

POLY(BUTYLENE SUCCINATE) MODIFIED BY DIMERIZED FATTY ACID FOR MEDICAL APPLICATION

AGNIESZKA KOZŁOWSKA*, MIROSLAWA EL FRAY

WEST POMERANIAN UNIVERSITY OF TECHNOLOGY IN SZCZECIN,
POLYMER INSTITUTE,
DIVISION OF BIOMATERIALS AND MICROBIOLOGICAL TECHNOLOGIES,
10 PULASKI STR., 70-322 SZCZECIN, POLAND
*MAILTO: AGAK@ZUT.EDU.PL

Abstract

The synthesis method, characterization and preliminary degradation studies of novel aliphatic polyesters based on dimerized fatty acid were presented. Hydrogenated dilinoleic acid, succinic acid and 1,4-butanediol were used for the synthesis. Preliminary results on selected properties as well as on hydrolytic degradation were discussed.

Keywords: aliphatic polyesters, poly(butylene succinate), hydrolytic degradation, dimerized fatty acid [Engineering of Biomaterials, 89-91, (2009), 255-256]

Introduction

BIONOLLE is commercially available biodegradable aliphatic polyester – poly(butylene succinate) (PBS) – with excellent characteristics such as good strength, toughness, processability and versatile commercial applications mainly as packaging material and for medical applications. Annual production of this polymer exceeds 3000 tons/year. However, there are many technical problems to be overcome before a full potential of this polymer can be realized and expanded to other applications, e.g. pressure sensitive adhesives, aqueous emulsions, coating to name just a few. For example, the elastic properties and biodegradation characteristics must be improved [1-3].

In general, the degradability of aliphatic polyesters depends mainly on their chemical structure and especially on the hydrolysable ester bonds in the main chain, which are susceptible to hydrolysis and microbial attack. Other factors, such as molecular weight, degree of crystallinity, stereoregularity and morphology also affect the rate of

No	Segment content		DP _{PBS}	[η]	T _{m1}	T _{m2}	d
	PBS (w _n)	DLA (w _s)					
1	100	0	192	0,861	113	115	1,431
2	70	30	9,3	0,879	107	110	1,324
3	60	40	6,0	0,910	102	107	1,245
4	50	50	4,0	0,816	97	102	1,231

w_s – content of DLA (dimerized fatty acid – saturated dilinoleic acid) soft segments, wt.-%
w_n – content of PBS (polybutylene succinate) hard segments, wt.-%
DP_{PBS} – degree of polymerisation of PBS hard segments
[η] – limiting viscosity number (in chloroform at 25°C), dl g⁻¹
T_{m1}, T_{m2} – melting point temperatures from Boetius apparatus, °C
d – density by picnometric method, g cm⁻³

TABLE 1. Composition and selected properties of synthesized materials.

polymer biodegradation [4].

To tailor the degradation characteristics of PBS, different modifications can be made, including copolymers. Thus, novel aliphatic copolyesters – multiblock thermoplastic elastomers – composed of poly(butylene succinate) (PBS) as hard segment and soft sequences containing flexible chains of butylene ester of dimerized fatty acid (saturated dilinoleic acid – DLA) were synthesized and some of their properties are discussed in this paper.

Experimental and methods

The synthesis method of polyesters, involving esterification and polycondensation from the melt, was described in previous publication [5]. Syntheses gave a series of PBS/DLA copolymers with variable hard/soft segments composition and selected properties from “pure” PBS – 100/0 to 50/50 copolymer as is presented in TABLE 1.

Differential scanning calorimetry (DSC) scans were performed with a TA Instruments (DSC-910) apparatus. The samples were dried in vacuum at 60°C, and then kept in a desiccator. The process was carried out in a triple cycle: first heating, then cooling, and second heating in the temperature range from –100°C to 50°C higher than melting point of each copolymer. The rate of heating and cooling was 10°C min⁻¹.

The tensile data were collected at room temperature with an Instron TM-M tensile tester equipped with a 500N load cell employing a crosshead speed of 100mm/min. The starting clamp distance was 25mm. The obtained results were averaged from 6 specimens with cross section of 0.5×4 mm.

Hydrolytic degradation test of incubated thin polymer films was carried out during 4 weeks in three types of solutions: alkaline, neutral and acidic in buffers (pH=9, pH=7,2 and pH=5) at 37°C. The mass loss of the polymer samples was

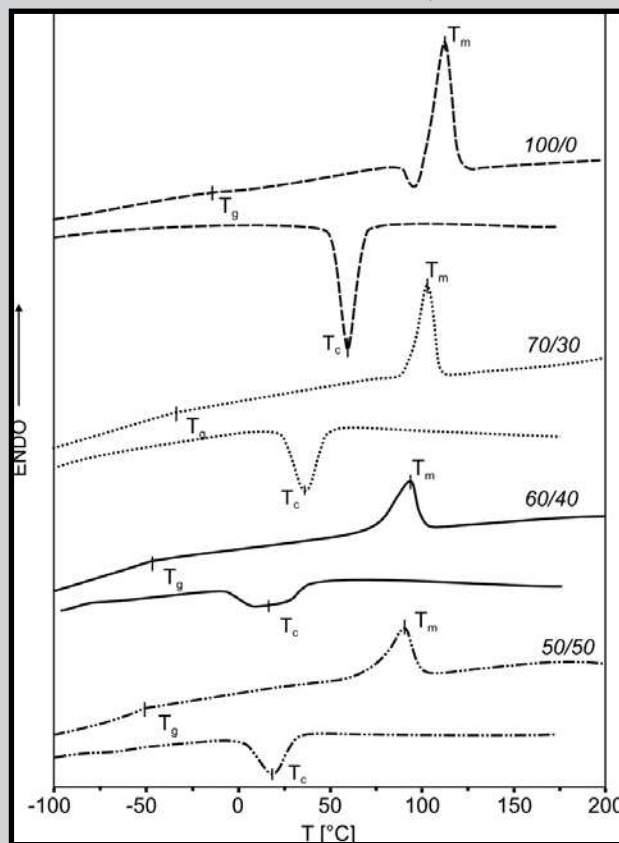


FIG.1 DSC scans from cooling and heating runs for PBS/DLA copolymers.

determined by comparing the dry weight (m_d) after hydrolysis with the initial weight (m_0) according to eq 1. The samples were dried for 2 weeks at reduced pressure before determination of the dry weight.

$$\Delta m_d = \frac{m_0 - m_d}{m_0} \times 100 \quad (1)$$

Results and discussion

Differential scanning calorimetry was carried out in a triple cycle heating/cooling/heating. Reported results collected from 2nd heating and cooling (FIG.1) clearly show that synthesised copolymers exhibit two main transition temperatures; low-temperature glass transition attributed to the soft block and high-temperature melting transition attributed to the hard block. At the same time, we can observe well-defined crystallization temperatures of hard segments. The thermograms of copolyesters show the occurrence of glass transitions in low temperature range from -61 to -37°C attributed to the amorphous soft phase. The observed Tg glass transition temperature shift corresponds well with the increase of the soft segments concentration. The endotherms occurred on the DSC curves in the range from 91 to 115°C, can be related to the melting transition of poly(butylene succinate) (PBS) hard domain (T_m). The

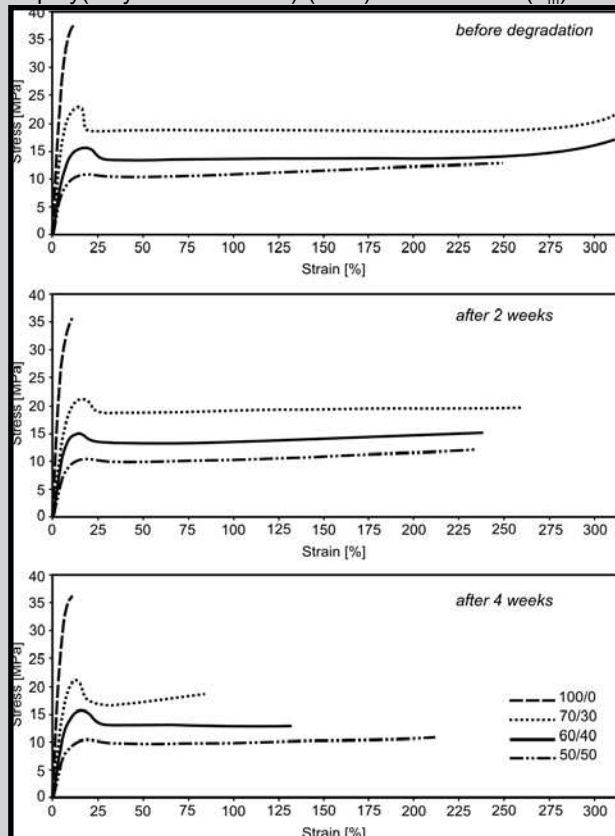


FIG.2. Stress-strain behaviour of PBS/DLA copolymers before and after degradation.

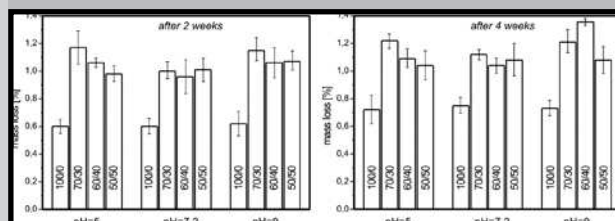


FIG.3. Mass loss of PBS/DLA copolymers after 2 and 4 weeks degradation.

maxima decrease and flatten along with the decrease of PBS sequence length. The crystallization transition of hard segments appears in all prepared polymers and similarly to melting endotherms, crystallization exotherms decrease with the decrease of PBS sequence length. The T_m melting temperature of hard domains as well as T_c crystallization temperature of hard segments decrease systematically with the decrease of PBS sequence length (respectively from 115 to 91 and from 65 to 28°C).

The tensile properties of investigated copolymers as typical stress-strain curves before and after degradation are shown in FIGURE 2. For samples before degradation, the highest strain was observed at about 40 % soft segment content. It is worth noting that this behaviour is similar to changes of the elongation for the majority of the multiblock thermoplastic elastomers [6]. After degradation (4 weeks in buffer (pH=7,2) at 37°C) we can observe decreasing of strain for copolymers with increasing soft segment content, while "pure" PBS keeps almost the same mechanical properties. This phenomenon suggests that the most changes occur in amorphous phase.

The mass loss for the different three kind of buffers (pH=9, pH=7,2 and pH=5) at 37°C after hydrolysis is shown in FIGURE 3. It can be seen that synthesized polymers shows weight loss during incubation time. Copolymer composition influenced the mass loss while the influence of solution type was not so significant. As it was expected, poly(butylene succinate) degrades slower as compared to copolymers with dimerized fatty acid.

Conclusions

In discussed paper, the results of preliminary hydrolytic degradation of degradable aliphatic copolyesters based on dimerized fatty acid (saturated dilinoleic acid), succinic acid and 1,4-butanediol were reported. Synthesized polymers are characterized by moderate melting temperatures. Introduction of dimerized fatty acid moieties decreases melting and crystallization temperature. The tensile properties (stress-strain curves) confirmed typical thermoplastic elastomer behaviour of the copolyesters. Synthesised polymers are susceptible to hydrolytic degradation as demonstrated by decrease of mechanical properties and mass loss.

References

- [1]. Kim M., Kim K., Jin H., Park J., Yoon J., Eur Polym J, Vol: 37, (2001), 1843-1847
- [2]. Jin H., Lee B., Kim M., Yoon J., J Appl Polym Sci, Vol: 38, (2000), 1504-1511
- [3]. Müller, R. J., Kleeberg I. Deckwer W.D. Journal of Biotechnology Vol: 86, 2001, 87 - 95
- [4]. Fujimaki T., Polym Degrad Stab Vol: 59, Issue: 1-3, 1998, 209-214
- [5]. Kozłowska A., Gromadzki D., Štěpánek P., El Fray M., Fibres & Textiles in Eastern Europe 2008, 6 (71), 85-88
- [6]. J. Slonecki, „Structure and some properties of copoly(ester-ether)”, Sci. Papers of Technical University of Szczecin 1992, 479