

The effect of catalyst and segmental composition on the crystallization of multiblock polyesters for biomedical applications (*Rapid Communication*)

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Abstract: In the present work, segmented thermoplastic elastomers (TPE) containing hard segments of poly(ethylene terephthalate) (PET) and soft segments comprising amorphous fatty acid ester sequences based on dilinoleic acid (DLA) were synthesized. The aim was to obtain transparent materials with high strength and flexibility. Thermal properties of the obtained PET/DLA copolymers were examined using differential scanning calorimetry (DSC). It was found that segmental composition and new type of catalyst used for the synthesis of PET/DLA copolymers has influence on materials transparency.

Keywords: thermoplastic elastomers, crystallization, biomedical applications, poly(ethylene terephthalate).

Wpływ typu katalizatora oraz udziału segmentów sztywnych i giętkich na krystalizację multiblokowych poliestrów przeznaczonych do zastosowań medycznych

Streszczenie: W ramach pracy zsyntezowano multiblokowe poliestrowe elastomery termoplastyczne (TPE), zawierające segmenty sztywne, takie jak w poli(tereftalanie etylenu) (PET), i segmenty giętkie zawierające amorficzne kwasy tłuszczowe na bazie kwasu dilinoleinowego (DLA). Celem było uzyskanie przezroczystych materiałów o dużej wytrzymałości i elastyczności. Właściwości termiczne otrzymanych kopolimerów PET/DLA zbadano za pomocą różnicowej kalorymetrii skaningowej (DSC). Stwierdzono, że wielkość udziału segmentów sztywnych i giętkich oraz zastosowanie nowego typu katalizatora do syntezy kopolimerów PET/DLA ma istotny wpływ na przezroczystość materiałów, a tym samym na ich właściwości użytkowe.

Słowa kluczowe: elastomery termoplastyczne, krystalizacja, zastosowania medyczne, poli(tereftalan etylenu).

It was clearly stated that the human body reaction on foreign body e.g. an implant is usually acute or/and chronic inflammatory response. Therefore, each biomaterial should be tested to evaluate the influence of human body environment on its certain properties [1, 2]. In the presence of physical and chemical conditions biomaterials can be unstable and lose their primary characteristics and may corrode or degrade [3]. Nowadays, new compounds and systems based on biopolymers have taken an advantage in the development of medical materials. Therefore, significant advances have been made in the preparation of implants, blood contacting devices, sensors or artificial organs. Because of the unique physicochemical and mechanical properties, multiblock thermoplastic elastomers

(TPE) are used in a wide range of medical applications [4]. Poly(aliphatic/aromatic-ester)s (PED) which have recently attracted attention are composed of poly(ethylene terephthalate) (PET) and dimerized fatty acid (DFA). The short-chain aromatic ester units of PET form hard segments, while the soft segments are derived from the aliphatic and amorphous DFA. These particular systems exhibit rubber elasticity and can be processed as thermoplastic resins by injection molding or extrusion [5, 6]. Their mechanical properties can be tailored by soft to hard segments ratio, from soft and elastic to rigid and tough materials. They show a very good solvent resistance at high content of hard segments and more importantly they exhibit excellent biocompatibility, thus they can have various possible biomedical applications such as flexor tendon prosthesis, heart patch for cell delivery and artificial heart assisting devices [7, 8]. A very important biofunctional property of the obtained materials is the transparency if they are applied in blood contacting devices (for visual inspection of blood clot formation). This

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feature can be found in thermoplastic polyurethanes known from decades [9, 10]. For that reason, it is a big challenge to produce transparent polyester-based thermoplastic elastomers since they are known to have high tendency to crystallize.

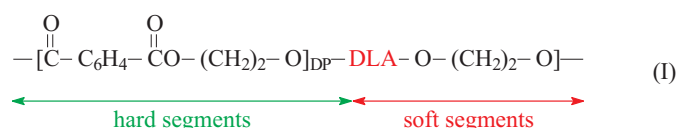
In the present work, segmented TPE containing hard segments of PET and soft segments comprising amorphous fatty acid ester sequences based on dilinoleic acid (DLA) were synthesized. We investigated the influence of DLA on the thermal properties of obtained polymers in a presence of a new catalyst. Previously, antimony trioxide was used as a catalyst in the synthesis of the described materials [11]. However, Sb_2O_3 has a high refractive index of 2.09 and is also used as an effective opacifier [12]. Therefore, to overcome the loss of transparency, we decided to use germanium dioxide as a catalyst. GeO_2 was already found to yield polymer products with better transparency than antimony catalysts which are acceptable for many uses where transparency is not of great importance [13].

The series of polymers was obtained with different hard to soft segment ratio (from 50 to 90 wt % of hard segments). The present paper reports on the differences in thermal properties of synthesized polymers. Total content of crystalline phase in polymer and content of crystalline phase in the hard segment phase was determined.

EXPERIMENTAL PART

Materials and synthesis

Series of multiblock elastomers with 50, 55, 60, 65, 70, 75, 80 and 90 wt % of hard segment content (W_h) were prepared and these percentage values are related to the names of materials in the following text. The synthesis of PET/DLA copolymers is a standard two stage melt polymerization. The first step is transesterification of dimethyl terephthalate (DMT, provided by Elana, Poland) and ethylene glycol (GE, provided by Sigma-Aldrich, Germany) carried out under normal pressure at the temperature about 200 °C and in the presence of zinc acetate as a catalyst. After the removal of methanol (95 % from stoichiometry), dimerized linoleic acid (DLA, Pripol 1009, provided by Croda, The Netherlands) was added. Polycondensation step was carried out under lower pressure at the temperature about 265 °C until the power consumption of stirrer motor has reached the highest value. The catalyst which has been used for the polycondensation step was germanium dioxide (provided by Sigma Aldrich, Germany). Chemical structure of synthesized PED is given by formula (I).



Methods of testing

Thermal properties were determined using differential scanning calorimetry (DSC) method with Q100, TA Instruments apparatus. The samples, whose weight varied between 10 and 20 mg, were dried in vacuum at 60 °C for 24 h. The measurements were carried out in a triple cycle “heating/cooling/heating” in the temperature range from -90 to 300 °C. Heating/cooling rate was 10 °C/min. DSC was applied to determine the heat capacity (ΔC_p), glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy of hard segments (ΔH_m) and crystallization enthalpy (ΔH_c). T_g was determined from the temperature diagrams as the temperature corresponding to the midpoint on the thermogram inflection. T_m and T_c were determined as values corresponding to the maximum of the endothermic and the minimum of the exothermic curve, respectively.

The transparency was examined using the UV-Vis JASCO 630 spectrometer on injection molded samples (4 mm thick).

RESULTS AND DISCUSSION

In the present work, segmented PET/DLA materials were synthesized. The aim was to obtain transparent products with high strength and flexibility, designed for biomedical applications and to characterize their thermal properties. Series of multiblock elastomers with 50, 55, 60, 65, 70, 75, 80 and 90 wt % of hard segment content (W_h) were prepared.

Thermal properties were studied to characterize obtained PET/DLA copolymers. The values of thermal properties, total content of the crystalline phase (W_c) and content of crystallites in the hard phase of PET ($W_{c,h}$) determined using DSC are listed in Table 1.

Table 1. Thermal properties of PET/DLA copolymers with various content of hard segments (W_h)

W_h wt %	ΔC_p J/(g·°C)	T_g °C	T_m °C	ΔH_m J/g	T_c °C	ΔH_c J/g	W_c %	$W_{c,h}$ %
50	0.47	-14.0	199.0	19.1	82.8	17.5	14	27
55	0.43	-7.0	208.0	22.7	88.8	17.9	16	29
60	0.42	-7.8	197.0	26.3	136.1	25.1	19	31
65	0.36	-1.9	222.7	33.8	136.6	32.1	24	37
70	0.29	9.0	223.3	39.2	178.0	36.4	28	40
75	0.22	14.0	236.7	34.3	147.8	32.8	25	35
80	0.33	24.0	237.4	42.2	149.0	40.0	30	38
90	0.24	45.0	244.2	44.5	160.5	42.0	32	35

DSC measurements showed the increase of ΔH_m with the increase of W_h . On the basis of ΔH_m and the melting enthalpy of the crystalline PET phase ΔH_f (140 J/g [14]),

the W_c value for the polymer was calculated from equation:

$$W_c = \frac{\Delta H_m}{\Delta H_f} \cdot 100 \% \quad (1)$$

The $W_{c,h}$ content for PET was calculated from:

$$W_{c,h} = \frac{\Delta H_m}{\Delta H_f \cdot W_h} \cdot 100 \% \quad (2)$$

Thermal properties of multiblock copolymers strongly depend on hard/soft segments ratio. Fig. 1 shows the DSC cooling thermograms of PET/DLA copolymers with different soft/hard segments ratio. For materials containing 50 and 55 wt % of PET sequences, the crystallization peaks were not observed. Above 60 wt % of hard segments content the crystallization temperature of copolymers shifts towards higher values. The presence of relatively high content of amorphous DLA disrupted the chain regularity due to aliphatic and randomly branched chains of DLA, thus the resulting copolyesters exhibited lower crystallinity and T_m [similar influence of DLA on crystallization temperature was observed for copolyesters with poly(butylene terephthalate) as hard segments] [15–17].

As presented in Fig. 2, T_m as well as ΔH_m of PET domains increase with the increasing content of hard seg-

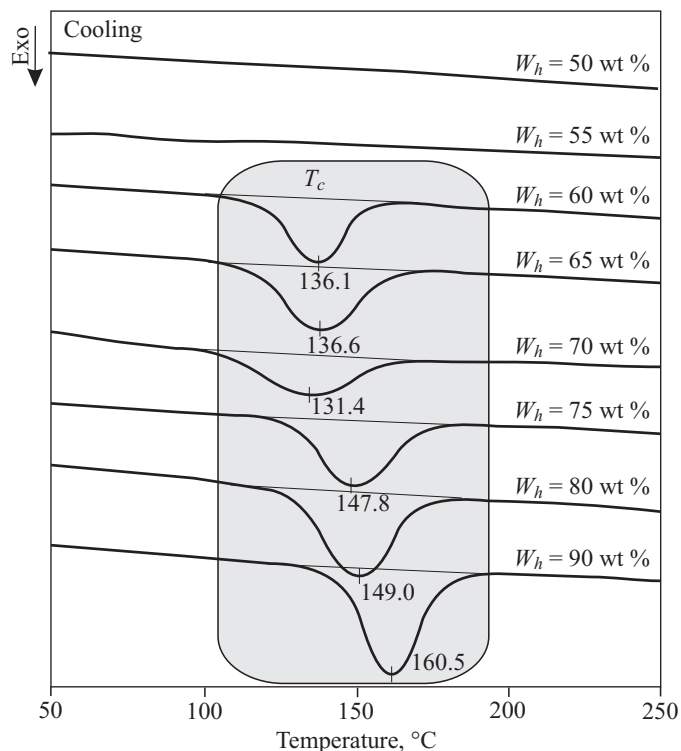


Fig. 1. Thermograms from cooling scans of PET/DLA copolymers with different content of hard segments (W_h)

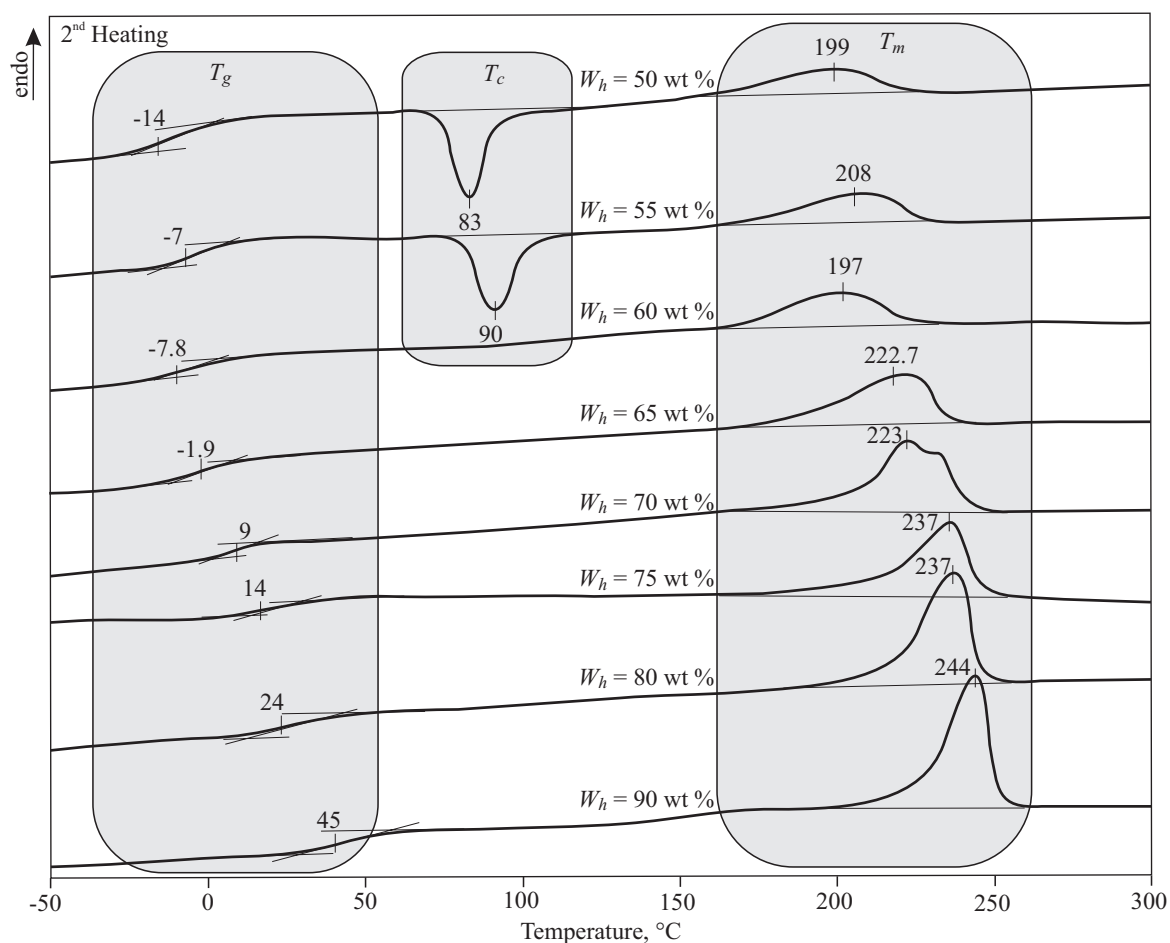


Fig. 2. Thermograms from scans for the second heating of PET/DLA copolymers with different content of hard segments (W_h)

ments. For copolymers with 50 and 55 wt % of hard segments content (degree of polycondensation of hard segments were 2.95 and 3.6, respectively) during the second heating step, also cold crystallization exotherms were observed. This transition occurs when the crystallization is too slow during the cooling step or is interfered by different factors. In PET/DLA systems with the lowest amount of hard segments, the crystallization process is hindered by a high amount of amorphous soft segments.

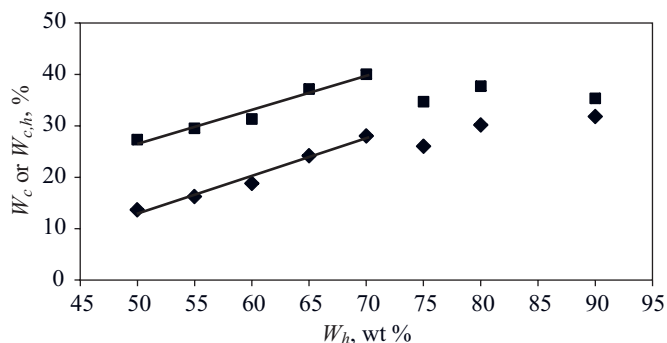


Fig. 3. Total content of crystalline phase in polymer (\blacklozenge) (W_c) and content of crystalline phase in the hard segment phase (\blacksquare) ($W_{c,h}$) as a function of hard segment content (W_h)

Fig. 3 shows W_c and $W_{c,h}$ correlated with W_h . The changes in W_c and $W_{c,h}$ crystallinity increase almost linearly up to 70 wt % of PET, and when W_c is still slightly increasing, the $W_{c,h}$ shows a plateau with further increase of the hard segments content. Probably, the PET oligomers have sufficiently high molar mass, therefore, no further and significant growth of hard segments is observed.

In Fig. 4 T_m as a function of W_c are shown. It should be noted that T_m increases almost proportionally with the increasing W_h in the polymer.

The properties of soft amorphous phase were correlated with T_g values and the corresponding plot was shown in Fig. 5. An increase of W_c in the polymer causes an increase of T_g values in the range from -55 °C (T_g of DLA) to 75 °C (T_g of PET). Moreover, there is no second glass

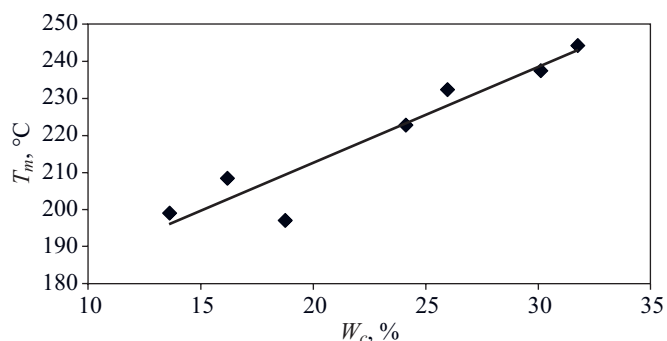


Fig. 4. Melting temperature (T_m) as a function of crystalline phase content in the polymer (W_c)

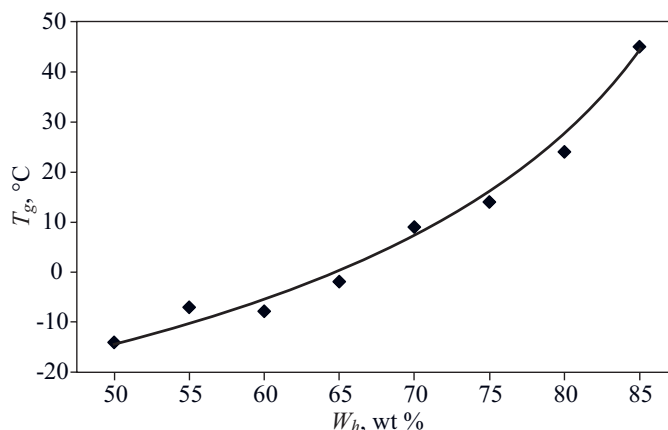


Fig. 5. The effect of hard segments content (W_h) on the glass transition temperature (T_g)

transition on DSC thermograms (see Fig. 2). This suggests the existence of a homogeneous mixture of non-crystalline sequences of PET and aliphatic residues of dimerized fatty acid in the soft amorphous phase.

The observed structural changes due to the changing soft/hard segments ratio are associated mainly with the crystallization. Polyester-based thermoplastic elastomers are known to have high tendency to crystallize. Therefore, our major challenge was to produce transparent materials. In order to determine the transparency of samples the series of injection molding samples was prepared. Parameters of PET/DLA processing are shown in Table 2.

Table 2. Parameters of PET/DLA copolymers injection molding process

Parameters	Value
Zone 1 temperature, °C	215–260
Zone 2 temperature, °C	215–260
Zone 3 temperature, °C	215–260
Zone 4 temperature, °C	170–200
Injection speed, mm/s	90
Clamping pressure, bar	400
Clamping time, s	8
Clamping pressure, bar	320
Molding temperature, °C	11
Cooling time, s	50

The changes of transparency with the increasing content of hard segments were observed macroscopically as shown in Fig. 6. The opacity of materials has decreased with the increasing W_h . A significant loss of transparency was noticed for materials with $W_h = 50, 55$ and 60 wt %. Transparent materials were obtained at higher W_h , namely from 65 to 90 wt %. This is probably due to the conditions of injection molding process. It is well known that PET is fully transparent when injected into a cold mold

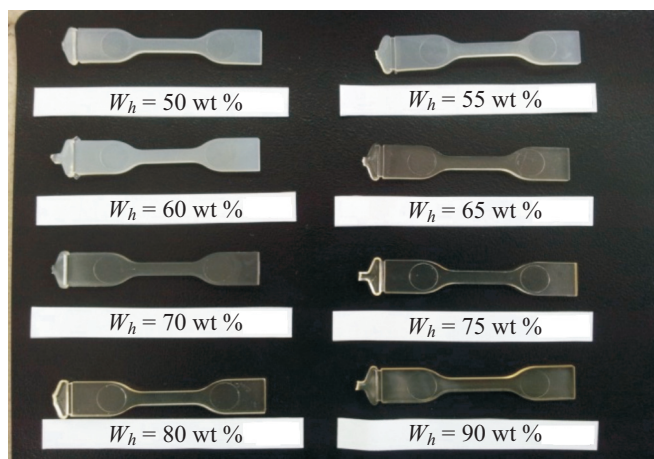


Fig. 6. The effect of hard segment content (W_h) on transparency of PET/DLA materials

(below T_g) [18]. In our case, materials with $W_h = 75, 80$ and 90 wt % have T_g higher than the mold temperature (Table 2). However, despite the fact that materials having $W_h = 65$ and 70 wt % seem to be transparent macroscopically, these polymers are slightly less transparent (Fig. 6) than materials with higher W_h .

The observed changes were verified by calculating the opacity index of prepared materials based on spectrophotometric measurements using the equation of Han and Floros [19]:

$$O = \frac{-\log T_{600}}{x} \quad (4)$$

where: O — the opacity, T_{600} — the fractional transmittance at 600 nm, x — the thickness of sample (mm).

The higher O value corresponds to the lower transparency of the material.

Fig. 7 shows O index of obtained materials calculated from eq. (4). The transparency of materials may be affected by various factors, including the thickness of samples, crystallinity or addition of nanoparticles e.g. SiO_2 . The

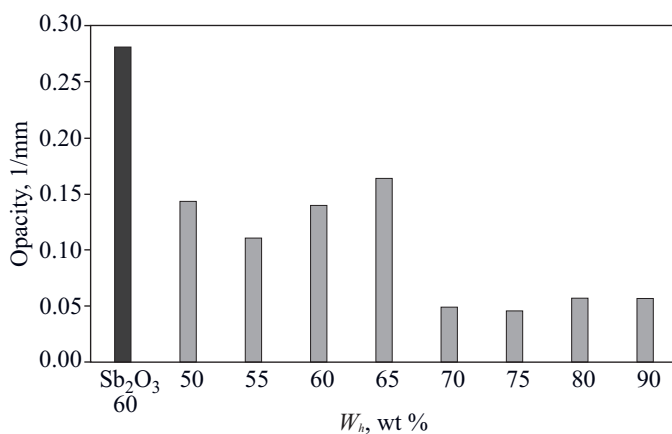


Fig. 7. The effect of hard segment content (W_h) on the opacity of materials synthesized with GeO_2 catalyst (gray) and with Sb_2O_3 catalyst (Sb_2O_3 , $W_h = 60$ %, black)

results showed that materials with $W_h = 70, 75, 80$ and 90 wt % of hard segments exhibited higher transparency than materials with $W_h \leq 65$ wt %. Moreover, we have prepared an additional material with $W_h = 60$ wt % synthesized by using Sb_2O_3 as a catalyst in order to underline better performance of GeO_2 catalyst in terms of obtaining transparent polymers. It can be seen from Fig. 7 that Sb_2O_3 has caused higher opaqueness in comparison with materials synthesized by using GeO_2 as a catalyst.

CONCLUSIONS

In the present work, segmented TPE containing hard segments of PET and soft segments comprising amorphous fatty acid ester sequences based on DLA were synthesized with the use of germanium oxide as a catalyst for polycondensation stage.

Thermal properties of the obtained PET/DLA copolymers were examined using DSC. It was found that T_m as well as ΔH_m of PET domains increases with the increasing concentration of hard segments. In PET/DLA systems with the lowest amount of hard segments crystallization the process was hindered by high amount of amorphous soft segments. It was also shown that the T_c , ΔH_m and ΔH_c increased gradually with the increasing W_h above 60 wt %.

Transparency of the materials depends on the soft segments content. In our studies, transparent PET/DLA materials with W_h from 65 to 90 wt % were obtained. These are promising results, thus indicating the composition window, where transparent polyester materials for biomedical devices can be synthesized.

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REFERENCES

- [1] Patel N.R., Gohil P.P.: *Int. J. Emerg. Technol. Adv. Eng.* **2012**, *2*, 2250.
- [2] Geetha M., Singh A.K., Asokamani R., Gogia A.K.: *Prog. Mater. Sci.* **2009**, *54*, 397, <http://dx.doi.org/10.1016/j.pmat-sci.2008.06.004>
- [3] El Fray M., Renke-Gluszko M.: *Biomaterials* **2004**, *25*, 21, <http://dx.doi.org/10.1016/j.biomaterials.2003.12.021>
- [4] Chen Q., Zhu C., Thouas G.A.: *Prog. Biomater.* **2012**, *1*, 2, <http://dx.doi.org/10.1186/2194-0517-1-2>
- [5] Drobny J.G.: "Handbook of Thermoplastic Elastomers", William Andrew Publishing 2007.
- [6] Fakirov S.: "Handbook of Condensation Thermoplastic Elastomers", Wiley-VCH Verlag GmbH & Co. KGaA 2006.
- [7] Wang B., Zhang Y., Guo Z., Cheng J.: *J. Polym. Res.* **2011**, *18*, 187.
- [8] El Fray M., Altstadt V.: *Polymer* **2003**, *44*, 4635, [http://dx.doi.org/10.1016/S0032-3861\(03\)00417-8](http://dx.doi.org/10.1016/S0032-3861(03)00417-8)
- [9] Lelah M.D., Cooper S.L.: "Polyurethanes in Medicine", CRC Press 1986.

- [10] Philips R.E., Smith M.C., Thoma R.J.: *J. Biomater. Appl.* **1988**, 3, 207, <http://dx.doi.org/10.1177/088532828800300204>
- [11] El Fray M.: *Polimery* **2011**, 56, 571.
- [12] *Pat. USA 7 476 704 B2* (2009).
- [13] Buttermann W.C., Jorgenson J.D.: "Germanium", U.S. Geological Survey, 2005.
- [14] van Krevelen D.W.: "Properties of Polymers, their Estimation and Correlation with Chemical Structure", Elsevier Sci. Pub. Co., 1996.
- [15] El Fray M., Slonecki J.: *Angew. Makromol. Chem.* **1996**, 234, 103.
- [16] Lembicz F., El Fray M.: *Polimery* **2002**, 47, 41.
- [17] El Fray M., Altstädt V.: *Des. Monomers Polym.* **2002**, 5, 353.
- [18] Fakirov S.: „Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends, and Composite: PET Fibers, Films, and Bottle", Wiley-VCH Verlag GmbH & Co., 2002.
- [19] Han J.H., Floros J.D.: *J. Plast. Film Sheet* **1997**, 13, 287.

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