

Agnieszka Kozłowska^{1*},
D. Gromadzki²,
Mirosława El Fray¹,
P. Štěpánek²

¹Szczecin University of Technology,
Polymer Institute,
Pulaskiego 10, 70-322 Szczecin, Poland

²Institute of Macromolecular Chemistry,
Academy of Sciences of the Czech Republic,
Heyrovsky Sq. 2, 162 06 Prague 6, Czech Republic

* Corresponding author: agak@ps.pl

Morphology Evaluation of Biodegradable Copolyesters Based on Dimerized Fatty Acid Studied by DSC, SAXS and WAXS

Abstract

Aliphatic copolyesters of succinic acid (SA) and dimerized fatty acid (saturated dilinoleic acid (DLA)) were synthesized via direct copolycondensation in the presence of 1,4-butanediol. The thermal and mechanical properties of these copolymers were investigated as a function of the hard/soft segments' ratio. The results of small-angle X-ray scattering (SAXS) investigations revealed that the characteristic d spacing of the copolyester supermolecular structure increases from 7 nm to 14 nm with increasing content of soft segments, DLA. It was found that the crystalline phase content determined by WAXS increases from 22 to 66% and was found to increase with increasing content in polybutylene succinate (PBS) sequences and increasing polybutylene succinate (PBS) sequence length. Also, it was shown that the synthesized polymers are susceptible to biodegradation and that the highest mass losses occurred for copolymers of lower crystallinity.

Key words: multiblock copolymers, DSC, WAXS, SAXS, biodegradation.

plastic disposal is to replace the bioreistant synthetic polymers, which are in use today, with biodegradable polymers. Hence, studying the modification of the biodegradation properties of these synthetic polymers has become extremely important. For this reason, many scientists have worked to develop new biodegradable polymers. Some of these biodegradable polymers have been commercialized [1-3].

Aliphatic polyesters are one of the most promising biodegradable materials because they are readily susceptible to biological attack. Poly(hydroxybutyrate) (PHB), poly(lactic acid) (PLA) and poly(caprolactone) (PCL) have been extensively investigated as biodegradable polyesters for a large number of biomedical applications [3]. These aliphatic polyesters are commercially produced by microorganisms, ring-opening polyaddition of cyclic dimer and ring-opening polymerization of lactones [4]. Limiting factors for the broader use of synthetic aliphatic polyesters derived from diols and diacids are their poor mechanical properties and low melting temperatures. There is a need to synthesize aliphatic polyesters with a high molecular weight and good mechanical properties, by some conventional method that could be used on an industrial scale.

To fulfil these requirements, novel aliphatic copolyesters – multiblock thermoplastic elastomers – composed of soft sequences containing flexible chains of butylene ester of dimerized fatty acid (saturated dilinoleic acid – DLA) and poly(butylene succinate) (PBS) as the

hard segment were synthesized and some of their properties are discussed in this paper.

Experimental Part

Materials

Dimerized fatty acid (DFA) – hydrogenated dilinoleic acid (DLA), trade name Pripol 1009, molecular weight $\sim 570 \text{ g}\cdot\text{mol}^{-1}$, (C36) (kindly provided by Uniqema BV, The Netherlands), 1,4-butanediol (BD, BASF), succinic acid (Aldrich Chemie).

Synthesis

Copolyesters were prepared by the typical melt polycondensation method. All the reactions were carried out in pressurized autoclaves designed and constructed at the laboratory of the Polymer Institute at the Szczecin University of Technology. Syntheses were carried out in a 1 dm^3 “pressure-vacuum” reactor made of stainless steel. A charge of components was 2/3 of the reactor capacity (about 650 g).

The esterification reaction between dimerized fatty acid (DFA), succinic acid and 1,4-butanediol (1,4-BD) in the molar ratio 1:2.2 was carried out in the presence of magnesium-titanate organometallic complex (Mg–Ti) as a catalyst using intensive stirring and upon the programmed temperature rising from $100 \text{ }^\circ\text{C}$ to $200 \text{ }^\circ\text{C}$ with a heating rate of $1.5 \text{ }^\circ\text{C}/\text{min}$. The reaction was finished when an acid value less than $2 \text{ mg KOH}\cdot\text{g}^{-1}$ had been reached.

The polycondensation reaction was carried out at $245\text{--}250 \text{ }^\circ\text{C}$, $\sim 0.4 \text{ hPa}$ and in

Introduction

The use of non-degradable synthetic plastics is nowadays widespread in almost all sectors of technology and modern society. However, the environmental concern is affecting international research on the development of novel polymers. One way to solve the pollution problem and

Table 1. Sample designation, compositional specification and selected properties of the PBS/DLA copolymers.

no	PBS, wt%	DLA, wt%	DP _n	M _n × 10 ³ , g/mol	PDI	T _g ^a , °C	T _m ^b , °C	T _c ^c , °C	X _c ^d , %	LVN, dl/g	d, g/cm ³
1	100	0	192	33	1.93	-37	115	65	48.9	0.861	1.4309
2	80	20	15.9	40	1.87	-48	110	50	39.1	0.841	1.3645
3	70	30	9.3	38	1.81	-50	105	47	31.4	0.879	1.3241
4	60	40	6.0	50	1.50	-58	94	24	21.6	0.910	1.2448
5	50	50	4.0	42	1.86	-61	91	28	22.5	0.819	1.2306
6	40	60	2.7	39	2.20	-62	78	-6	12.4	1.023	1.2107

DLA – content of dilinoleic acid,
 PBS – content of butylene succinate,
 DP_n – degree of polymerization of PBS segment
 M_n – molecular weights from GPC (PS standards),
 PDI – polydispersity index,
 T_g, T_m, T_c – glass transition, melting and crystallization temperatures as measured by DSC,
 X_c – calculated degree of crystallization of hard phase from DSC,
 LVN – limiting viscosity number of the polymers in chloroform at 25 °C,
 d – density by picnometric method.

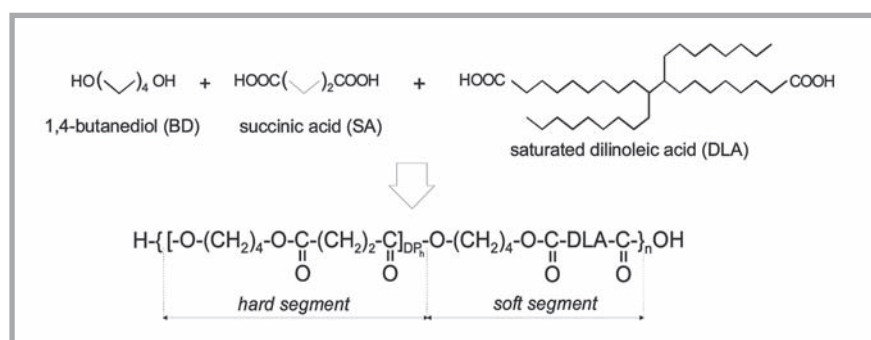


Figure 1. Scheme of copolyester synthesis.

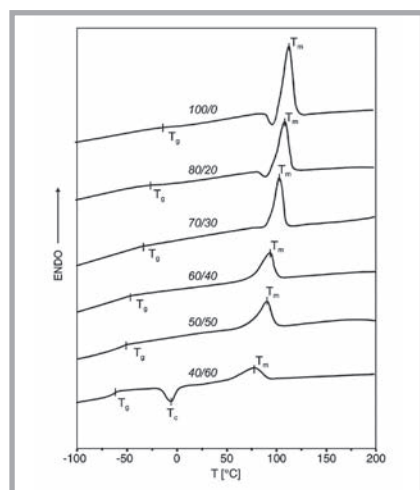


Figure 2. DSC thermograms of the 2nd heating of the PBS/DLA copolymers.

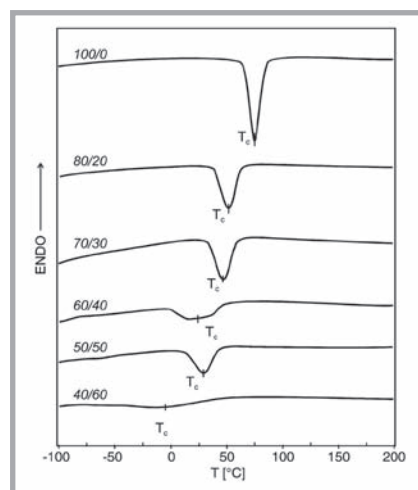


Figure 3. DSC cooling thermograms of the PBS/DLA copolymers.

the presence of the Mg–Ti catalyst. The process was considered complete when the observed power consumption of the stirrer motor signalled that the polymer of the highest melt viscosity had been obtained. The reaction mass was extruded by means of compressed nitrogen. Syntheses gave a series of PBS/DLA copolymers with variable hard/soft segment composition from 80/20 to 40/60 (see **Figure 1**).

Measurements

The limiting viscosity number ([η], LVN) of the polymers in chloroform at 25 °C was determined by a Ubbelohde viscometer IIA. The density was measured by the picnometry method.

The microcalorimetric examinations were carried out with DSC-910 apparatus from TA Instruments. The samples were examined in a triple cycle (heating-

cooling-heating) in the temperature range from –150 °C to +200 °C. The heating and cooling rates were 10 °C min⁻¹.

SAXS experiments were performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental set-ups were used to cover the *q* range of 0.007–1.1 Å⁻¹ (*q* = (4π/λ) sin Θ/2), where λ is the wavelength and Θ is the scattering angle. The copolyester films were prepared by pouring 8% chloroform solutions into a Petri dish followed by evaporation of the solvent for a duration of two days.

The tensile data were collected with an Instron TM-M tensile tester at a cross-head speed of 20 cm/min.

Biodegradation tests were carried out on thin polymer films (60×60×0.5 mm) in controlled conditions at 50 °C for 3 months in a mixture of sand and compost (1:1) [5].

Results and discussion

The composition and selected properties of the investigated copolymers are presented in **Table 1**.

The DSC thermograms from the 2nd heating and cooling are shown in **Figures 2** and **3**, respectively.

The thermograms of the copolymers (**Figure 2**) show the occurrence of glass transitions in the low temperature range from –62 to –37 °C attributed to the amorphous soft phase. The observed shift of the T_g glass transition temperature corresponds well to the increase of the soft segments' concentration. The endotherms occurring on the DSC curves in the range from 78 to 115 °C can be related to the melting transition of poly(butylene succinate) (PBS) hard domains (T_m). The maxima decreases and flattens along with the decrease of the PBS sequence length. The crystallization transition of hard segments appears in all the prepared polymers (**Figure 3**) and, similarly, the melting endotherms and crystallization exotherms decrease with a decreasing PBS sequence length. The melting temperature, T_m, of the hard domains as well as the crystallization temperature, T_c, of the hard segments decrease systematically with the decrease

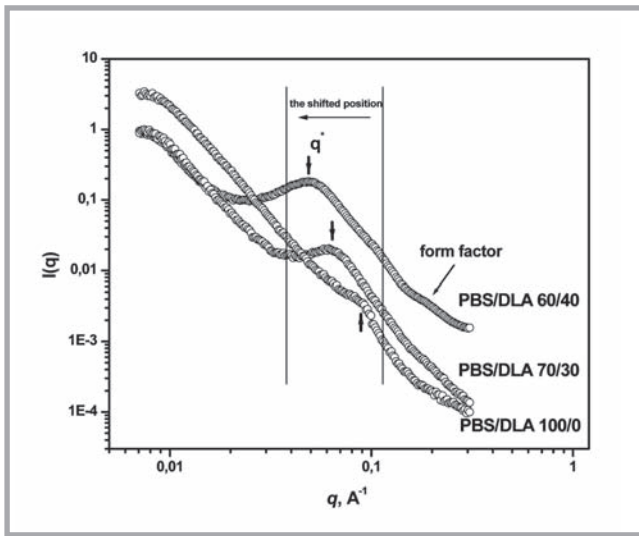


Figure 4. SAXS scattering curves of the neat PBS and PBS/DLA copolymers containing 30 and 40 wt% soft DLA segments.

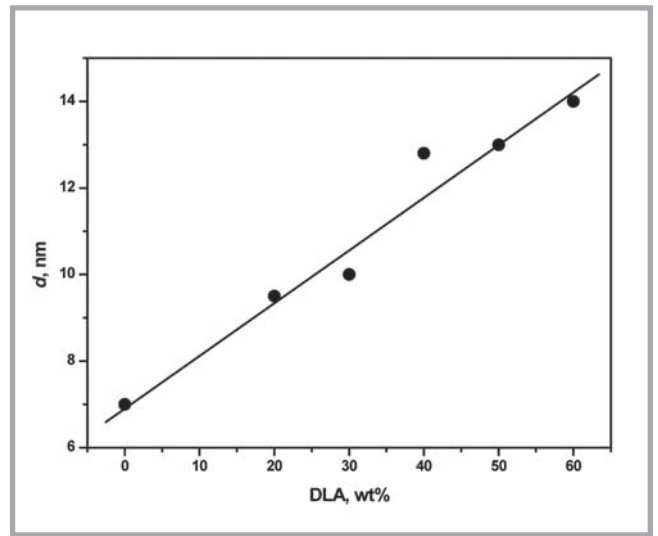


Figure 5. The plot of the characteristic d spacing of the copolymers' supermolecular structure vs. the DLA content (wt%).

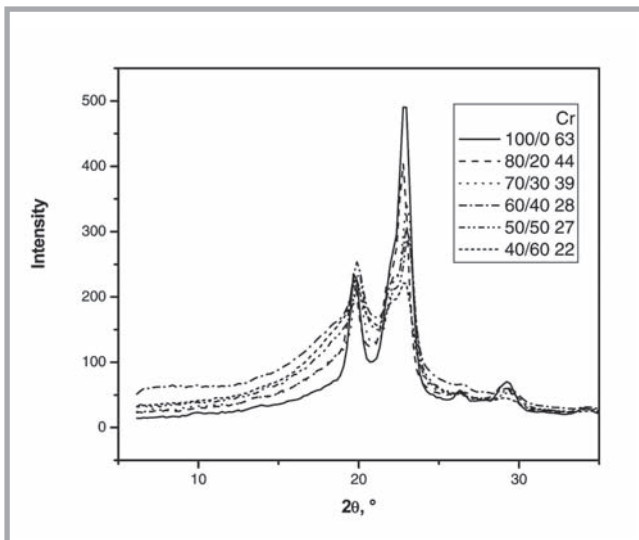


Figure 6. WAXS diffraction patterns of synthesized copolymers along with WAXS data determining the degree of crystallinity, X_c .

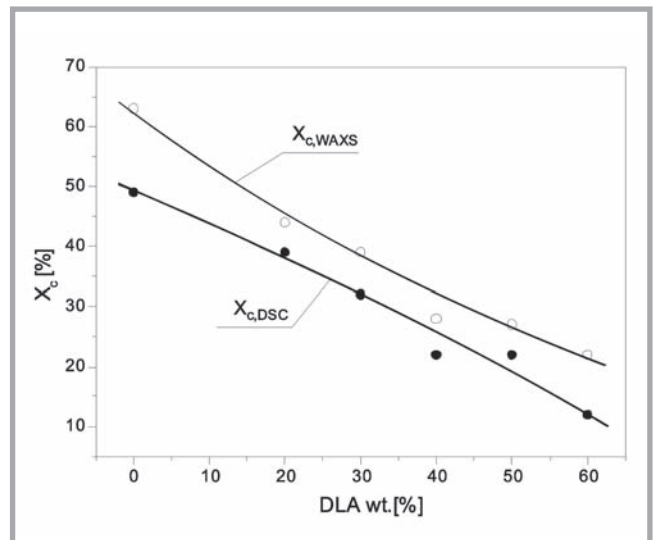


Figure 7. The plot of the degree of crystallinity determined by DSC and WAXS vs. the DLA content.

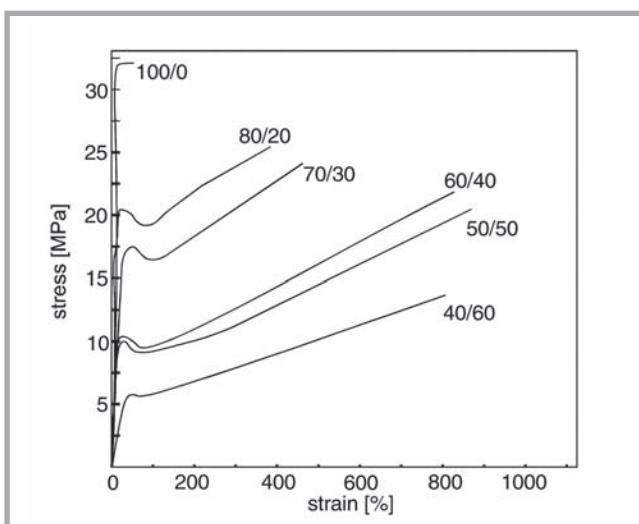


Figure 8. Stress-strain curves for the investigated copolymers.

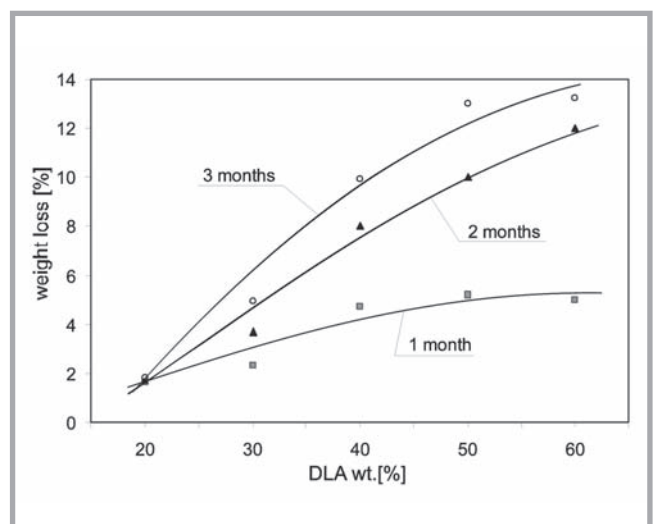


Figure 9. Weight losses of the PBS/DLA copolymers vs. biodegradation periods.

of the PBS sequence length (respectively from 115 to 78 °C and from 65 to -6 °C).

The morphology of the solution cast copolyester films was investigated by X-ray scattering techniques to clarify the change of the higher-order structure. In this study, no special treatment of the samples was performed (e.g. thermo-annealing); thus, the X-ray measurements were carried out for as-cast films. At the small-angle region, a clear structure peak was observed for all the copolyester samples, the position of which shifted towards lower scattering angles with a DLA soft block content and increased as is shown in **Figure 4** (see page 87). This shift results in an increase in the characteristic *d* spacing of the copolymers' supermolecular structure, as shown in **Figure 5**.

The wide-angle X-ray scattering (WAXS) patterns shown in **Figure 6** are characterized by two strong reflections at 2θ equal to 19.67° and 22.77°, for which the Bragg spacing equals, respectively, 0.452 nm and 0.391 nm. In accordance with the data presented in [6], one may suppose that these peaks are, respectively, the (020) and (110) peaks of the crystalline structure of the PBS hard domains.

The changes observed in the DSC thermograms as well as in the WAXS diffraction patterns allowed the determination of the degree of crystallinity, as illustrated in **Figure 7**. As it was expected, the PBS crystalline phase content is strongly dependent on the copolymer composition and increases with the increase in the PBS content.

The tensile properties of the investigated copolymers as typical stress-strain curves are shown in **Figure 8**. The highest strain was observed at about 50% soft segment content. It is worth noting that this behaviour is similar to the changes of the elongation for the majority of the multiblock thermoplastic elastomers [7, 8]. Poly(butylene succinate-dilinoleate)s are a class of materials combining some of the strength of engineering plastics with some of the elasticity of rubber; therefore, they can be best described as engineering thermoplastic elastomers.

A preliminary study of the susceptibility to biodegradation of the prepared copolyesters was carried out under controlled laboratory conditions. **Figure 9** displays the dependences of the weight losses as the function of the DLA content at differ-

ent incubation times. The weight losses are higher for samples with a lower content of crystallizable succinate sequences. It can be concluded that weight losses of up to 14 wt% are achieved within 3 months of incubation.

Conclusions

Multiblock copolyesters based on butylene esters of succinic acid (PBS) and dimerized fatty acid (DLA) were synthesized. The copolymers showed a wide range of softnesses and processing flexibilities. The DSC results show that the synthesized copolymers exhibit two main transition temperatures, the low-temperature glass transition attributed to the DLA soft domains and the high-temperature melting transition attributed to the PBS crystalline domains. These results have indicated at least the two-phase structure of these materials. The characteristic *d* spacing of the copolymers' supermolecular structure ranges from 7 to 14 nm, as measured by SAXS.

The tensile properties (stress-strain curves) confirmed a typical thermoplastic elastomer behaviour of the synthesized copolyesters. The preliminary results from the composting test confirmed the susceptibility of the copolyesters to biodegradation.

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For more information please contact

Iwona-Dusio Kraska,
tel. +48 42 6374400,
www.moratex.eu