



The influence of of cross-linking process on the physicochemical properties of new copolyesters containing xylitol



Marta Piątek-Hnat*, Kuba Bomba

West Pomeranian University of Technology, Faculty of Chemical Technology and Engineering, Department of Polymer and Biomaterials Science, Piastów Ave. 42, 71-065 Szczecin, Poland

ARTICLE INFO

Keywords:

Ester elastomers
Esterification
Renewable sources
Crosslinking
Mechanical properties

ABSTRACT

The goal of this research was developing biodegradable and biocompatible xylitol-based copolymers with improved mechanical properties, and investigating the change in their thermal and chemical properties with progress of the cross-linking process. Using a raw material of natural origin such as xylitol, a prepolymer was obtained by esterification and polycondensation. Then, at subsequent stages of the crosslinking process in a vacuum dryer, samples of materials were taken to determine the progress of the process using Fourier transform infrared spectroscopy. The method of differential scanning calorimetry also defined changes in the ranges of phase changes occurring at each stage of the crosslinking process. After the crosslinking process, ester materials based on sebacic and succinic acid were characterized in terms of mechanical and surface properties.

1. Introduction

Polyester materials are very popular among many research teams in the world. This is due to the fact that these materials can be obtained from easily available raw materials and the method of their synthesis allows you to modify them in the direction of the desired properties. Among many types of polyesters, succinic acid copolyesters and sebacic acid copolyesters deserve attention. These copolymers belong to the group of biodegradable aliphatic polyesters.

Despite many advantages, widespread use of biodegradable polyesters is limited due to the limited range of mechanical properties and the difficulty of their modification due to the lack of reactive functional groups. In this paper [1] describes a new class of multiblock copolymers composed of PBF poly (butylene fumarate and PBS poly (butylene succinate). The obtained materials have good thermal and mechanical properties, and as the authors describe the increase in biodegradability. The rate of copolymer degradation was significantly accelerated by copolymerization of PBF with PBS, especially at 50% and higher its share in the copolymer. It has been found that both segments are compatible in both the amorphous and crystalline region, and isomorphous co-crystallization between PBF and PBS occurs in the crystal region, which was the first time. It is noteworthy that the reactive C–C bond found in the copolymer backbone allows the physicochemical properties to be modified as needed.

The article [2] describes the method of preparation and properties

of multiblock copolymers composed of poly (butylene succinate) PBS and poly (ϵ -caprolactone) PCL and with hexamethylene diisocyanate (HDI) as a chain extender. According to the authors, such copolymers could be used in the field of biodegradable polymeric materials. PBS and PCL do not show miscibility in the amorphous phase. However, in the high temperature area two melting temperature of the crystalline phase can be observed. The thermal stability of the copolymers increases with the increase of PBS. However, the mechanical properties can be well regulated by changing the proportion of PBS and PCL, obtaining rigid materials characterized by a high value of stress to break, to elastic elastomers, which is characterized by a high value of strain to break. The authors emphasize that copolymers with 10–30% PCL are characterized by optimal mechanical properties and impact resistance.

Examples of multiblock copolymers are those consisting of crystalline poly (butylene succinate) (PBS) and amorphous poly (1,2-propylene succinate) (PPSu), which were synthesized by chain elongation using hexamethylene diisocyanate (HDI) [3]. Authors of studies ^{13}C NMR confirmed the receipt of copolymers with a sequential structure. They also confirmed that block copolymers have very good mechanical and thermal properties as well as excellent impact strength. The use of the amorphous soft PPSu segment not only gives the copolymers higher impact resistance without lowering the melting point, but also increases the rate of enzymatic degradation.

In the article [4], the authors describe a biodegradable copolymer of

* Corresponding author.

E-mail address: marp@zut.edu.pl (M. Piątek-Hnat).

<https://doi.org/10.1016/j.mtcomm.2019.100734>

Received 30 June 2019; Received in revised form 28 October 2019; Accepted 30 October 2019

Available online 04 November 2019

2352-4928/ © 2019 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

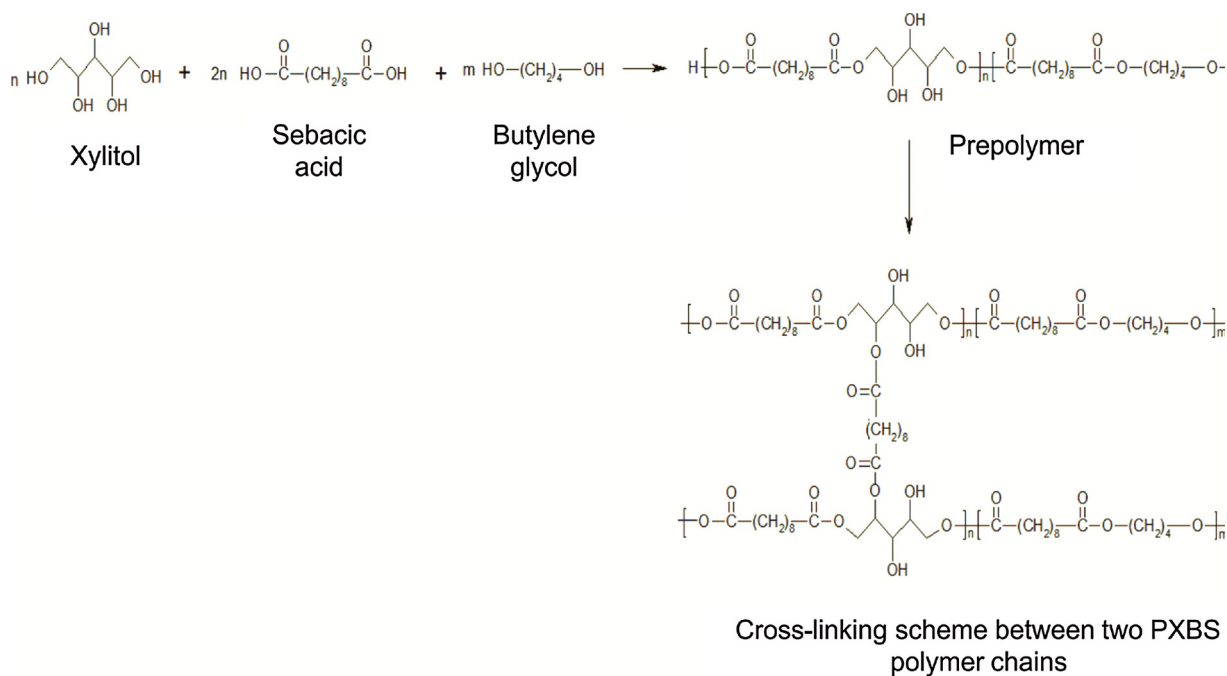


Fig. 1. Scheme of poly(xylitol sebacate-co-butylene sebacate)PXBS structure.

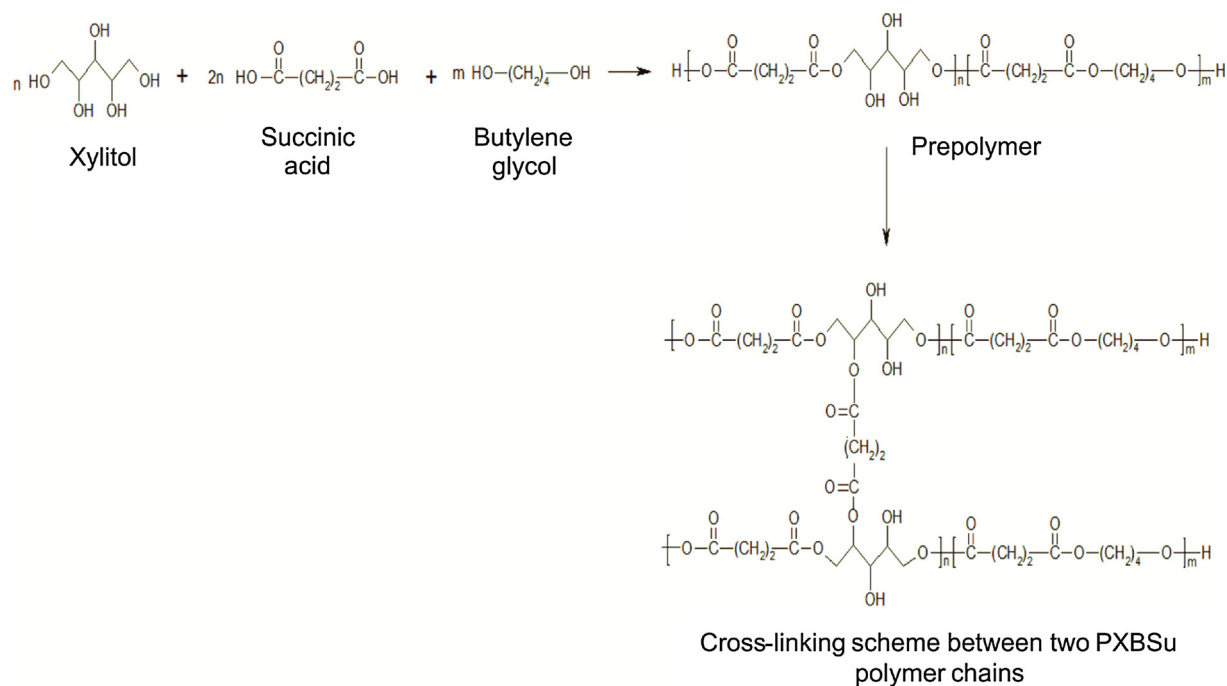


Fig. 2. Scheme of poly(xylitol succinate-co-butylene succinate)PXBSu structure.

Table 1

Composition and selected properties of poly(xylitol sebacate-co-butylene sebacate) PXBS after 288 h crosslinking.

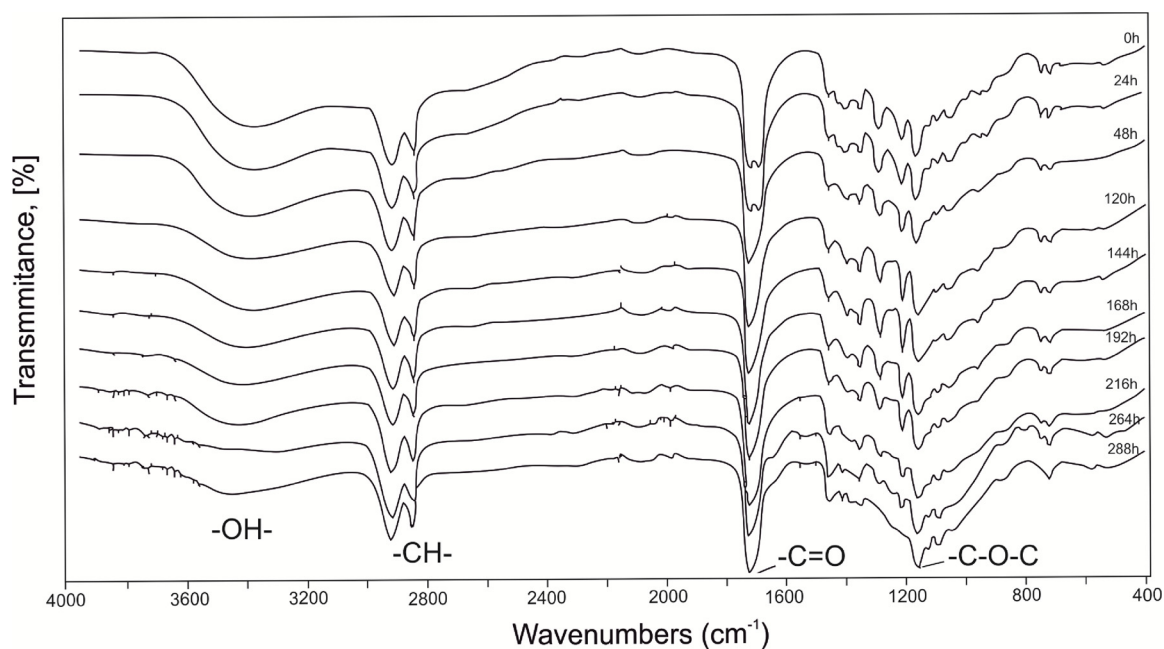
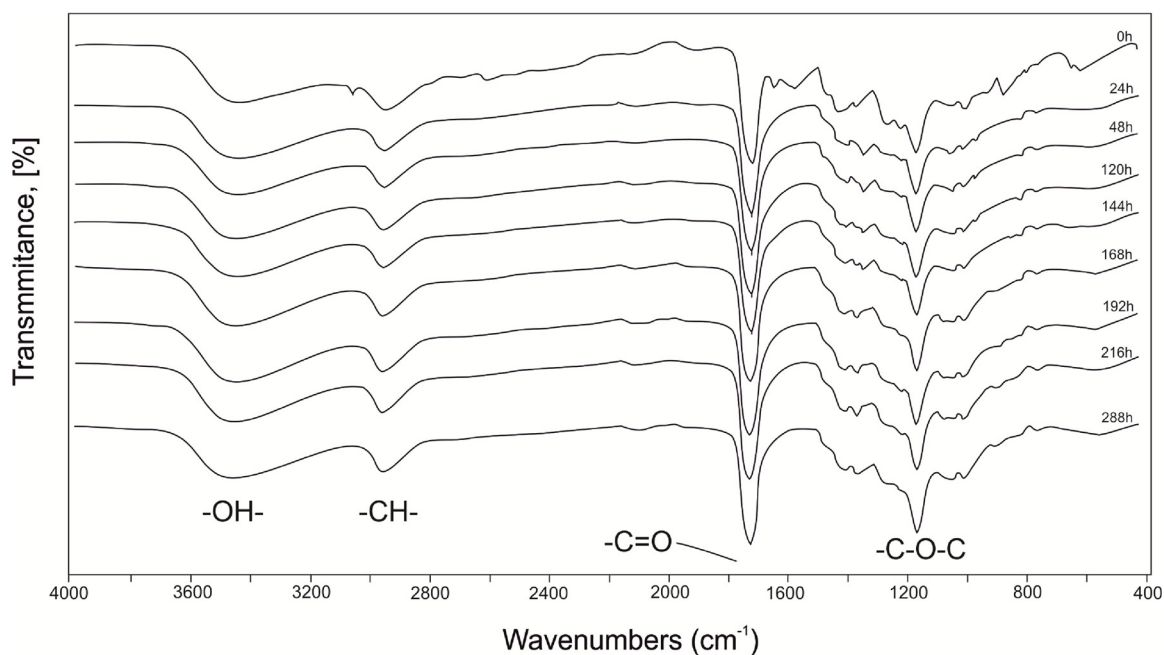
Polymer sample	Molar Composition [mol]			H ShA	σ_r MPa	ϵ_r %	X %	CA
	Sebacic acid	Xylitol	Butylene glycol					
poly(xylitol sebacate-co-butylene sebacate) PXBS	2	1	1	36 +/- 0.42	0.93 +/- 0.25	306 +/- 63	91	46

where: H - Hardness, σ_r - Stress in break, ϵ_r - Elongation, X - Gel fraction, CA - Contact angle.

Table 2

Composition and selected properties of poly(xylitol succinate-co-butylene succinate) PXBSu after 288 h crosslinking.

Polymer sample	Molar Composition [mol]			H ShA	σ_r MPa	ϵ_r %	X %	CA
	Succinic acid	Xylitol	Butylene glycol					
poly(xylitol sebacate-co-butylene sebacate) PXBSu	2	1	1	46 +/- 0.68	1.5 +/- 0.19	248 +/- 83	96	69

where: H - Hardness, σ_r - Stress in break, ϵ_r - Elongation, X - Gel fraction, CA - Contact angle.**Fig. 3.** Spectrum ATR-FTIR spectra of pre- PXBS (0 h) and PXBS during the crosslinking process (24 h–288 h).**Fig. 4.** Spectrum ATR-FTIR spectra of pre- PXBSu (0 h) and PXBSu during the crosslinking process (24 h–288 h).

poly (butylene succinate) and a butylene ester of dilinoleic acid (PBS/DLA), which were the coating for multi-component controlled release fertilizer (NPK). It has been shown that the studied PBS/DLA are very interesting materials in the processes of nutrient release due to their biodegradability, which can be extremely important in agricultural

cultivation.

Poly(polyol sebacate) polyesters are biocompatible and biodegradable elastomers exhibiting a wide range of potential biomedical applications like scaffolds for treating cartilage defects [5] vascular tissue engineering [6], myocardial tissue engineering [7], and retinal

Table 3
Thermal properties of the poly(xylitol sebacate-co-butylene sebacate) PXBS.

Cross-linking time	First heating				Cooling		Second heating					
	T_{m1} [°C]	ΔH_{m1} [J/g]	T_{m2} [°C]	ΔH_{m2} [J/g]	T_{c1} [°C]	ΔH_{c1} [J/g]	T_{g1} [°C]	Δc_p [J/g°C]	T_{m3} [°C]	ΔH_{m3} [J/g]	T_{m4} [°C]	ΔH_{m4} [J/g]
0 h	19	24.17	44.9	50.89	-3.9	65.87	-13.1	0.558	22.6	61.3	50.7	3.17
24 h	18.5	28.29	42	34.38	-5	54.27	-12	0.292	21.4	61.2	n.o.	n.o.
48 h	19.5	23.28	43.5	41.56	-6.3	47.16	-12.8	0.128	21.1	53.15	n.o.	n.o.
120 h	15.8	40.09	39.9	10.86	-7.4	46.93	-18.4	0.339	17.5	49.84	n.o.	n.o.
144 h	17.2	34.1	41	18.18	-8.8	42.77	-19.3	0.426	18.3	48.41	n.o.	n.o.
168 h	16.4	36.8	40.7	10.28	-10.9	39.12	-21.7	0.371	17.5	45.74	n.o.	n.o.
192 h	18.9	28.67	42.9	9.76	-13.3	30.3	-20.5	0.264	19.9	35.52	n.o.	n.o.
216 h	16.5	34.35	40.6	6.42	-14.3	27.87	-22.9	0.209	18.2	36.04	n.o.	n.o.
264 h	19.5	32.15	43.3	3.54	-18.7	25.42	-26.3	0.336	20.3	34.48	n.o.	n.o.
288 h	17.5	24.01	41.2	0.66	-19	15.87	-28	0.248	17.6	23.18	n.o.	n.o.

n.o. - not observed, where: T_{g1} - glass transition temperatures; Δc_p - change of the heat capacity at glass transition, T_{m1} , T_{m2} , T_{m3} , T_{m4} - melting temperature; T_{c1} - crystallization temperatures; ΔH_{m1} , ΔH_{m2} , ΔH_{m3} , ΔH_{m4} - heat of melting at T_{m1} , T_{m2} , T_{m3} , T_{m4} ; ΔH_{c1} - crystallization heat in T_{c1} .

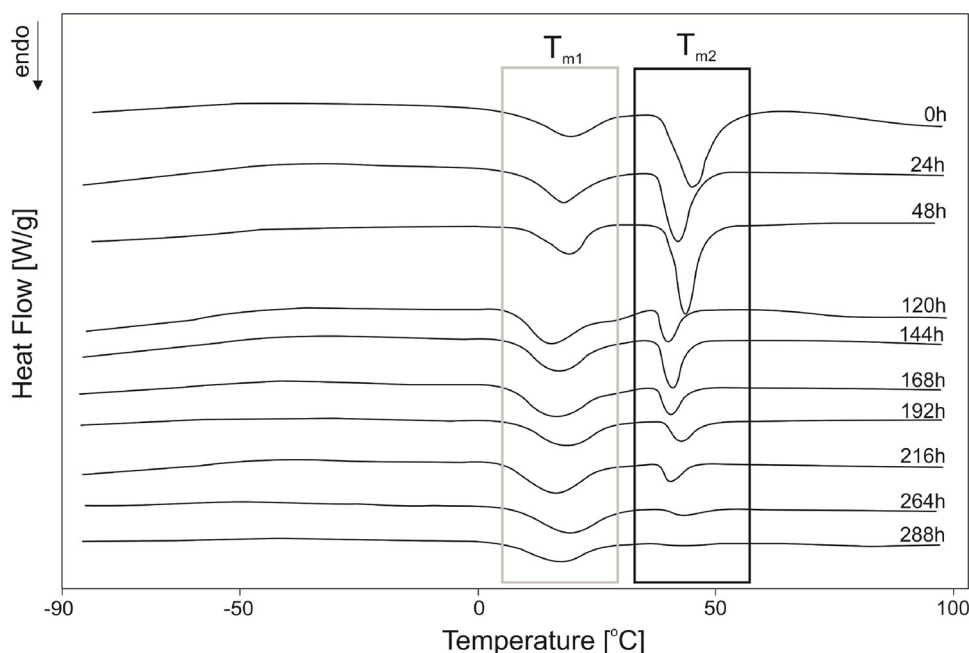


Fig. 5. DSC thermograms of poly(xylitol sebacate-co-butylene sebacate) PXBS at the crosslinking stages subjected to first heating.

progenitor cell grafting [8]. They also have potential applications as contact guidance materials [9], hollow conduit neural guides [10], and drug delivery [11]. Polyesters with similar properties to poly(glycerol sebacate) can be synthesized by substituting glycerol with natural polyols like mannitol, sorbitol and xylitol [12]. One of the possible monomers for biodegradable polyester synthesis, xylitol is a sugar alcohol found naturally in fruits and vegetables like lettuce, cauliflower, raspberry, grape, banana and strawberry. It can also be found in yeast, lichens, mushrooms, and seaweed. It is an intermediate in human carbohydrate metabolism, produced by human adults between 5 and 15 g/day [13]. Xylitol-based polymers are of great interest to biomaterials science due to their biocompatibility, and biodegradability. Poly(xylitol sebacate) has been shown to possess in vitro and in vivo biocompatibility comparable to poly(L-lactic-co-glycolic acid) (PLGA) [14–16]. Furthermore, both mechanical properties and degradation rate of polyesters containing xylitol can be fine-tuned by adjusting xylitol: dicarboxylic acid ratio [15,17]. Those properties can also be fine-tuned by adjusting curing time and dicarboxylic acid chain length. [17]. To the best of our knowledge, poly(xylitol sebacate-co-butylene sebacate) and poly(xylitol succinate-co-butylene succinate) have not been previously synthesized by other authors, and are novelty materials. Using butylene glycol as an additional monomer in polyester synthesis

allowed us to obtain copolyesters with improved mechanical properties compared to polyesters synthesized using only polyol and dicarboxylic acid.

2. Material and experimental methods

2.1. Synthesis and characterization of xylitol-based copolymers

All chemicals except xylitol were purchased from Sigma–Aldrich (St. Louis, MO, USA). Two copolymers containing xylitol were synthesized: poly(xylitol sebacate-co-butylene sebacate) with sebacic acid: butylene glycol: xylitol ratio of 2:1:1 (PXBS), and poly(xylitol succinate-co-butylene succinate) with succinic acid: butylene glycol: xylitol ratio of 2:1:1 (PXBSu) Monomers were melted in a round bottom flask in a temperature above 100 °C under a blanket of N₂. Following that, esterification reaction was performed for 13,5 h in 150 °C under a blanket of N₂, catalyzed by Ti(OBu)₄. Then, polycondensation reaction was conducted in 150 °C under vacuum. Prepolymers were then cross-linked in a vacuum-dryer in 100 °C under 100 mBar for 288 h. Samples were taken directly after polycondensation reaction ended, and at consecutive stages of cross-linking process.

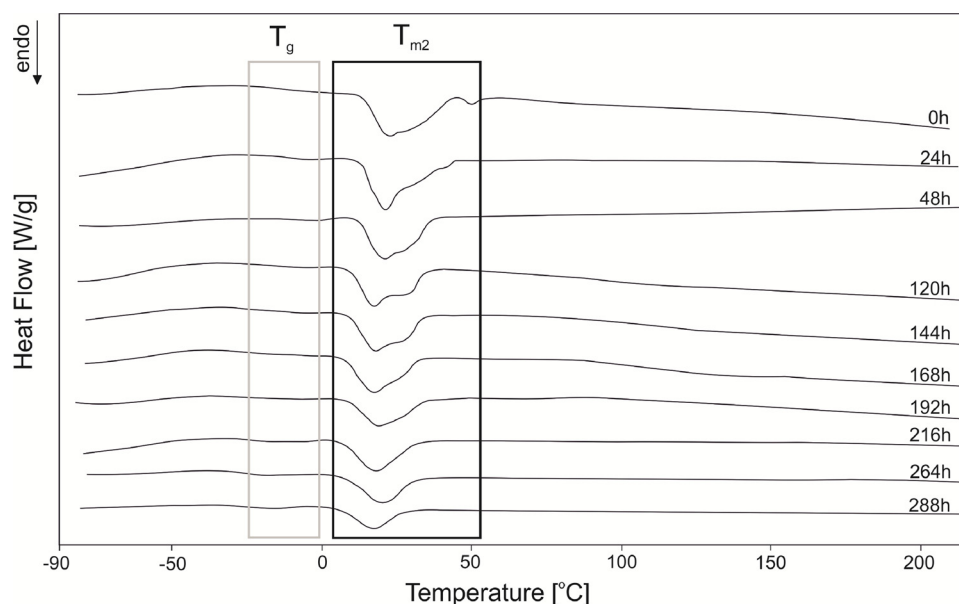


Fig. 7. DSC thermograms of poly(xylitol sebacate-co-butylene sebacate) PXBS at the crosslinking stages subjected to second heating.

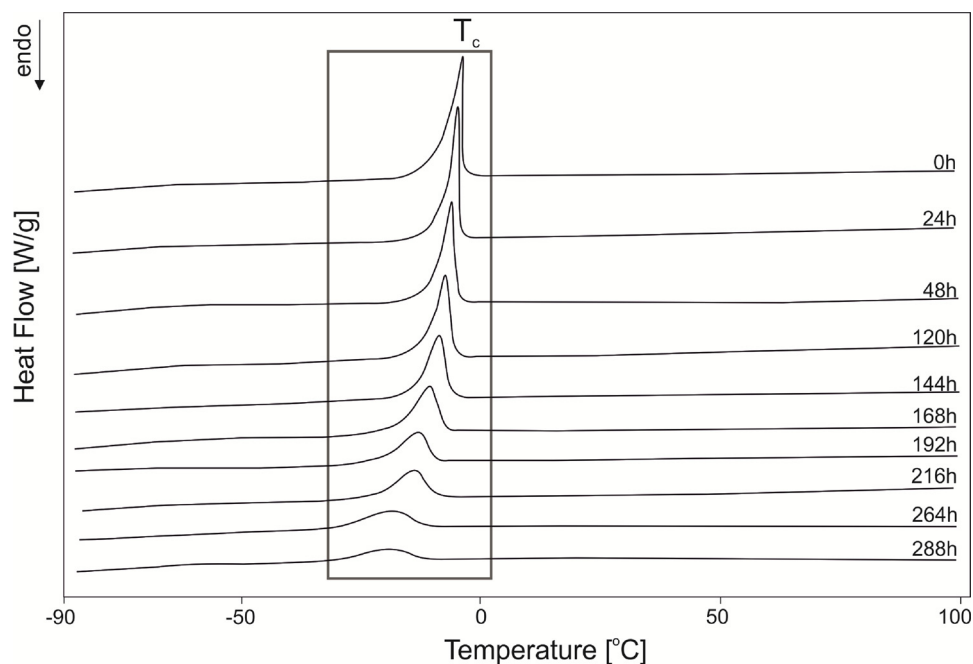


Fig. 6. DSC thermograms of poly(xylitol sebacate-co-butylene sebacate) PXBS at the crosslinking stages subjected to cooling.

Table 4

Thermal properties of the poly(xylitol succinate-co-butylene succinate)) PXBSu.

Cross-linking time	First heating				Cooling		Second heating	
	T _{g1} [°C]	Δc _{p1} [J/g°C]	T _{m1} [°C]	ΔH _{m1} [J/g]	T _{g2} [°C]	Δc _{p2} [J/g°C]	T _{g3} [°C]	Δc _{p3} [J/g°C]
0 h	-19.9	0.522	46.8	15.41	-26.4	0.84	-15.7	0.57
24 h	-19.2	0.48	48.1	12.82	-23.5	0.606	-16.9	0.519
48 h	-18.6	0.533	48.4	13.92	-24.8	0.542	-18.8	0.651
120 h	-17.8	0.533	47.8	12.12	-23.4	0.7	-17.6	0.617
144 h	-17.6	0.596	48.5	12.32	-22.5	0.668	-17.5	0.719
168 h	-14.2	0.588	49.8	8.52	-18	0.709	-10.4	0.596
192 h	-12.2	0.449	50.9	7.77	-18.9	0.897	-5.2	0.475
216 h	-12	0.604	53.2	4.14	-18.2	0.695	-9.8	0.612
288 h	-7	0.572	n.o.	n.o.	-18.6	0.624	-2.8	0.543

n.o. - not observed, where: T_{g1,2,3} - glass transition temperatures; Δc_{p1,2,3} - change of the heat capacity at glass transition T_{g1}, T_{g2}, T_{g3}; T_{m1} - melting temperature; ΔH_{m1} - heat of melting at T_{m1}.

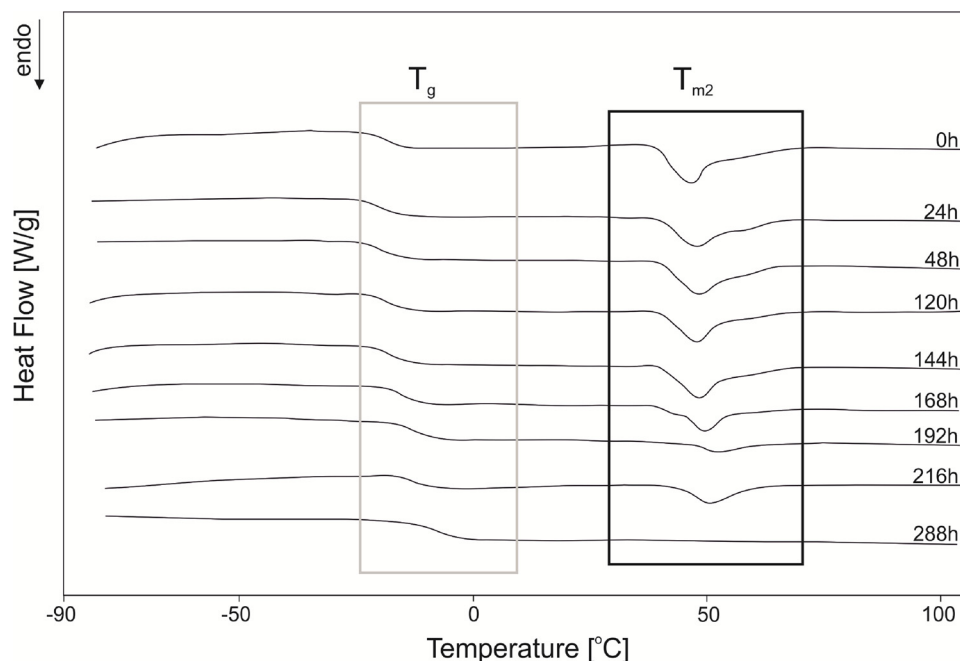


Fig. 8. DSC thermograms of poly(xylitol succinate-co-butylene succinate) PXBSu at the crosslinking stages subjected to first heating.

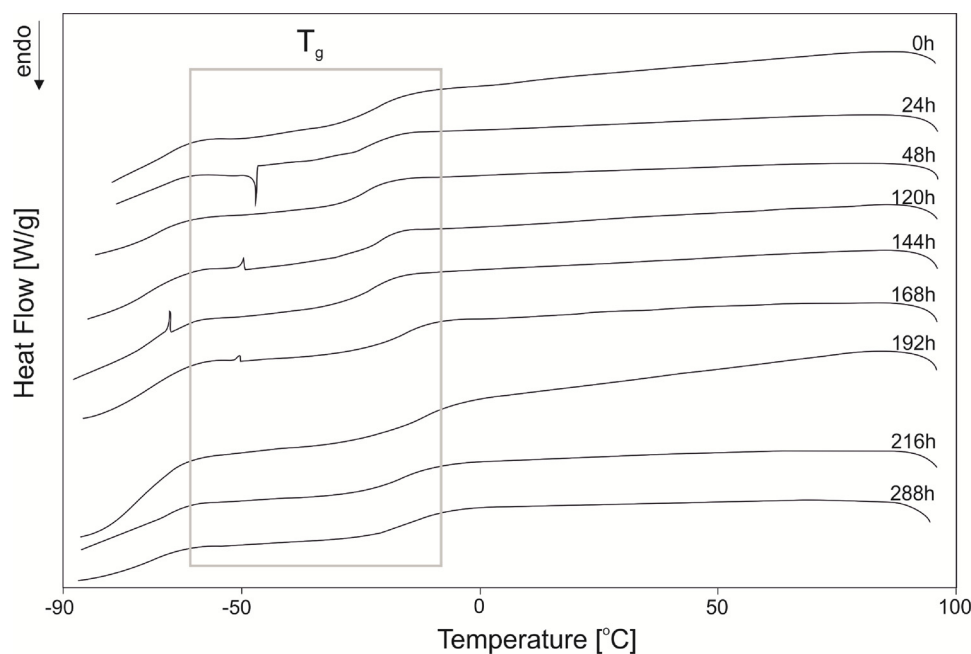


Fig. 9. DSC thermograms of poly(xylitol succinate-co-butylene succinate) PXBSu at the crosslinking stages subjected to cooling.

2.2. Experimental methods

2.2.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectrometry (ATR FTIR Alpha spectrometer, Bruker) was used to examine the chemical structure of all materials obtained at subsequent stages of the crosslinking process. FTIR transmission spectra were recorded between 400 and 4000 cm^{-1} , with 2 cm^{-1} resolution. The test results were developed using Omnic software.

2.2.2. Differential scanning calorimetry (DSC)

Thermal properties were determined using differential scanning calorimetry (DSC) (Q100, TA Instruments apparatus). The measurement was carried out in a cycle heating in the temperature range from

– 100 to 200 °C.

2.2.3. Mechanical properties

Mechanical tests were carried out with an Instron 3366 instrument equipped with a 500 N load cell in accordance with standard PN-EN-ISO 527/1:1996 (crosshead speed of 100 mm/min, at 25 °C and 50% of relative humidity).

2.2.4. Hardness

Hardness (H) for materials after 288 h was measured using a Zwick/Material Testing 3100 Shore A hardness tester.

2.2.5. Water contact angle

The water contact angle was measured by using a KRUS DSA100

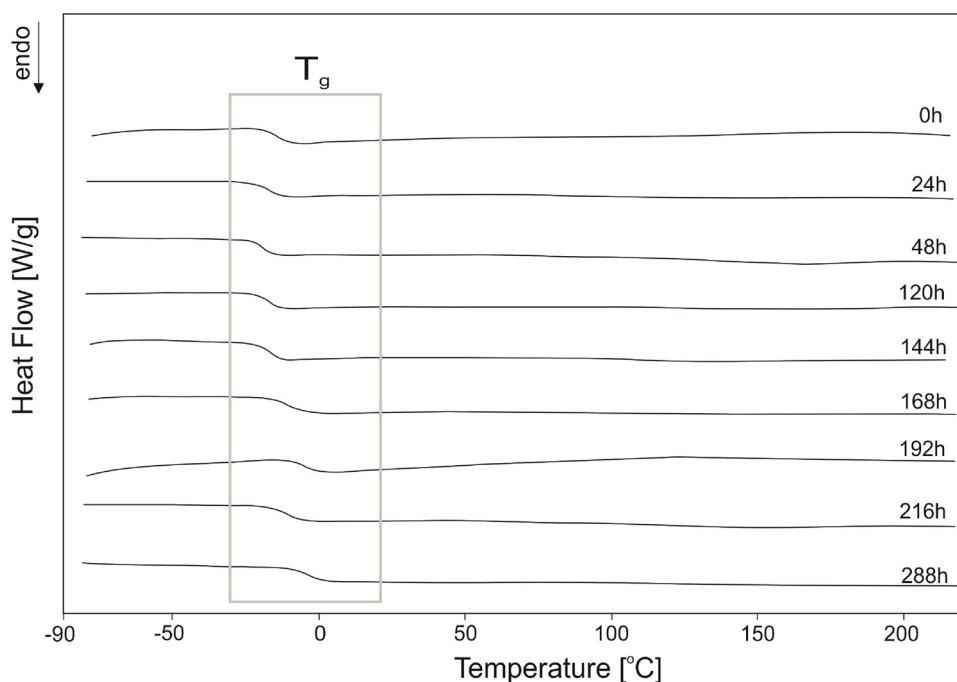


Fig. 10. DSC thermograms of poly(xylitol succinate-co-butylene succinate) PXBSu at the crosslinking stages subjected to second heating.

digital goniometer. Static contact angle measurements were performed on the surface of degreased materials after 288 h crosslinking by placing a 2 μ L droplet of deionized water using the automatic dispenser of the goniometer. Contact angle was calculated using Kruss drop shape analysis software (DSA4).

2.2.6. Gel fraction

Determination of gel fraction of elastomers after 288 h was made by the extraction method. PN-EN 579: 2001. Material samples after 288 h crosslinking (about 1 g) were placed in Schott type P2 crucible and subjected to extraction in boiling tetrahydrofuran (100 cm³) for 3 h. After extraction, the samples were dried in a vacuum oven at 25 °C for 3 h and then in a desiccator. Three determinations were made for each elastomer. The content of gel fractions was calculated from formula (1) as the mean of three measurements:

$$X = m_1/m_0 \cdot 100\% \quad (1)$$

where: m_1 - sample mass after extraction, m_0 - sample mass before extraction.

3. Results and discussion

As a result of the described synthesis, two ester elastomers were obtained, the reactions of which are shown in Figs. 1 and 2. In Tables 1 and 2 the basic physicochemical properties of PXBS and PXBSu were compared after 288 h of crosslinking (the third stage of the preparation process - crosslinking).

3.1. Fourier transform infrared spectroscopy (FTIR)

The obtained spectra show bands typical for polyester structure. For both materials four transmittance peaks can be observed (Fig. 3 (PXBS) and Fig. 4 (PXBSu)): $-C-O-C$ group at about 1150 cm⁻¹ wavelength, $-C=O$ group at about 1706 cm⁻¹ wavelength, $-CH$ at about 2944 cm⁻¹ wavelength, and intermolecularly associated $-OH$ groups at about 3435 cm⁻¹ wavelength. Peak intensity of $-OH$ groups decreases, and peak intensity of $-C-O-C$ groups increases with the cross-linking progress. It is the result of bonding between molecules in the adjacent polymer chains.

3.2. Differential scanning calorimetry (DSC)

3.2.1. Poly(xylitol sebacate-co-butylene sebacate)

Table 3 contains the values of the characteristic temperatures of phase transitions with thermal effects at subsequent stages of PXBS crosslinking.

On the first-heating thermograms (Fig. 5) two melting temperatures can be observed, T_{m1} is the result of melting of poly(xylitol sebacate), and T_{m2} is the result of melting of poly(butylene sebacate). Second melting enthalpy value decreases with the cross-linking progress. On the second-heating thermograms (Fig. 7) T_{m2} can only be observed for the non-crosslinked polymer. Glass transition temperature can be observed on the second-heating thermograms. Cooling thermograms (Fig. 6) show crystallization temperatures. Both the temperatures and enthalpies of crystallization decrease with the cross-linking progress.

3.2.2. Poly(xylitol succinate-co-butylene succinate) PXBSu

Table 4 contains the values of the characteristic temperatures of phase transitions with thermal effects at subsequent stages of PXBSu crosslinking.

On the first-heating thermogram glass transition temperature and melting temperature can be observed. Glass transition temperature increases with the cross-linking progress. Melting temperature increases, and melting enthalpy decreases with the cross-linking progress. For the completely cross-linked material melting temperature cannot be observed (Fig. 8). On the cooling thermograms (Fig. 9) glass transition temperature can be observed. Fig. 9 shows a wide range of glass transition, which is probably associated with the overlap of certain effects associated with the crystallization of other crystalline forms. On the second-heating thermograms (Fig. 10) thermogram only glass transition temperature can be observed. Melting temperature cannot be observed which is probably the result of thermal cross-linking that occurred during DSC analysis.

3.3. Mechanical properties

The mechanical properties of the PXBS and PXBSu elastomers after 288 h of crosslinking are shown in Tables 1 and 2. An elastomer based on succinic acid (PXBSu) 288 h after the crosslinking process has a

much higher value of tensile strength of 1.5 MPa than the elastomer PXBS (0.93 MPa). Elongation material PXBS is higher relative to the material as is evident PXBSu the observed values of tensile strength.

3.4. Hardness

Tables 1 and 2 show the hardness results for PXBS and PXBS after 288 h of crosslinking. It can be observed that both materials have a very low Shore A value and can be included in soft elastomers similar to cross-linked silicone rubber.

3.5. Water contact angle

Wetting properties of polymeric materials are very important for their applications in medicine. Therefore, it is important that the designed materials determine their hydrophilicity or hydrophobicity. Hydrophilic surfaces potentially improve biocompatibility. To investigate the wetting characteristics of the surfaces of our materials, the water contact angle measurements were made for ester elastomers after 288 h of the crosslinking process and the results are presented in Tables 1 and 2. Both the PXBS and PXBS material are characterized by a hydrophilic surface. However, for an ester elastomer based on sebacic acid, the surface of the material exhibits a significantly higher wettability compared to an elastomer based on succinic acid.

3.6. Gel fraction

The results of the gel fraction for ester materials presented in Table 1 and 2 after 288 h of cross-linking indicate obtaining materials characterized by a high degree of cross-linking. Both PXBS and PXBSu achieved gel fraction values of 91 and 96%, respectively. Slightly lower value can be observed for the PXBS material, which is directly related to the fact that the material shows an endothermic melting transformation visible on DSC thermograms after the crosslinking process (Figs. 5, 7). The PXBSu material does not show such a conversion, while DSC thermograms show the glass transition temperature, which is typical for elastomeric materials.

4. Conclusions

Copolymers synthesized by us exhibit better mechanical properties than materials synthesized using only xylitol and dicarboxylic acid, while retaining their biocompatibility and biodegradability. Mechanical properties, and change in thermal and chemical properties with progress of the cross-linking process were investigated. Different temperatures and thermal effects corresponding to various phase transitions were recorded at consecutive stages of the cross-linking process. Bonding between adjacent polymer chains lead to decreasing peak intensity of intermolecularly associated $-OH$ groups and increasing peak intensity of $-C-O-C$ groups in FTIR analysis with progress of the cross-linking process.

Conflicts of interest

The authors declared that they have no conflict of interest.

References

- [1] L. Zheng, Z. Wang, S. Wu, Ch. Li, D. Zhang, Y. Xiao, Novel poly(butylene fumarate) and poly(butylene succinate) multiblock copolymers bearing reactive carbon-carbon double bonds: synthesis, characterization, cocrystallization, and properties, *Ind. Eng. Chem. Res.* 52 (2013) 6147–6155, <https://doi.org/10.1021/ie303573d>.
- [2] L. Zheng, Li Ch, Z. Wang, J. Wang, Y. Xiao, D. Zhang, G. Guan, Novel biodegradable and double crystalline multiblock copolymers comprising of poly(butylene succinate) and poly(ϵ -caprolactone): synthesis, characterization, and properties, *Ind. Eng. Chem. Res.* 51 (2012) 7264–7272, <https://doi.org/10.1021/ie300576z>.
- [3] L. Zheng, Ch. Li, W. Huang, X. Huang, D. Zhang, G. Guan, Y. Xiao, D. Wang, Synthesis of high-impact biodegradable multiblock copolymers comprising of poly(butylene succinate) and poly(1,2-propylene succinate) with hexamethylene diisocyanate as chain extender, *Polym. Adv. Technol.* 22 (2011) 279–285, <https://doi.org/10.1002/pat.1530>.
- [4] K. Lubkowski, A. Smorowska, B. Grzmil, A. Kozłowska, Controlled-release fertilizer prepared using a biodegradable aliphatic copolyester of poly(butylene succinate) and dimerized fatty acid, *J. Agric. Food Chem.* 63 (2015) 2597–2605, <https://doi.org/10.1021/acs.jafc.5b00518>.
- [5] J.M. Kempainen, S.J. Hollister, Tailoring the mechanical properties of 3D-designed poly(glycerol sebacate cartilage applications) scaffolds for, *J. Biomed. Mater. Res. - Part A* 94 (2010) 9–18, <https://doi.org/10.1002/jbm.a.3265>.
- [6] D. Motlagh, J. Yang, K.Y. Lui, A.R. Webb, G.A. Ameer, Hemocompatibility evaluation of poly(glycerol-sebacate) in vitro for vascular tissue engineering, *Biomaterials* 27 (2006) 4315–4324, <https://doi.org/10.1016/j.biomaterials.2006.04.010>.
- [7] Q.Z. Chen, A. Bismarck, U. Hansen, S. Junaid, M.Q. Tran, S.E. Harding, N.N. Ali, A.R. Boccaccini, Characterisation of a soft elastomer poly(glycerol sebacate) designed to match the mechanical properties of myocardial tissue, *Biomaterials* 29 (2008) 47–57 <https://doi.org/10.1016/j.biomaterials.2007.09.010>.
- [8] W.L. Neeley, S. Redenti, H. Klassen, S. Tao, T. Desai, M.J. Young, R. Langer, A microfabricated scaffold for retinal progenitor cell grafting, *Biomaterials* 29 (2008) 418–426, <https://doi.org/10.1016/j.biomaterials.2007.10.007>.
- [9] C.J. Bettinger, B. Orrick, A. Misra, R. Langer, J.T. Borenstein, Microfabrication of poly (glycerol-sebacate) for contact guidance applications, *Biomaterials* 27 (2006) 2558–2565 <https://doi.org/10.1016/j.biomaterials.2005.11.029>.
- [10] C.A. Sundback, J.Y. Shyu, Y. Wang, W.C. Faquin, R.S. Langer, J.P. Vacanti, T.A. Hadlock, Biocompatibility analysis of poly(glycerol sebacate) as a nerve guide material, *Biomaterials* 26 (2005) 5454–5464 <https://doi.org/10.1016/j.biomaterials.2005.02.004>.
- [11] Z.J. Sun, C. Chen, M.Z. Sun, C.H. Ai, X.L. Lu, Y.F. Zheng, B.F. Yang, D.L. Dong, The application of poly (glycerol-sebacate) as biodegradable drug carrier, *Biomaterials* 30 (2009) 5209–5214 <https://doi.org/10.1016/j.biomaterials.2009.06.007>.
- [12] Z.Y. Ning, Q.S. Zhang, Q.P. Wu, Y.Z. Li, D.X. Ma, J.Z. Chen, Efficient synthesis of hydroxyl functionalized polyesters from natural polyols and sebacic acid, *Chin. Chem. Lett.* 22 (2011) 635–638, <https://doi.org/10.1016/j.ccl.2010.12.033>.
- [13] J.C. Paraji, H. Dominguez, J.M. Dominguez, Biotechnological production of xylitol. Part 1: interest of xylitol and fundamentals of its biosynthesis, *Bioresour. Technol.* 65 (1998) 191–201, [https://doi.org/10.1016/S0960-8524\(98\)00038-8](https://doi.org/10.1016/S0960-8524(98)00038-8).
- [14] J.P. Bruggeman, C.J. Bettinger, C.L.E. Nijst, D.S. Kohane, R. Langer, Biodegradable xylitol-based polymers, *Adv. Mater.* 20 (2008) 1922–1927, <https://doi.org/10.1002/adma.200702377>.
- [15] J.P. Bruggeman, C.J. Bettinger, R. Langer, Biodegradable xylitol-based elastomers: in vivo behavior and biocompatibility, *J. Biomed. Mater. Res. - Part A* 95 (2010) 92–104, <https://doi.org/10.1002/jbm.a.32733>.
- [16] J.P. Bruggeman, B.J. de Bruin, C.J. Bettinger, R. Langer, Biodegradable poly(polyol sebacate) polymers, *Biomaterials* 29 (2008) 4726–4735, <https://doi.org/10.1016/j.biomaterials.2008.08.037>.
- [17] Q. Dasgupta, K. Chatterjee, G. Madras, Combinatorial approach to develop tailored biodegradable poly(xylitol dicarboxylate) polyesters, *Biomacromolecules* 15 (2014) 4302–4313, <https://doi.org/10.1021/bm5013025>.