Influence of the addition of citric acid on the physico-chemical properties of poly(sorbitol sebacate-*co*- butylene sebacate)

Marta Piątek-Hnat

Abstract— The article presents the results of the physicochemical properties of poly(sorbitol sebacate- co-butylene sebacate) (PSBS) obtained with 0.25; 0.5; 0.75; 1 mol of citric acid (KC). It was shown that PSBS obtained with 0.25 and 0.5 mol KC is characterized by the most optimal mechanical and thermal properties. As a result of the study, it was found that the use of sorbitol and citric acid allows obtaining ester materials with properties that can meet the material requirements of products for mwdical applications (scaffolds, drug delivery systems). The poly(sorbiotol sebacate- co- butylene sebacate) are hydrophilic and, despite the high content of the gel fraction (high degree of cross-linking), are susceptible to hydrolytic degradation.

Index Terms— ester elastomers, polycondensation, citric acid, physico-chemical properties, sugar alcohol, cross-linking

1 Introduction

Poly(sorbitol sebacate- co- butylene sebacate) PSBS is a material obtained as a result of the reaction of sebacic acid 1,4-butanediol with a sugar alcohol - sorbitol. The use of products derived from natural sources for the synthesis of new materials is of great interest, and therefore many scientists conduct research in this direction by modifying the composition of materials and the types of monomers used. PSBS is characterized by good physicochemical properties while being susceptible to hydrolytic degradation, which allows application in the direction of medical applications. The aim of the work was to obtain poly(sorbitol sebacate- co-butylene sebacate) in the mass polycondensation reaction using sebacic acid as a monomer, sugar alcohol-sorbitol, 1,4-butanediol and as a modifier - citric acid with various molar participation. The modifiers used were aimed at improving the properties of poly(sorbitol sebacate- co- butylene sebacate). The resulting polymers with variable molar participation were characterized for changes in physicochemical properties. Due to the multifunctionality of the sorbitol used, the obtained elastomers were characterized by a high degree of cross-linking, also dependent on the molar proportion of citric acid. [1-9].

2. MATERIAL AND METHODS

2.1 Synthesis of poly(sorbitol sebacate-co-butylenesebacate) with citric acid

The technological process of obtaining ester elastomers is three-stage. In the first stage, an esterification reaction takes place between sebacic acid (Sigma-Aldrich, Poland), sorbitol (Sigma-Aldrich, Poland), butylene glycol (1,4-butanediol) (Sigma-Aldrich, Poland) citric acid (Fluka) catalyzed by $Ti(BuO)_4$ (Fluka), at a temperature of 150- 160 ^{o}C. In the second step, polycondensation occurs under reduced pressure. The third step leading to obtaining a crosslinked elastomer takes place in a vacuum dryer [10-11].

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2.2 Methods

Determination of gel fraction of elastomers was made by the extraction method. PN-EN 579: 2001. Material samples (about 1 g) were placed in Schott type P2 crucible and subjected to extraction in boiling tetrahydrofuran (100 cm^3) for 3 hours. After extraction, the samples were dried in a vacuum oven at 25 °C for 3 hours 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:

$$X = m1/m0\ 100\% \qquad (1)$$

where: m1 - sample mass after extraction, m0 - sample mass before extraction

Mechanical tests were carried out with an Instron 3366 instrunents 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 ^{o}C and 50 % of relative humidity)

The stady of the contact angle of the surface of the materials was made with deionized water using the Haas Contact Angle Analyzer apparatus on the Phoenix Mini model.

The method involves placing a drop of water on the surface of the material and determining the angle between them.

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 150 ^{o}C.

3. RESULTS AND DISCUSSION

Figure 1 shows the results of the gel fraction content determination. Gel fraction values for unmodified material and at a content of 0.25 and 0.5 moles of citric acid oscillate between 90-95%. For PSBS containing 0.75 and 1 mole of citric acid we observe a decrease in the gel fraction value

Differential DSC scanning calorimetry was performed to determine the thermal properties of poly(sorbitol sebacate- co-butylene sebacate). (PSBS) with a different molar content of citric acid.

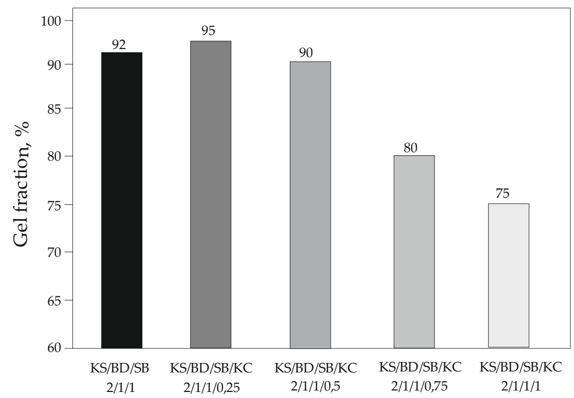

Fig. 1. Gel fraction of poly(sorbitol sebacate-co- butylene sebacate) (PSBS) with 0,25; 0,5; 0,75; 1 mol citric acid, where: KS- sebacic acid, BD- butylene glycol (1,4- butanediol), SB- sorbitol, KC- citric acid.

DSC thermograms (Fig. 2) of the obtained materials, a low-temperature transformation can be observed which is associated with the transformation of the glass transition of the amorphous phase. The glass transition temperature (T_g) associated with this transformation oscillates between -34 ° C and -17 ° C. It can be seen that as its content increases, its value increases. The DSC thermogram of elastomers with a content of 0.75 and 1 mole of citric acid at 57 °C has an endothermic peak associated with the melting temperature of the crystalline phase probably derived from sebacic acid. The results of these tests correspond very well with the analysis of gel fraction content, where it was observed a decrease in materials with a content of 0.75 and 1 mole of citric acid.

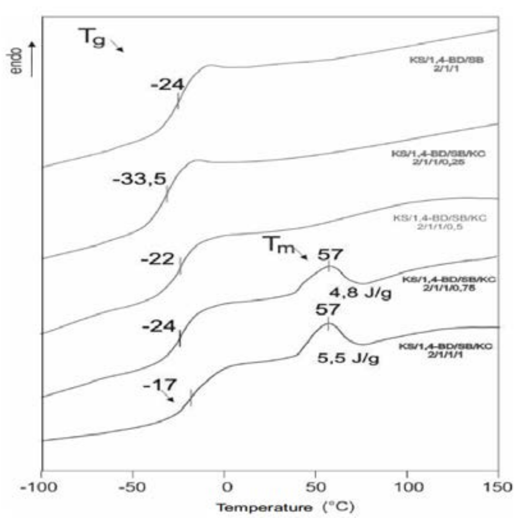

Fig. 2. DSC thermograms of poly(sorbitol sebacate-co- butylene sebacate) (PSBS) with 0,25; 0,5; 0,75; 1 mol citric acid, where: KS- sebacic acid, BD- butylene glycol (1,4- butanediol), SB- sorbitol, KC- citric acid.

The surface properties (Fig.3.) of poly(sorbitol sebacate- co-butylene sebacate) (PSBS) All obtained elastomers are characterized by the hydrophilic nature of the surface, while the lowest value of the contact angle was observed for unmodified PSBS and containing 0.25 moles of citric acid

Fig. 4 presents the results of tests of mechanical properties for PSBS unmodified and modified with 0.25 and 0.5 moles citric acid. On the basis of the obtained results of mechanical tests, it can be stated that the unmodified material is characterized by stress values up to breakage of 1.4 MPa and elongation to break at the level of approx. 400%. After modification with 0.25 and 0.5 mol of citric acid, the value of both tension and elongation decreases.

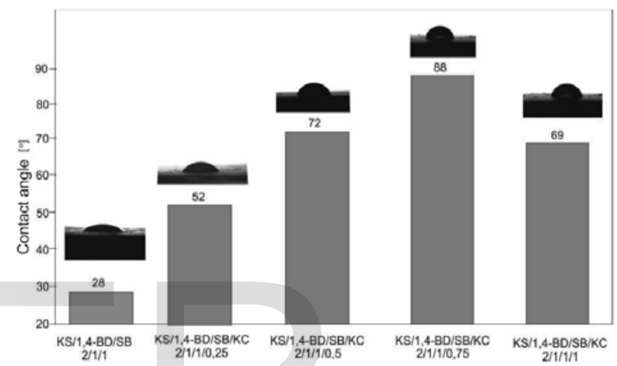

Fig. 3. Contact angle of poly(sorbitol sebacate-co- butylene sebacate) (PSBS) with 0,25; 0,5; 0,75; 1 mol citric acid, where: KS- sebacic acid, BD- butylene glycol (1,4- butanediol), SB- sorbitol, KC- citric acid.

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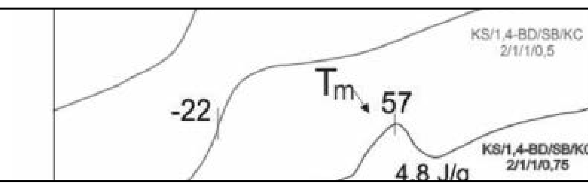

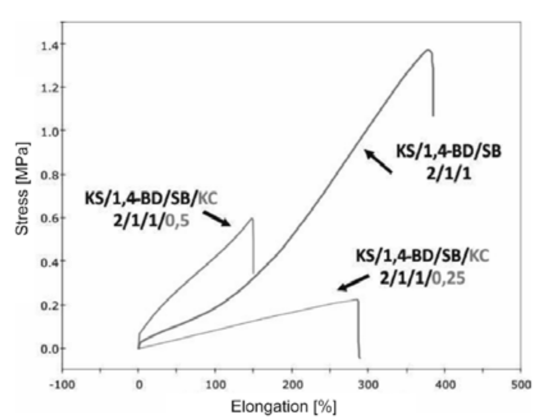

Fig. 4. Mechanical properties of poly(sorbitol sebacate-co- butylene sebacate) (PSBS) with 0,25; 0,5; 0,75; 1 mol citric acid, where: KS- sebacic acid, BD- butylene glycol (1,4- butanediol), SB- sorbitol, KC-

4 Conclusion

The study examined physicochemical properties (PSBS) with the participation of 0.25-1 molar citric acid. It can be concluded that the PSBS obtained with 0.25 and 0.5 moles of KC is characterized by the most optimal physicochemical properties. As a result of the conducted tests, it was found that the use of sorbitol and variable molar fraction of citric acid allows obtaining ester materials with interesting properties. The ester materials obtained are characterized by high hydrophilicity and, despite the high content of the gel fraction (high degree of cross-linking), they are susceptible to hydrolytic degradation.

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