

MONIKA KNITTER\*, JOANNA ZEMBRZUSKA\*\*, MONIKA  
DOBRZYŃSKA-MIZERA\*

## INFLUENCE OF PLASTICIZER TYPE ON PROPERTIES OF RENEWABLE ENGINEERING MATERIALS

Polymers and their composites are commonly used as engineering materials. They reveal a number of beneficial properties that allow their use in many industries. However, the main disadvantage of polymeric materials is their long degradation time in environment. For this reason, there is a need to replace synthetic polymers with renewable ones which are of plant or animal origin. Potato starch-based polymer was produced and characterized in this study. An influence of plasticizers on rheological, thermal and morphological properties of the plasticized starch was studied herein.

**Key words:** natural polymer, starch, glycerol.

### 1. INTRODUCTION

Polymers have been an important subgroup of engineering materials for many years. They reveal a number of beneficial properties which allow them to be used in a variety of industries including: mechanical engineering, aerospace, automotive, packaging and construction [2,4,10,13]. The main disadvantage of polymers is their long degradation which is a serious environmental issue. Hence, polymers of natural origin are gaining ground nowadays [11]. These polymers are mainly based on polysaccharides or polypeptides and include among others: starch, cellulose, chitin and collagen [12]. Among the above-mentioned biopolymers, the most promising one is native starch due to its availability, annual renewal and competitive price [6]. Furthermore, an appropriate modification of native starch allows to obtain polymer with thermoplastic properties, known as thermoplastic starch (TPS).

- \* Polymer Processing Division, Poznan University of Technology,  
monika.knitter@put.poznan.pl, monika.dobrzynska-mizera@put.poznan.pl
- \*\* Institute of Chemistry and Technical Electrochemistry, Poznan University of  
Technology, joanna.zembrzuska@put.poznan.pl

Apart from the above features, this material is characterized by unfavorable, from a practical point of view, high hydrophilicity which causes low dimensional stability of starch during use at room temperature. This characteristic provoked researchers to conduct a number of technological and research work in order to improve starch processability, mechanical properties and extend its dimensional stability [14,15].

The aim of this work is to produce thermoplastic starch based on native starch using conventional methods of processing. Moreover, an influence of plasticizers on rheological, thermal and morphological properties was studied herein.

## 2. EXPERIMENTAL WORKS

The commercial Superior Standard potato starch, with the defined content of pure starch in dry mass at a minimum level of 97%, from PEPEES S.A. (Poland) was used in our studies. The starch was in a form of white powder with moisture content of maximum 20%. Two different glycerol types of plant origin, with various contents of impurities, were used as plasticizers. The first one, of 99.5% purity and 99.87% of glycerol, abbreviated *P*, was produced by Galvet Sp.z.o.o (Poland). The second one, ultra-pure for analysis (99.5%), henceforth *UP*, was produced by P.P.H. „STANLAB” s.j (Poland).

Processing of thermoplastic starch was conducted in two steps: premixing and extrusion in a molten state. The first step was carried out using the rotary mixer Retsch GM 200. Starch and glycerol were premixed for 60 s at 200 rpm. Then, the mixture was stored in sealed plastic bags and conditioned for 72h. Homogenization of the premixed blends was assured by molten state extrusion with a Zamak EH-16.2D corotating twin screw extruder equipped with a single-channel head with a nozzle diameter of 5.3 mm. The extruder operated at a temperature range between 50 and 150°C and 130 rpm. Then, formed samples were cooled down to room temperature (22.6°C) at humidity of 40%RH. Six different compositions of thermoplastic starch were obtained and presented in Table 1.

Table 1

Compositions and symbols of the samples

Weight proportion glycerol:starch	Glycerol type	Symbol
15:85	Pure glycerol	TPS15_P
20:80		TPS20_P
30:70		TPS30_P
15:85	Ultra-pure glycerol	TPS15_UP
20:80		TPS20_UP
30:70		TPS30_UP

### 3. METHODOLOGY

Preliminary evaluation of the input materials was conducted using liquid chromatography (LC) performed for both types of glycerol. Moreover, an influence of plasticizer type and concentration on melt flow rate, degradation temperature and residual mass were analyzed. Morphological properties were determined by optical microscopy.

LC analyses were performed using the UltiMate 3000 RSLC chromatographic system produced by Dionex (Sunnyvale, CA, USA). Ten  $\mu\text{L}$  samples were injected into a Kinetex 2.6 $\mu$  Hilic 100A analytical column (50 x 2.1 mm, bead size 2.6  $\mu\text{m}$ ) (Phenomenex, USA). In the majority of experiments, the column maintained the temperature of 35°C and the mobile phase was 5 mM ammonium acetate in water (A) and acetonitrile (B), at a flow rate of 0.3 mL min<sup>-1</sup>. The following gradients were used: 0 min 90% B, 2 min 50% B.

The LC system was connected to the API 4000 QTRAP triple quadrupole mass spectrometer produced by AB Sciex (Foster City, CA, USA). Glycerol was characterized by electrospray ionization mass spectrometry (ESI-MS) operated in a positive ion mode. The analyte was detected using the following settings for the ion source and mass spectrometer: curtain gas 10 psi, nebulizer gas 20 psi, auxiliary gas 20 psi, temperature 280°C, ion spray voltage 5500 V and collision gas set to medium.

The MS/MS multiple reaction monitoring mode (MRM) parameters, used for quantitative glycerol determination, are shown in Table 2. In majority of experiments  $[\text{M}+\text{H}]^+$  complex of glycerol was used as ions' precursor.

**Table 2**

Optimum MS/MS working parameters for compounds

Precursor ion $m/z$	Declustering potential [V]	MRM 1 transitions-quantitation ion (precursor ion $m/z \rightarrow$ product ion $m/z$ )	Collision energy [V]	MRM 2 transitions-confirmation ion (precursor ion $m/z \rightarrow$ product ion $m/z$ )	Collision energy [V]
93 [M+H] <sup>+</sup>	41	93→57	13	93→75	9

Melt flow rate (MFR) test was performed using a load plastometer produced by Dynisco, Model 4003 as per EN ISO 1133: 2006, method A. Thermoplastic starch was extruded using a nozzle with a diameter of 2.095 mm and length of 8 mm. Measurements were conducted for ten samples at 200°C under a load of 2.16 kg. Plasticization time was dependent on the composition type and was in a range between 60 and 240 s.

Thermogravimetric studies were conducted as per ISO 11358 using a thermogravimetric analyzer Netzsch TG 209 F1 Libra®. The measurements were carried out in the temperature range between 25 and 600°C at a heating rate of 20°C/min under nitrogen flow. The sample mass was equal to 10 ± 0.5 mg. Residual mass was determined at 600°C.

The microscopic photographs of thermoplastic starch, at a magnification of 100x, were taken with optical microscope Nikon Eclipse E 400, cooperating with Opta-Tech camera and OptaView software. Specimens in a form of shavings with a thickness of 30 microns were prepared using a Leica RM 2265 microtome.

#### 4. RESULTS

The ESI mass spectra reveal very similar patterns for all studied samples. Figure 1 a-b presents ESI mass spectra for ultra-pure and pure glycerol. Typical glycerol ions, such as: [M+H]<sup>+</sup> at  $m/z = 93$ , [M+NH<sub>4</sub>]<sup>+</sup> at  $m/z = 110$ , [M+Na]<sup>+</sup> at  $m/z = 115$ , two ion products obtained from fragmentation of protonated ion at  $m/z = 75$  and  $57$  and dimer containing potassium at  $m/z = 223$ , are observed [3,8]. The mass spectrum of pure glycerol reveals lower intensity of characteristic ions for glycerol. In addition to these ions, intense impurities at  $m/z = 167.8$  and  $184$  were observed (Fig. 2b).

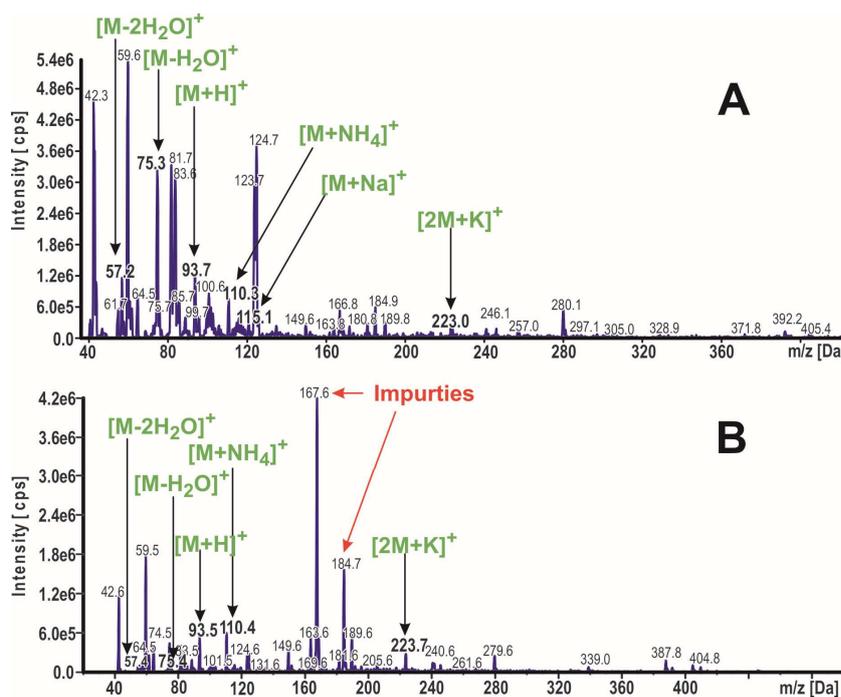


Fig. 1 Positive electrospray spectrum of a) ultra-pure glycerol, b) pure glycerol

Solutions of both glycerols were analyzed by LC-MS/MS method. Calculated peak areas prove an increased amount of glycerol in the ultra-pure sample, being  $1.7075 \cdot 10^5$  cps, in comparison with  $1.5038 \cdot 10^5$  cps for the pure one.

The results of MFR measurements for both thermoplastic starch types (TPS\_P and TPS\_UP) are shown in Figure 2. The experiment for TPS15\_P composition was not performed due to a lack of polymer plastification, although parameters such as: temperature, time and load have been readjusted. The analysis reveals that regardless of a glycerol type, increasing amount of plasticizer raises MFR values and results in a decrease in dynamic viscosity of modified starch.

Various MFR values, depending on a glycerol type, are noted herein, the higher the amount of plasticizer in a composition, the greater the MFR value. In case of TPS\_UP samples, the MFR values are in a range from 41 to 59 g/10 min, and from 48 to 72 g/10 min for the TPS\_P starch. An increase in the values with

glycerol content probably occurs due to enhanced mobility of macromolecules in thermoplastic starch and raised free volume between them resulting from presence of large amount of plasticizer.

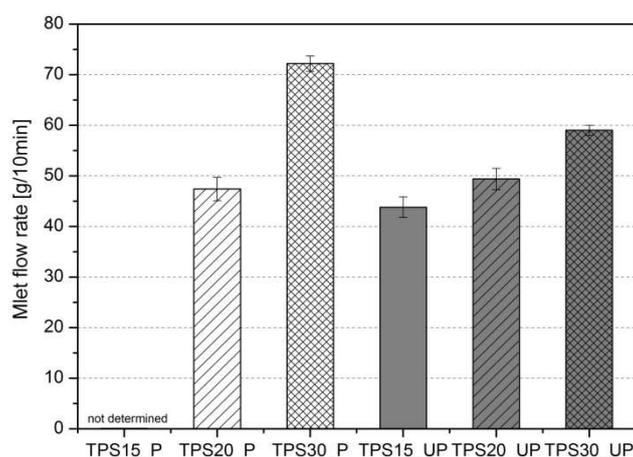


Fig. 2. Melt flow rate in a function of thermoplastic starch composition

Growth in melt flow rate values directly translates into a decrease in viscosity and facilitates flow. Hence, plastification of native starch facilitates material to flow easier through a plastometer nozzle (enhanced slip down the walls of processing equipment). The abovementioned phenomenon is described in the literature as the lubricity theory [1,5,9]. The plasticizer acts as a lubricant to reduce friction and facilitates polymer chain mobility past one another.

Thermogravimetric analyses were performed for samples containing both pure and ultra-pure glycerols and are presented in Figure 3. Temperatures for 5 and 50% mass loss as well as polymer residual masses are summarized in Table 3.

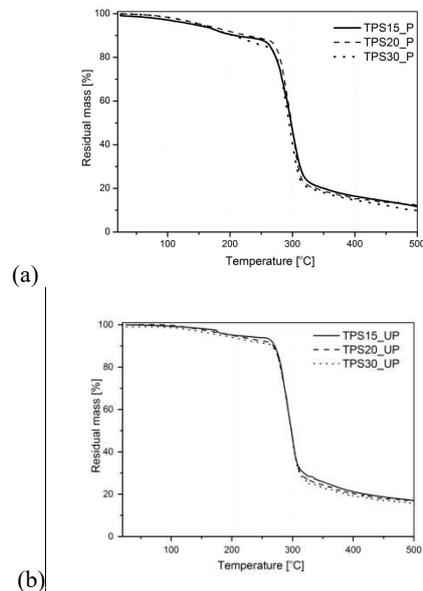


Fig. 3. TGA thermograms a) TPS\_P b) TPS\_UP

It is noted that 5% mass loss ( $T_{5\%}$ ) for starch plasticized with pure glycerol occurs at a temperature of 150°C and approx. 50°C higher for the TPS modified with the ultra-pure one. It is assumed that this phenomenon is related to the fact that pure glycerol contains more impurities and volatile compounds with low molecular mass, which evaporate at lower temperature as indicated by liquid chromatography. However, irrespective of a type and concentration of glycerol in a composition, 50% mass loss ( $T_{50\%}$ ) occurs at about 298°C.

Table 3

Influence of glycerol concentration on TPS thermal stability

Sample	T5%	T50%
	[°C]	
TPS15_P	143.6	298.0
TPS20_P	156.4	294.5
TPS30_P	152.9	298.8
TPS15_UP	205.2	298.1
TPS20_UP	201.4	298.4
TPS30_UP	203.1	298.4

The TGA result analysis reveals that thermoplastic starch degrades in a single stage process. Furthermore, mass loss is observed from the beginning of the experiment what is associated with evaporation of water and glycerol. Residual mass for all studied samples is in a range between 10 and 15%, regardless of the amount and type of plasticizer. Similar results were described in the literature with other organic fillers, such as: bamboo, wood or kenaf [6].

Microscopic images were taken to illustrate morphological properties of TPS\_P and TPS\_UP and are presented in Figure 4 and 5.

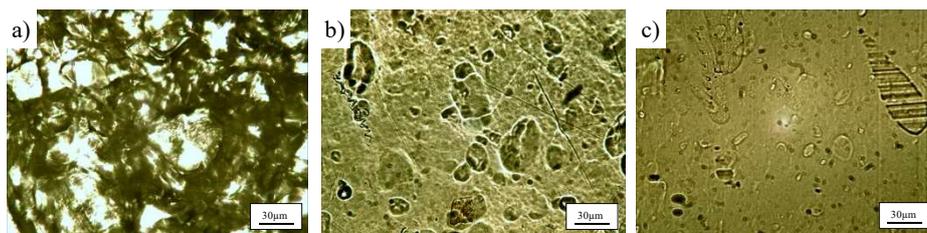


Fig. 4. Microscopic images of TPS\_P: a) TPS15\_P, b) TPS20\_P, c) TPS30\_P



Fig. 5. Microscopic images of TPS\_UP: a) TPS15\_UP, b) TPS20\_UP, c) TPS30\_UP

Figure 4a presents clearly separated regions of pure glycerol in starch matrix. The addition of 20 wt% of glycerol results in better plasticizer distribution, however two different phases are still visible in the structure (Fig. 4b). The highest degree of homogenization is obtained for the TPS30\_P sample and presented in Fig 4c. Hence, an increasing amount of glycerol in TPS\_P samples results in better homogenization. Conversely, upon the addition of ultra-pure glycerol, structure uniformity worsens (Fig. 5 a-c). Although, the samples containing 15 and 20 wt% of the plasticizer are quite smooth, the TPS30\_UP sample reveals large clusters of glycerol visible throughout the analyzed area.

## 5. CONCLUSIONS

The results prove that purity and concentration of glycerol is of prime importance in case of selecting plasticizer for thermoplastic starch. Different rheological, thermal and morphological properties are noted for the samples that contained various types and amounts of plasticizer. Better homogenization and higher melt flow rate values were obtained for compositions modified with pure glycerol (P). However, starch modified with ultra-pure plasticizer reveals higher thermal stability, at least for the studied range. The conducted research indicated that the selection of plasticizer for starch modification is crucial due to its influence on processing properties.

## REFERENCES

- [1] **Ferguson J., Kembłowski Z.**, Reologia stosowana płynów, Łódź, Wyd. Marcus 1995.
- [2] **Grabowska B.**, Termodynamicznie stabilne kompozycje biopolimerowe do zastosowania w odlewnictwie, *Archiwum Technologii Maszyn i Automatykacji*, 2009, vol. 29, nr 3, s. 33-40.
- [3] **Hong W. E. Ch., Zhen Y. J.**, Determination of sugar compounds in atmospheric aerosols by liquid chromatography combined with positive electrospray ionization mass spectrometry, *Journal of Chromatography A*, 2006, vol. 1107, s. 175-181.
- [4] **Kelar K., Mencil K., Olejniczak J.**, Modyfikacja polietylenu haloizytowymi nanorurkami. Cz. I. Struktura kompozytów, *Archiwum Technologii Maszyn i Automatykacji*, 2011, vol. 31, nr 1, s. 103-111.
- [5] **Kembłowski Z.**, Reometria płynów nienewtonowskich, Warszawa, WNT 1973.
- [6] **Liu X., Wang Y., Yu L., Tong Z., Chen L., Liu H., Li X.**, Thermal degradation and stability of starch under different processing conditions, *Starch*, 2013, vol. 65, nr 1-2, s. 48-60.
- [7] **Lu D. R., Xiao C. M., Xu S. J.**, Starch-based completely biodegradable polymer materials, *EXPRESS Polymer Letters*, 2009, vol. 3, nr 6, s.366-375.
- [8] **McIntosh T.S., Davis H.M., Matthews D.E.**, A liquid chromatography-mass spectrometry methods to measure isotopic tracer enrichments of glycerol and glucose in human serum, *Analytical Biochemistry*, 2002, vol. 300, s. 163-169.
- [9] **Mekonnen T, Mussone, P., Khalilb H., Bressler D.**, Progress in bio-based plastics and plasticizing modifications, *Journal of Materials Chemistry A*, 2013, vol. 1, s. 13379-13398

- [10] **Oleksy M., Oliwa R., Heneczkowski M., Mossety-Leszczak B., Galina H., Budzik G.**, Kompozyty żywicy epoksydowej zmodyfikowanymi bentonitami dla potrzeb przemysłu lotniczego, *Polimery*, 2012, vol. 57, nr 3, s. 228-235.
- [11] **Petersen K., Vaeggemose Nielsen P., Bertelsen G., Lawther M., Olsen M.B., Nilsson N.H., Mortensen G.**, Potential of Biobased Materials for Food Packaging, *Trends in Food Science and Technology*, 1999, vol. 10, nr 2, s. 52-68.
- [12] **Ryzenkov A. V., Klassen N. V., Masalov V. M.**, Features of structure and properties of biopolymer composites with inorganic nanoparticles, *Inorganic Materials: Applied Research*, 2014, vol. 5, nr 4, s. 312–317.
- [13] **Szostak M.**, Recycling of PP/EPDM/Talc car bumpers, *Chemicke Listy*, 2011, vol. 105, s. 307-309.
- [14] **Van Soest J. J. G., Knooren N.**, Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging, *Journal of Applied Polymer Science*, 1997, vol. 64, nr 7, s. 1411–1422.
- [15] **Wilpiszewska K., Sychaj T.**, Termoplastyfikacja skrobi na drodze wyłaczania w obecności plastyfikatorów, *Polimery*, 2006, nr 5, s. 325–404.

## WPLYW RODZAJU PLASTYFIKATORA NA WŁAŚCIWOŚCI ODNAWIALNYCH MATERIAŁÓW INŻYNIERSKICH

### S t r e s z c z e n i e

Polimery i ich kompozyty to powszechnie stosowane materiały inżynierskie. Mają one szereg korzystnych właściwości, które umożliwiają stosowanie ich w wielu gałęziach przemysłu. Podstawową wadą materiałów polimerowych jest ich długi czas degradacji w środowisku naturalnym. Z tego powodu dąży się do zastępowania polimerów syntetycznych odnawialnymi polimerami pochodzenia roślinnego lub zwierzęcego. W pracy wytworzono i scharakteryzowany polimer na bazie skrobi ziemniaczanej. Oceniono wpływ plastyfikatora na wybrane właściwości reologiczne, cieplne i morfologiczne materiału polimerowego.

**Słowa kluczowe:** polimery naturalne, skrobia, gliceryna