification and polycondensation from the melt. Terpolymers were prepared in a presence of thermal stabilizer (α-tocopherol). DSC investigations showed microseparated two-phase structure of TEEE characteristic for thermoplastic elastomers, with amorphous and crystallizable soft segments and crystalline hard segments. Tensile properties of synthesized terpolymers were strongly dependent on the molecular weight of PEG. Crystallizable PEG_{4600} soft segments increased significantly tensile strength and elongation at break in comparison to PEG_{1000}.

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Received 14 III 2008.