

AGNIESZKA PIEGAT, MIROŚLAWA EL FRAY^{*)}

Szczecin University of Technology

Polymer Institute

Division of Biomaterials and Microbiological Technologies

ul. Pułaskiego 10, 70-322 Szczecin

Poly(ethylene terephthalate) modification with the monomer from renewable resources

RAPID COMMUNICATION

Summary — An emerging problem related to the development of biodegradable polymers from renewable resources was brought up in this work. Modification of petrochemical-based poly(ethylene terephthalate)(PET) with the use of bio-based monomer, namely dilinoleic acid (DLA) was presented. Series of multiblock copolymers containing oligo-PET as hard segments and DLA as soft segments was obtained in typical process of PET synthesis *via* polycondensation from the melt. PET/DLA copolymers containing $W_h = 30$ —90 wt. % of hard segments were characterized with respect to their mechanical, thermal and processing properties. It was demonstrated that at high concentration of DLA ($W_h = 30$ —40 wt. %) materials are susceptible to hydrolytic degradation.

Key words: poly(ethylene terephthalate), biodegradable polyesters, dilinoleic acid, copolymer, thermal properties, mechanical properties.

MODYFIKACJA POLI(TEREFTALANU ETYLENU) ZA POMOCĄ MONOMERU ZE ŹRÓDEŁ ODNAWIALNYCH

Streszczenie — Zaproponowano metodę otrzymywania z zastosowaniem surowców odnawialnych polimerów zdolnych do biodegradacji. Zastosowano poli(tereftalan etylenu)(PET), będący produktem petrochemicznym, który modyfikowano za pomocą kwasu dilinolowego (DLA) będącego monomerem bio-pochodnym, stanowiącym dimer kwasu tłuszczowego. Metodą polikondensacji w stopie otrzymano serię kopolimerów zawierających oligomery PET jako segmenty sztywne oraz DLA jako segmenty giętkie. Kopolimery PET/DLA zawierały $W_h = 30$ —90 wt. % segmentów sztywnych. Zbadano ich właściwości mechaniczne, termiczne oraz przetwórcze. Wykazano, że wysoka zawartość DLA ($W_h = 30$ —40 wt. %) sprzyja degradacji hydrolytycznej polimerów.

Słowa kluczowe: poli(tereftalan etylenu), biodegradowalne poliestry, kwas dilinolowy, kopolimer, właściwości termiczne, właściwości mechaniczne.

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer, which is widely used in the textile and packing industry [1]. Fibers made of this polymer are used for production of unwoven fabrics and threads *e.g.* Terylene & Trevira[®]. They are also used in medicine as nondegradable sutures or prostheses elements *e.g.* Dacron. Their high stability in human body and very low susceptibility to enzymatic and hydrolytic degradation are often ones of the biggest disadvantages of this material. Therefore, an extended research on PET modification led to the commercialization of aliphatic-aromatic copolyesters by global suppliers [2]. Unlike other petrochemical-based polymers that take a very long time to degrade after disposal, these polyesters break down ra-

pidly to CO₂ and water in appropriate conditions (about twelve weeks during aerobic degradation). It was possible to obtain such materials by incorporating aliphatic monomers such as adipic or sebacic acid into the polymer chain [3]. Degradation rate of these copolymers depend on the weight ratio of aliphatic and aromatic components (segments). Higher susceptibility to chemical hydrolysis was observed for the systems containing adipic acid, because of higher acidity of this monomer. Another approach involved usage of 1,3-propanediol or 1,4-butanediol instead of 1,2-ethanediol in the transesterification step [4]. Oligomers based on dimethyl terephthalate (DMT) and these three glycols were obtained at different weight ratio of DMT/glycol. It was observed that degradation time depends mainly on the molecular weight of oligomers rather than on the type of glycol.

^{*)} Author for correspondence; email: mirfray@ps.pl

These investigations confirmed that it was possible to combine the degradability of aliphatic (components, soft segments) polyesters with the outstanding properties of aromatic (component, hard segments) ones thus giving "tailor-made" materials, where polymer properties such as tensile strength, melting point as well as susceptibility to degradation could be easily controlled by the weight ratio of the components (hard and soft segments) on the feed.

Another effective method of thermoplastics modification is the use of polymers from renewable resources, such as poly(glycolic acid) (PGA), poly(lactic acid) (PLA) or poly(β -hydroxybutyrate) (PHB) that usually are biodegradable in the environment [5]. PET was modified with L-lactic acid by ester-ester exchange between both PET and poly(L-lactic acid) (PLLA) polymers or by polycondensation of PET and L-lactic acid (L-LA) [6]. The degradation process was evaluated on the basis of the weight loss and decrease in relative viscosity of polymer solution. The highest weight loss as well as reduction of intrinsic viscosity were observed for copolymer containing 41 wt. % of L-LA.

Another interesting group of modifying agents are bio-based monomers, especially low-molecular weight dicarboxylic acids or higher unsaturated fatty acids obtained from vegetable oils. Dimer fatty acids, such as dilinoleic acid (DLA) or their diols, derived from triglycerides are widely used as components of commercially available adhesives, coating materials or polyurethanes. They were also successfully used for modification of polyamides [7, 8] or polyesters [9, 10] giving the materials classified as thermoplastic elastomers (TPE), where they occur as soft segments components. Modification of TPEs, where hard segment was made of poly(butylene terephthalate) (PBT) with DLA resulted in enhanced elasticity, processing properties as well as susceptibility to degradation [11]. It was already demonstrated, that

mechanical and processing properties of biodegradable multiblock poly(aliphatic/aromatic-ester) copolymers containing different weight ratio of hard (PET) and soft (DLA) segments.

EXPERIMENTAL

Materials

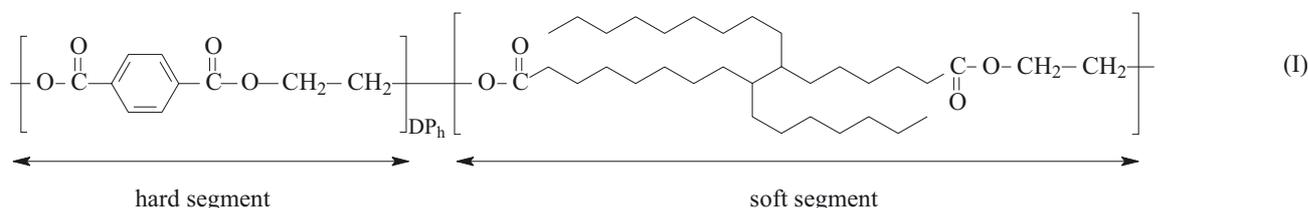
The following materials were used in this work:

- dimethyl terephthalate (DMT, Elana SA, Poland),
- 1,2-ethanediol (ED, POCh, Poland),
- $\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, 99,99 %),
- dilinoleic acid (DLA, "Pripol 1009", Uniquema B. U., The Netherlands),
- phenol (99 %, POCh),
- trichloroethylene (99,5 %, POCh),
- benzene (99,7 %, POCh).

Reagents were used without purification.

Synthesis

Series of multiblock copolymers with oligomeric sequences as in poly(ethylene terephthalate) (PET) constituting hard segments and dilinoleic acid as soft segments were synthesized by two-step process, namely transesterification and polycondensation from the melt. Transesterification stage was carried out in the presence of ethylene glycol and dimethyl terephthalate and was catalyzed by $\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}$, at temperature 180 °C, until 95 % of stoichiometric (calculated) amount of methanol was collected. Before polycondensation step, DLA was added to the reaction mixture, then the pressure was decreased to 0.2–0.5 hPa and the temperature increased to 280 °C. Due to excellent thermal stability of DLA, process was carried out without the use of thermal stabilizers. The progress of polycondensation



DLA could also be successfully applied for modification of PET-based systems at high concentration of DLA [12]. First trials of multiblock TPE copolymer synthesis with PET hard segments and DLA soft segments showed that at high concentration of DLA (70 wt. %) polymer obtained showed excellent mechanical properties and was susceptible to hydrolytic degradation.

In this work we present the syntheses of PET/DLA copolymers and the investigation of an influence of DLA, a monomer from renewable resources on thermal,

reaction was observed by power consumption of the stirrer and reaction was finished when the power consumption increased significantly. Copolymers, with chemical structure shown by formula [I] contained 30, 40, 50, 60, 70, 80 or 90 wt. % of PET hard segments (W_H).

Methods of testing

Intrinsic viscosity (η) was measured in phenol/trichloroethylene mixture (1/1 by volume) as a solvent at

temp. 30 °C using Ubbelohde capillary viscometer immersed in water bath. All polymers were dissolved at room temperature.

To determine swelling of copolymers in benzene, approximately 1g of polymer sample was immersed in benzene at room temperature for 72 h. After this time, sample was dried and mass of dry (w_d) and swollen (w_s) samples were estimated. The swelling (S) was calculated from the following equation:

$$S = \frac{w_s - w_d}{w_d} \cdot 100 \% \quad (1)$$

Thermal properties were determined with the use of differential scanning calorimetry (DSC) using a TA Instruments Q1000 apparatus. The process was carried out in a triple cycle: first heating, subsequent cooling and second heating, in the temperature range from -100 °C to 300 °C at a constant heating rate for all runs of 10 °C/min. From DSC curves glass transition temperature (T_g), melting temperature (T_m) and melting enthalpy (ΔH_m) of copolymer were determined. Degree of crystallinity (DC) was calculated according to the following equation:

$$DC = \frac{\Delta H_m}{\Delta H_{mPET}} \cdot 100 \% \quad (2)$$

where: $\Delta H_{mPET} = 130.2 \text{ J/g}$ [13] — enthalpy of melting of crystalline PET phase.

Mechanical properties were investigated for the samples in the shape of dumbbells prepared by injection molding (parallel length 35 mm and cross-section 12 mm²) and compression molding (thin films 0.5 mm thick, parallel length 20 mm and cross-section 2 mm²), and were tested using Instron 1161 testing machine equipped with a 500 N load cell at a crosshead speed of 200 mm/min according to standard PN-EN ISO 527-1. Strain at break of tested material was taken as the total clamp displacement.

Hardness was measured using Shore D apparatus (Zwick, type 3100) according to DIN 53505 (ISO 868) standard.

RESULTS AND DISCUSSION

It is already known that properties of TPE polyesters can be controlled by the hard/soft segments ratio [14—16]. Due to the preparation of a series of PET/DLA copolymers with subsequently changing segments' weight ratio, we also noticed this characteristic change of the properties. The soft/hard segment ratio had strong influence on physicochemical behavior of copolymers. The highest value of intrinsic viscosity $\eta = 0.765 \text{ dl/g}$ was found for copolymer with $W_h = 50 \text{ wt. \%}$, while the lowest value $\eta = 0.544 \text{ dl/g}$ was observed for copolymer with $W_h = 30 \text{ wt. \%}$.

The changes of η were not as regular as for swelling in benzene. These values increased with decreasing content of hard segments in polymer matrix from 120 % for

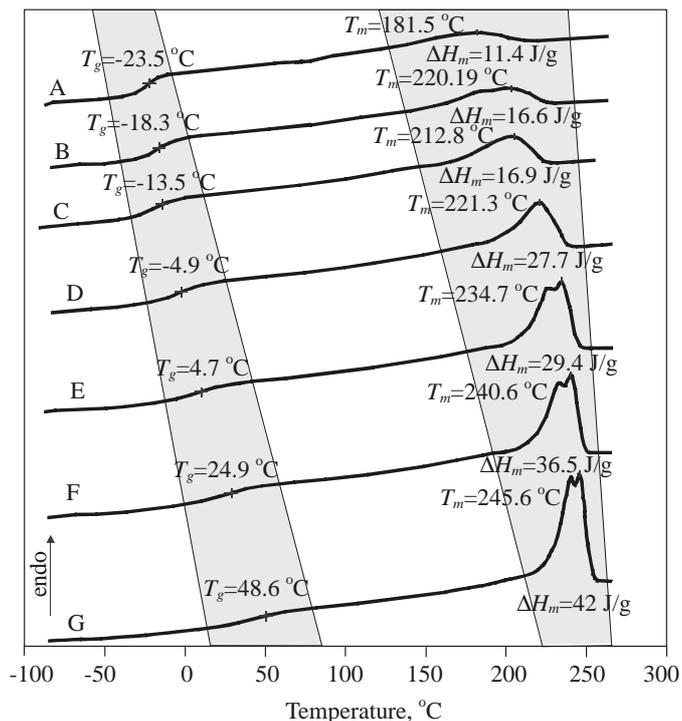


Fig. 1. DSC curves of second heating cycle of PET/DLA copolymers with different content of hard segments; description of curves according to symbols of samples defined in Table 1

copolymer with $W_h = 90 \text{ wt. \%}$ to 340 % for this with $W_h = 30 \text{ wt. \%}$. Such behavior can be connected with the high amount of amorphous phase, which is more susceptible to organic solvents penetration.

Thermal properties were determined with the use of DSC method. The results of second heating cycle are shown in Figure 1. It was noticed that values T_m as well as ΔH_m of copolymers increased with increasing concentration of hard segments. These changes reflect also an increase in DC values from 8.7 % to 32 % (Table 1). The peaks ascribed to melting temperature, become sharper and the temperature range corresponding to melting is becoming narrow. During second heating only one T_g was observed for each copolymer and the value was shifting from -23.5 °C to 48.6 °C with increasing W_h . Such observation suggests that amorphous phases of DLA and PET are mixed, and depending on the soft segments concentration, T_g value is closer either to the neat DLA ($T_g = -55 \text{ °C}$) or to PET ($T_g = 77.4 \text{ °C}$).

High concentration of amorphous phase enhanced also susceptibility of these copolymers to hydrolysis. Because hydrolysis in the solid state depends mainly on the chain mobility and permeability, it is favorable for the hydrolysis, to have polymers with low value of T_g [5]. This assumption was confirmed for copolymer with $W_h = 30 \text{ wt. \%}$ characterized by $T_g = -23.5 \text{ °C}$ which showed degradation during 6 months in phosphate buffer saline (PBS). After this period, weight-average molecular weight (M_w) decreased from 34 350 to 10 700, what is over 68 % of initial M_w . This confirms that DLA

can be successfully used as bio-based modifier to obtain degradable PET.

Table 1. Selected properties of samples multiblock PET/DLA copolymers prepared by injection molding

Symbol of sample	W_h wt. %	Elongation at break, %	Stress at break MPa	Hardness Shore D	DC %
A	30	380	15.9	38	8.7
B	40	475	25.0	47	12.7
C	50	620	33.0	53	13.0
D	60	610	35.0	57	21.3
E	70	350	24.6	65	22.7
F	80	N	13.6 ^{a)}	78	28.0
G	90	N	5.1 ^{a)}	84	32.0

N — not identified;

^{a)} — measurements at crosshead speed of 50 mm/min.

Table 1 summarizes mechanical properties of PET/DLA copolymers series. Depending on the hard/soft segment ratio, mechanical behavior of thermoplastic elastomers can be similar to vulcanized rubber or to rigid thermoplastics [17]. Such behavior was also observed for PET/DLA copolymers. However, the optimum mechanical properties in term of elongation at break as well as stress at break were found for copolymers containing 50 and 60 wt. % of hard segments, prepared by injection molding (for compression molded samples, the optimum mechanical properties were found for samples containing 40 and 50 wt. % of hard segments, Figure 2). This behavior showing a “peak” of mechanical properties can be explained by specific arrangement of rigid and amorphous phases within the polymer matrix. Changes of mechanical properties have a bell-shape character similar to phase diagrams for

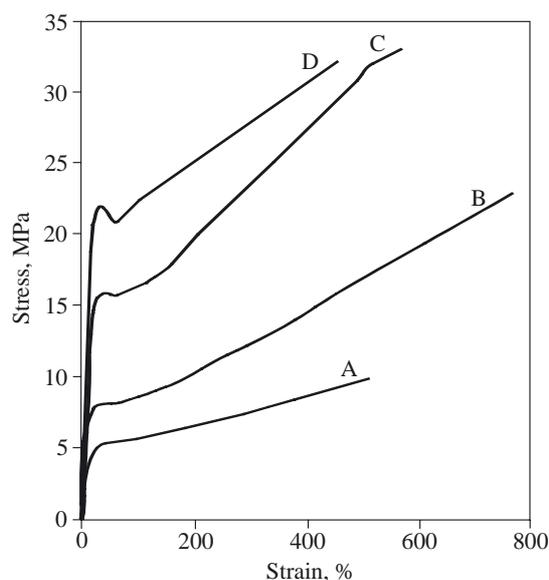


Fig. 2. Stress-strain curves for selected samples of copolymers with different content of hard segments; description of curves as in Fig. 1

block copolymers with Lorenzian peak (spinodal) at equal monomer volumes, what can suggest that PET/DLA system can undergo a second-order phase transition from the disordered (at wings of phase diagrams, where poor mechanical properties are observed) to well organized lamellar phase. This prediction, however, requires more detailed investigations with small-angle X-ray scattering method (SAXS) in order to find correlation among polymer composition, morphology and mechanical properties [16]. The hardness value increases with increasing W_h , due to higher degree of crystallinity as can be seen in Table 1.

In conclusion we can say that PET/DLA copolymers with different soft/hard segments weight ratio were synthesized by melt polycondensation reaction. Thermal properties as well as mechanical behavior can be controlled by initial monomers concentrations. Such tailoring of PET properties was successfully realized by incorporation of bio-based monomer from renewable resources, which additionally had significant influence on copolymers' susceptibility to biodegradation.

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