

Polyesters from renewable sources

Sylvia Dworakowska, Wiktor Kasprzyk, Szczepan Bednarz, Dariusz Bogdał

Faculty of Chemical Engineering and Technology, Politechnika Krakowska, Warszawska 24,
31-155 Krakow, Poland
pcbogdal@cyf-kr.edu.pl

Abstract

Aliphatic polyesters are one of the classes of materials that can potentially meet the varying requirements put for tissue scaffolds. In recent years, much attention was paid to design biocompatible scaffolds for tissues that would have the similarity to natural tissues in terms of stiffness, flexibility and endurance. Polyesters of citric acid and diols are promising materials for tissue scaffolds. They are characterized by simplicity of synthesis, use of low-cost and non-toxic monomers as well as ease of controlling properties of obtained products by polymerization process operating conditions. Many attempts at modification of polyesters based on citric acid with natural polyols such as xylitol and mannitol have been observed in recent years. Synthetic polyesters can also be modified with vegetable oil-based polyols being diverse in terms of hydroxyl number and functionality, which leads to change of mechanical properties of obtained polyesters. In this work, the effect of rapeseed oil-based polyols addition on the properties of citric acid-based polyesters has been investigated. It has been found that modification with polyols leads to improvement of tensile strength of obtained materials and additionally in a reduction of elongation at break values. However, the modification had no significant influence on swelling properties of achieved polyesters.

Keywords

polyesters, vegetable oil-based polyols

Introduction

The chemical industry is now focusing on environmental protection. The depletion of natural resources as well as high oil and gas prices have a significant impact on increasing use of renewable raw materials in world production of polymers. The application of natural raw materials of plant origin in organic synthesis is compatible with sustainable development being a rational model of technological development including environmental aspects.

Vegetable oils are a mixture containing mostly esters of glycerol and higher fatty acids, which, due to the presence of double bonds, as a result of the modification are capable of reacting with isocyanate or carboxyl groups. The production of vegetable oil-based polyols refers to conversion of double bonds to hydroxyl groups. Polyols vary in functionality, which affects the mechanical properties of polymeric materials [1,2].

Recently biodegradable polyester elastomers have been of interests for pharmaceutical and medical applications because of their biocompatibility, mechanical and chemical properties [3,4]. Two types of biodegradable elastomers include thermosets and thermoplastics. The crystallized hard regions which can be found in thermoplastic elastomers slow their biodegradation and often cause a nonlinear loss of mechanical properties during the

degradation process. On the other hand, thermoset elastomers characterize more uniform speed of biodegradation and the loss of mechanical properties during degradation is more linear which is desirable in tissue engineering scaffolds [5,6].

Some of those thermoset elastomers have been reported, which include poly(glycerol sebacate) [7,8], polyesteramide [9], starpoly(ϵ -caprolactone-*co*-D,L-lactide) [10], poly(trimethylene carbonate-*co*- ϵ -caprolactone) [11]. High cost of substrates, catalysts and harsh conditions of synthesis of those materials are main limitations in their use in tissue scaffold processing industry.

Other kind of promising polyester elastomers are poly(diols-citrates). Those elastomers can be easily fabricated under mild conditions using simple and viable procedure, without a catalyst what is a significant advantage over those mentioned earlier. Moreover mechanical properties of this polymer can be controlled by the post-polymerization conditions and use of different length diols or other polyols [12].

In this work, polyesters of citric acid and 1,6-hexanediol were synthesized using rapeseed oil-based polyols via two-step esterification. At first stage a prepolymer was prepared by carrying out controlled condensation reaction between 1,6-hexanediol and citric acid in molar ratio 1:1. At second stage the prepolymer was post-polymerized by crosslinking by diol in molar ratio of COOH:OH approximately 1:1. In order to form a porous microstructure, salt was used as a porogen. Fig. 1 shows scheme of prepolymer synthesis as well as postpolymerization reaction.

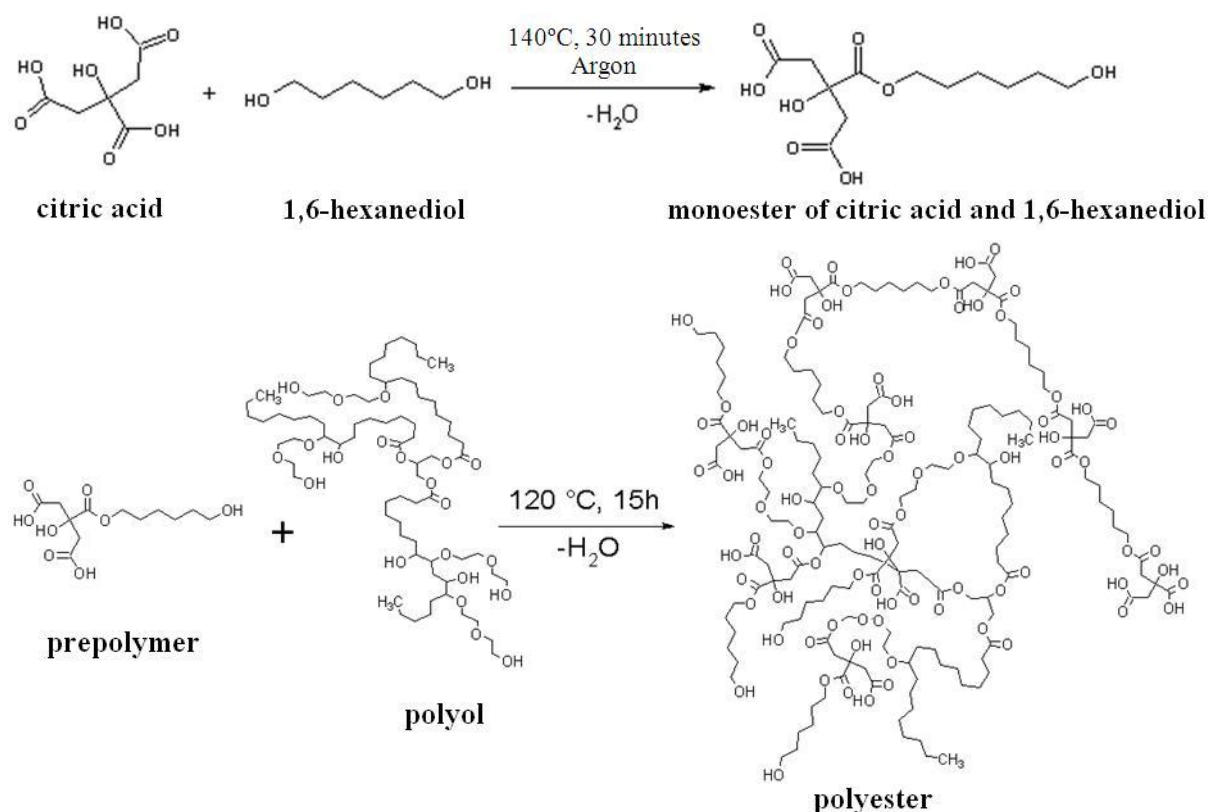


Fig. 1. Schematic representation of prepolymer synthesis and postpolymerization reaction

To evaluate the properties of tested materials in terms of their suitability for use in bone tissue engineering several techniques including observations on microscopy and determination of tensile strength and elongation at break values were used.

Experimental procedure

Materials

The following raw materials were used in the syntheses: citric acid, 1,6-hexanediol (Sigma Aldrich), sodium chloride (POCh Gliwice) and rapeseed oil-based polyols RDEG 1 and RDEG 2 with hydroxyl values, 196 mg KOH/g and 114 mg KOH/g, respectively. Polyols were obtained by a two-stage method by epoxidation of rapeseed oil and then complete oxirane ring opening under microwave irradiation [2].

Synthesis of polyesters

Equimolar amounts of citric acid (371.6 g) and 1,6-hexanediol (228.4 g) were mixed together and then triturated in a mortar. Prepolymer synthesis proceeded in a 1L three-neck round bottom flask at 140°C for 30 minutes under the protection of argon and by means of silicon oil bath. The obtained prepolymer was cooled to room temperature. Postpolymerization reaction was carried out in three teflon molds (A,B,C). To each of them 99 g of the prepolymer were weighed. Additionally 1 g of rapeseed oil-based polyols was weighed to the molds (polyol RDEG 1 to mold B and polyol RDEG 2 to mold C). The components in the molds were mixed and then 280 g of sodium chloride were added to each mold and mixed again. The obtained mixtures were cured at 120°C for 15 hours in air. Polyesters were cooled and then sodium chloride was leached from them using water in order to obtain elastomers with porous structure.

Methods

The acid content as the measure of carboxyl endgroups in 1 g of polyesters was determined and expressed in mmol COOH/g. 100 mg of prepolymer sample was placed in an Erlenmeyer flask and dissolved in 100 ml of 96% ethanol with addition of 3-5 drops of 1% phenolphthalein. The mixture was titrated with 0.5 M potassium hydroxide/96% ethanol solution. The acid number was calculated as mmol of carboxylic groups per 1g of a sample.

Swelling properties of obtained polyesters were defined as water absorbability and reported in a wt. % and calculated using the formula $W = [(A-B)/B] \times 100\%$, where: W – water absorbability (wt. %), A – mass of sample upon wetting (g), B – mass of sample before wetting (g).

The FTIR analysis was conducted using FT-IR BIORAD FTS-165 spectrophotometer. Spectrum was recorded on KBr discs in the wavenumber range of 4000-400 cm^{-1} .

The GPC chromatography was carried out using Knauer GPC chromatograph equipped in Refractive index detector Smartline2300 and gel permeation chromatography column Polysep-GFC-P4000. The chromatographic conditions were as follows: flow rate = 0.5 mL/min, eluent = distilled water, temperature of analysis = 35°C.

The cell structure was studied using the optical microscope with 2,5x magnification.

The tensile strength and elongation at break values of polyesters were carried out using Zwick Testing Machine (model 1445) according to Polish Norm PN-EN ISO 1798:2009.

Results and discussion

Received prepolymer of citric acid and 1,6-hexanediol was a clear, viscous liquid. Its FTIR spectrum (Fig.2) shows characteristic stretching vibrations of unsaturated bonds at 1730 cm^{-1} ($\text{C}=\text{O}$), what is confirmation of ester bonds formation. Broad absorption band related to hydroxyl groups is observed in the range of $3500\text{-}3000\text{ cm}^{-1}$. It can result from the presence of water in the prepolymer.

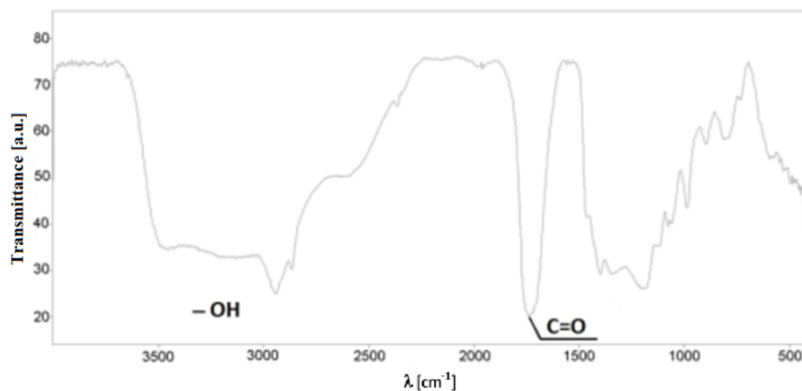


Fig. 2. FTIR spectrum of prepolymer

Reduction in the acid content of product (56 mmol COOH/g) according to the mixture of substrates (97 mmol COOH/g) also proves formation of ester bonds. The GPC chromatograms (Fig. 3) indicate that the resulting product consisted of two types of esters with retention times equal to 13,5 and 16 minutes. There were no peaks originating from citric acid and 1,6-hexanediol, indicated absence of unreacted substrates in the prepolymer.

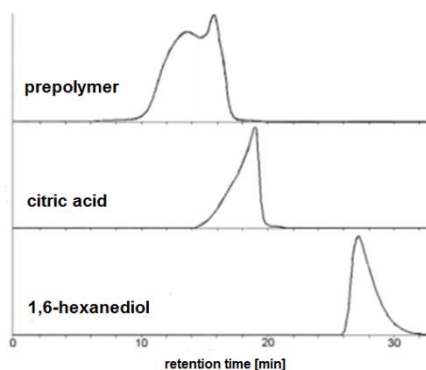


Fig. 3. GPC traces for prepolymer, citric acid and 1,6-hexanediol

Polyesters obtained after postpolymerization process were porous elastic solids with white and yellow colors (Fig. 4). Darker yellow color probably result from presence of double bonds in unsaturated fatty acids of polyols.

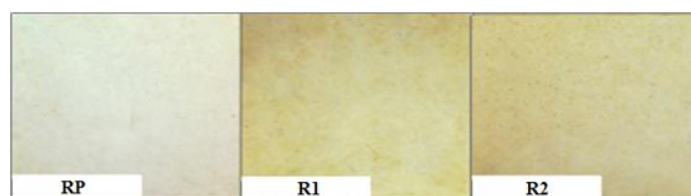


Fig. 4. Macroscopic structure of the polyesters; RP – reference polyester, R1 – polyester modified with RDEG 1, R2 – polyester modified with RDEG 2

Microscopic structure of a representative sample of the polyester is presented in Fig. 5, where can be observed the pores.

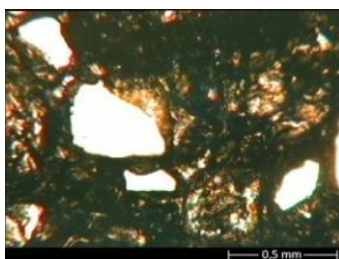


Fig. 5. Optical micrograph of cross-sectioned polyester (x2.5)

The mechanical properties of obtained materials are presented in Table 1. It was found beneficial effect of rapeseed oil-based polyol addition on elongation at break values of polyesters. Water absorbability test results show that one-percent addition of polyols in the synthesis of polyesters has no significant effect on this parameter.

Table 1 Properties of the polyesters

Parameter	RP reference polyester	R2 polyester modified with RDEG 2	R1 polyester modified with RDEG 1
Tensile strength, kPa	46.6	49.3	49.2
Elongation at break, %	70.8	62.6	63.6
Water absorbability, %	190	170	180

Conclusions

Citric acid derived biodegradable elastomers have promising potential in application for soft tissue engineering. The relatively simple synthesis that can be carried out under mild conditions without addition of toxic catalysts makes poly[(glycerol-citrate)diol] modified with vegetable oil-based polyols a good candidate for drug delivery and as biomaterials. The analysis of results showed that introducing the rapeseed oil-based polyols to the polyesters can improve tensile strength of the materials.

References

1. Gunstone F.D., Vegetable Oils in Food Technology: Composition, Properties and Uses, Blackwell Publishing, Oxford, 2002, 99-110.
2. Dworakowska S., Bogdał D., Prociak A., Synthesis of polyols from rapeseed oil, Proceedings of ECSOC-14, The Fourteenth Electronic Conference on Synthetic Organic Chemistry, Basel, Switzerland, 1-30.11.2010.
3. Barrett D.G., Thermosets synthesized by thermal polyesterification for tissue engineering applications, Soft Matter., 2010, 6(20), 5026.
4. Amsden B., Wang S., Wyss U., Biomacromolecules, 2004, 5, 1399.

5. Barrett D.G., Design and applications of biodegradable polyester tissue scaffolds based on endogenous monomers found in human metabolism. *Molecules* (Basel, Switzerland), 2009, 14(10), 4022-4050.
6. Synthesis, characterization and in vitro degradation study of a novel and rapidly degradable elastomer, *Polym. Degrad. Stab.*, 2006, 91(4), 733-739.
7. Wang Y., Ameer G.A., Sheppard B.J., Langer R., *Nat Biotechnol.*, 2002, 6, 602.
8. Nijst C.L.E., Bruggeman J.P., Karp J.M., Ferreira L., Zumbuehl A., Bettinger C.J., Langer R., *Biomacromolecules*, 2007, 8, 3067.
9. Bettinger C.J., Bruggeman J.P., Borenstein J.T., Langer R.S., *Biomaterials*, 2008, 29, 2315.
10. Amsden B.G., Tse M.Y., Tumer N.D., Knight D.K., Pang S.C., *Biomacromolecules*, 2006, 1, 365.
11. Pêgo A.P., Siebum B., Van M.J., Gallego Y., Van Seijen X.J., Poot A.A., Grijpma D.W., Feijen J., *Tissue Eng.*, 2003, 5, 981.
12. Djordjevic I., Synthesis and characterization of novel citric acid-based polyester elastomers, *Polymer*, 2009, 50(7), 1682, 1691.