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Biodegradable copolyester/starch blends — preparation, mechanical properties, wettability, biodegradation course

Summary — A set of blends of an aromatic-aliphatic copolyester containing 35 mol. % of aromatic ester units and plasticized wheat starch has been prepared. The copolyester used in this process was synthesized by polycondensation of the product of solvolysis of polyethyleneterephthalate (PET) from disposed beverage bottles by an aqueous solution of lactic acid. The blends copolyester/starch were characterized by their tensile strength and wetting behavior. Biodegradability of the blends was tested by using of mixed culture of microorganisms of digested sludge from wastewater treatment plant under anaerobic thermophilic conditions (55 °C).

Key words: food packaging, aromatic-aliphatic copolyester, plasticized starch, blends, biodegradation.

BIODEGRADOWALNE MIESZANINY KOPOLIESTER/SKROBIA — OTRZYMYWANIE, WŁAŚCIWOŚCI MECHANICZNE, ZWILŻALNOŚĆ, PRZEBIEG BIODEGRADACJI

Streszczenie — Otrzymano szereg mieszanin aromatyczno-alifatycznych kopoliestrów zawierających 35 % mol. fragmentów aromatycznych z plastyfikowaną gliceryną skrobią pszeniczną (tabela 1). Kopoliester był produktem solwolizy poli(tereftalanu etylenu) (PET z butelek po napojach) w wodnym roztworze kwasu mlekowego. Zbadano go metodami ¹H NMR (rys. 2) i DSC (rys. 3). Określono wpływ składu mieszanin (zawierających 55—75 % mas. kopoliestru) na ich właściwości sorpcyjne w stosunku do wody oraz właściwości mechaniczne przy rozciąganiu (tabela 1) a także na — istotną z punktu widzenia zastosowania do celów opakowaniowych — zwilżalność charakteryzowaną wartościami energii powierzchniowej i krytycznego napięcia powierzchniowego obliczonymi na podstawie wartości kąta zwilżania (rys. 4). Biodegradowalność mieszanin badano w beztlenowych warunkach termofilnych (55 °C) z zastosowaniem mieszanej kultury mikroorganizmów w osadach z oczyszczalni ścieków. Oceniano intensywność procesu wydzielania biogazu w funkcji czasu biodegradacji (rys. 5) jak również spowodowaną tym procesem zmianę lepkości zredukowanej frakcji poliestru w mieszaninie (tabela 2).

Słowa kluczowe: opakowania żywności, aromatyczno-alifatyczny kopoliester, skrobia plastyfikowana, mieszaniny, biodegradacja.

Synthetic polymers have become the basis of modern packaging industry in the last three decades. About one third of the world plastics' production has been recently used for packaging. Unfortunately, the increasing consumption of plastics for packaging of the products of short life cycle leads to growing problems concerning the accumulation of plastic waste. Polyethylene, polypropylene, polystyrene, poly(ethylene terephthalate) and rigid poly(vinyl chloride) are the most common plastics used for the above mentioned applications. Low density, good mechanical and barrier properties, water resistance, transparency as well as relatively low costs are the main benefits of these polymers. The resistance of

named materials to the attack of microorganisms is a valuable feature from the viewpoint of their application, but it turns to a disadvantage when the packaging becomes waste. The use of biodegradable polymers in packaging would be an ecologically affordable alternative allowing reducing the solid plastics waste. Beside the synthetic biodegradable polymers suitable for technical use, a lot of attention is paid to natural polymers, namely starch.

Starch is one of the cheapest biopolymers which can be obtained from the large number of vegetable sources. Native starch can be transformed into a thermoplastic material, commonly called "thermoplastic starch" (TPS) under thermomechanical and plasticizer treatment [1, 2]. In contrast to native starch, the supermolecular structure

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of TPS or of destructured starch is less organized due to destruction of intermolecular hydrogen bonds between starch macromolecules. It leads to the reduction of melting and glass transition temperatures of TPS compared to native starch. For this reason TPS can be easily processed by typical techniques used for synthetic plastics. The main disadvantages of destructured starch are poor mechanical properties and too high hydrophilicity. These properties can be improved with unchanged biodegradability by blending of TPS with more hydrophobic synthetic biodegradable polymers, namely polyesters [3, 4] or poly(vinyl alcohol) [5].

We focused our interest on the blends of starch with an aromatic-aliphatic copolyester based on poly(ethylene terephthalate) (PET) from used beverage bottles and lactic acid. This type of copolyester (PET/PLA) has been found to degrade under action of active biological system under both aerobic and anaerobic conditions [6, 7].

EXPERIMENTAL

Copolyester synthesis

Washed PET flakes from colorless postconsumer bottles (20 g) were treated with aqueous L-lactic acid (85 wt. %) solution (20 cm³) at 250 °C in the presence of 0.2 wt. % of zinc acetate as catalyst for 30 min. Following polycondensation of the solvolytic product at 250 °C and reduced pressure (reduced stepwise to ≈ 1 Pa) leads after 3 hours to the formation of a copolyester PET/PLA containing 35 mol. % of aromatic ester units. Cresole solution of prepared copolyester (0.25 wt. %) is characterized by reduced viscosity $\eta_{red} = 60 \text{ cm}^3/\text{g}$.

Preparation of copolyester/starch blends

In the first step native wheat starch containing 12 wt. % of water was plasticized with glycerol (native starch/glycerol: 70:30, 80:20, 85:15 by weight) using Brabender Plasti-Corder Labstation (130 °C, 50 rpm, 10 min). A set of nine blends containing 25 to 45 wt. % of plasticized starch (TPS) and 75–55 wt. % of copolyester was prepared under conditions analogous to preparation of TPS. The films made of blends (thickness of 0.45 or 0.2 mm) were prepared by pressing between Teflon films at 120 °C. Glycerol contents in TPS and its blends with copolyester were determined in aqueous extracts by high pressure liquid chromatography (HPLC). Samples of TPS and blends were extracted with HPLC grade water under vigorous stirring at 80 °C twice for 15 min to achieve complete diffusion of glycerol to the solution. A Supelco column (250×4.6 mm i.d., packed with Supercosil LC-8-DB 5 μm), UV detector ($\lambda=190 \text{ nm}$) and methanol-water (vol. ratio 5:95) mixture as eluent were used for HPLC analyses of the extracts. The solvent flow rate was 0.6 cm³/min.

Methods of testing

Viscometric measurements

Reduced viscosity values of tricresol polymer solutions (concentration 0.25 wt. %) were determined by using an Ubbelohde viscometer at 25 °C with measuring precision $\pm 0.2 \text{ cm}^3/\text{g}$.

¹H NMR analysis

¹H NMR spectra were recorded with the aid of NMR Spectrometer Bruker Avance DRX 500, Work Station SGI Indy.

Thermal properties

For evaluation of thermal properties by DSC method, the DSC 2920 modulated differential scanning calorimeter TA Instruments was used. Measurements were carried out in the temperature range of 20–260 °C, with heating rate of 10 °C/min and nitrogen purge (50 cm³min⁻¹).

Water sorption

Samples of copolyester/starch blends were deposited in a desiccator over the saturated solution of NaNO₂ (relative humidity RH 66 %) or ZnSO₄ (RH 90 %) for 8 days at 23 °C and afterwards weighted (m). Then the samples were dried over P₂O₅ to the constant weight (m₀). On this base the content of absorbed water (x, wt. %) was calculated as $[(m-m_0)/m_0] \cdot 100 \%$.

Tensile strength

The tests were carried out with standardized tensile test specimens using the instrument Instron 3365. The test specimens were equilibrated before the measurement at RH 66 % and 23 °C for 8 days.

Contact angle measurements

Static contact angle measurements with the sessile drop method were performed using Lucia G device involving digital camera and image analysis software (Fig. 1). Contact angles were measured immediately after the

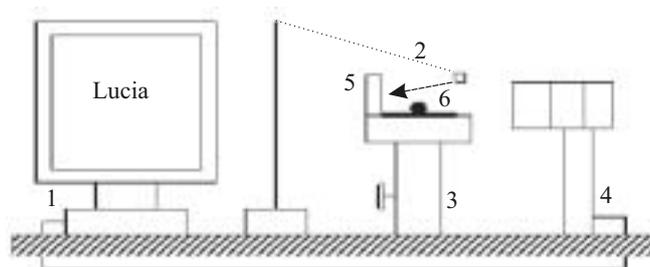


Fig. 1 Scheme of device for measuring contact angles on the surface of copolyester/starch blends: 1 — computer with software Lucia G, 2 — dot-lit lamp, 3 — adjustable holder, 4 — digital camera, 5 — shade, 6 — sample with a droplet test liquid

deposition of the test liquid droplet onto the surface of copolyester/starch films (equilibrated at RH 66 %, 23 °C) by means of a micropipette. Glycerol, ethan-1,2-diole, distilled water and formamide were used as test-liquids. Contact angles used for the calculation of surface free energies were the average values of at least 5 measurements.

Biodegradation test under anaerobic conditions

Films of copolyester/starch blends were placed into serum bottles with digested sludge from wastewater treatment plant under nitrogen atmosphere at 55 °C. The amount of biogas evolved as a product of tested samples degradation under action of this mixed thermophilic culture of microorganisms was determined by the volumetric measurements. The biogas was analyzed by gas-liquid chromatography (GLC, CE Instruments, TYPE: GC8000 Top).

RESULTS AND DISCUSSION

According to 1H NMR spectrum (Fig. 2) the copolyester used for blending contains 35 mol. % of aromatic ester units. As follows from the result of thermal analysis (DSC) this copolyester is completely amorphous; its glass transition temperature is $T_g = 63$ °C (Fig. 3).

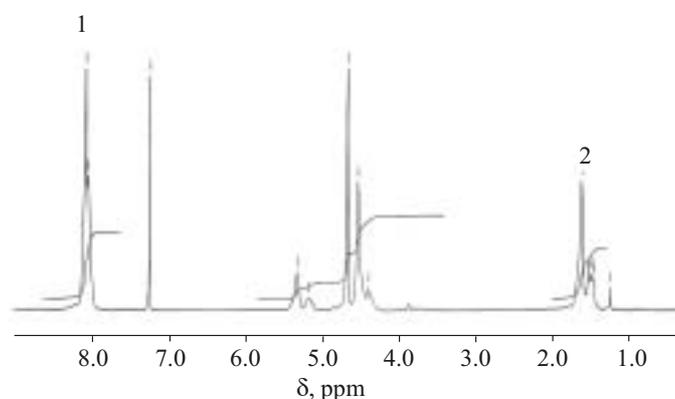


Fig. 2 1H NMR spectrum of the aromatic-aliphatic copolyester PET/PLA in solution of $CDCl_3$: 1 — aromatic ring, 2 — CH_3 -group in the lactid acid structural unit

Copolyesters containing structural units of ethylene terephthalate and lactic acid are, as mentioned above, sensitive to active biological systems. Their structures are effectively degraded during composting [6] as well as under action of mixed thermophilic culture of microorganisms of digested sludge from wastewater treatment plants [7].

Table 1 shows the compositions and some properties of the blends prepared from thermoplastic starch (25—45 wt. %) and the aromatic-aliphatic copolyester (75, 65 or 55 wt. %). Wheat starch was plasticized by

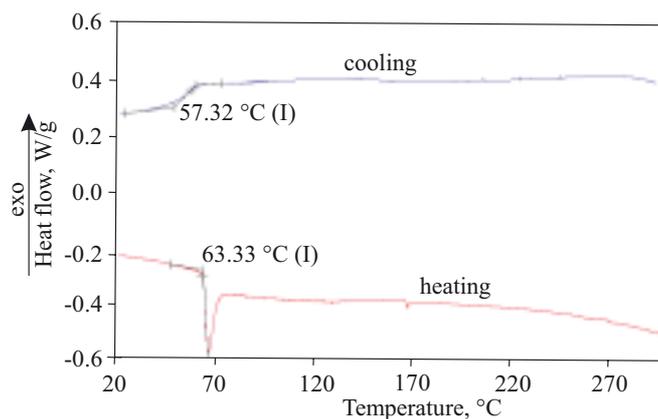


Fig. 3 DSC thermogram of the aromatic-aliphatic copolyester containing 35 mol. % of aromatic ester units and 65 mol. % of lactic acid units

30 wt. % (symbols A, B, C) 20 wt. % (D, E, F) or 15 wt. % (G, H, I) of glycerol.

Table 1. Compositions of copolyester/starch blends and their tensile and sorption properties

Blend	Blend composition (wt. %)			Tensile strength (MPa)	Water sorption (wt. %)	
	copolyester (PET/PLA)	native starch	glycerol		RH 66 %	RH 90 %
A	75	17	8	13	4.6	10.5
B	65	24	11	13	6.6	15.3
C	55	31	14	10	8.1	22
D	75	20	5	30	3.6	9.7
E	65	28	7	20	4.8	13.3
F	55	36	9	12	6.2	16.1
G	75	21	4	11	4.3	9.6
H	65	30	5	9	5.2	12.3
I	55	38	7	8	6.3	12.8

The films made of these blends (thickness of 0.2 mm) were exposed to the atmosphere with RH 66 % and RH 90 % at 23 °C. Their water sorption logically increases with the decreasing copolyester content in the blends with starch plasticized by 30, 20 or 15 wt. % of glycerol ($A < B < C$, $D < E < F$, $G < H < I$) (Table 1). At RH 66 % the values of water sorption vary from 3.6 to 8.1 wt. %, at RH 90 % from 9.6 to 22 wt. %. Slightly higher water sorption of blends in the set with TPS containing 15 wt. % of glycerol (G, H, I) at RH 66 % compared to those prepared with TPS plasticized with 20 wt. % of glycerol is somewhat unexpected. There are no traces of sweated-out glycerol on the surface of films equilibrated at RH 66 % contrary to the films with the content of glycerol 9 or more wt. % which were conditioned at RH 90 %. In these cases small droplets of glycerol were displaced to the surface by the sorbed water.

Mechanical properties of prepared blends were characterized by tensile tests. The specimens used for measurements were equilibrated at RH 66 % and 23 °C. The copolyester used for blending with TPS is brittle and it was not possible to characterize its tensile strength under conditions comparable with those applied for the characterization of the blends. Table 1 shows good tensile strength of the copolyester/starch blends. It can be seen that blends containing TPS plasticized with 20 wt. % of glycerol (D, E, F) are distinguished by the highest values of this parameter. In the series of these blends the tensile strength logically decreases depending on the increasing starch content. The trend towards reduction of mechanical strength is less significant in the series of blends prepared with TPS containing 30 wt. % of glycerol (A, B, C). The destructure of starch grains is supposed to be incomplete in TPS plasticized by 15 wt. % of glycerol (G, H, I). The properties of blends with this low plasticizer content can be explained by antiplastification effect occurring. This effect may be a consequence of strong interactions between plasticizer and starch to the detriment of interactions between plasticizer and copolyester. Thus, the material reinforcement is obtained instead of its plastification. Similar effect was further described by Lourdin [8].

All blends' elongation at break values are very low and do not exceed 2 %. It can be concluded that the mechanical properties of the prepared blends are close to those of polystyrene.

Beside mechanical properties, wettability of polymer material is an important parameter especially from the point of view of their potential use in packaging. As it was described before (see Experimental), the surface energies of selected copolyester/starch blends, TPS and PET were determined *via* contact angle measurements.

Contact angle values were then used to calculate surface free energies (SE) according to two different methods. The interactions between two phases can be divided into polar, dispersive or hydrogen bonding contributions. There are some methods like Owens-Wendt-Rabel-Kaelble method (OWRK) [9, 10] that distinguish a polar and a dispersive fractions of the surface energy. In contrast to this one, the Neumann's method [11] does not discern the type of interactions (polar or dispersive) and is therefore less accurate. This method is based on an empirical expression for the surface free energy solid liquid interface. At least the Zisman method [12] was used for calculation of the critical surface tension (γ_c) values which are derived from a plot of contact angle cosinus ($\cos\theta$) *versus* the test liquid's surface tension. The linear regression extrapolated value of the liquid's surface tension at $\cos\theta=1$ equals γ_c . This method, similarly to Neumann's one, is less accurate and applicable to mainly disperse liquid-solid systems. Fig. 4 shows the values of surface free energy and critical surface tension for the tested films, calculated according to the methods mentioned above. Because of the different mathematical ap-

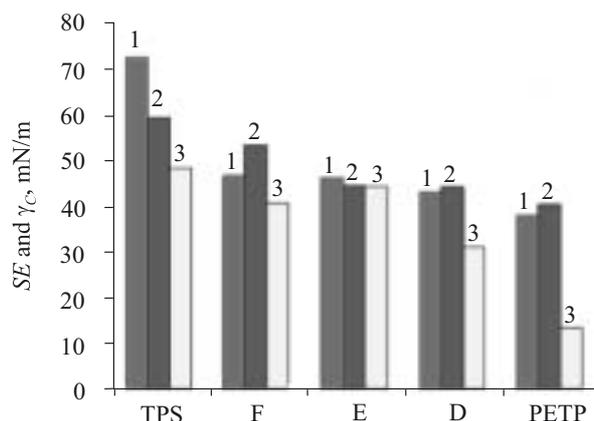


Fig. 4 Surface free energy (SE) and critical surface tension (γ_c) values of copolyester/starch blends (D, E, F in Table 1), starch plasticized with 20 wt. % of glycerol (TPS) and PET: 1 — SE according to Owens-Wendt-Rabel-Kaelbe method, 2 — SE according to Neumann's method, 3 — γ_c according to Zisman's method

proaches of the methods used the variations in the results obtained are not surprising. Nevertheless it can be summarized that the values of surface free energy of the tested blends containing 55–75 wt. % of the aromatic-aliphatic copolyester (Table 1, samples D, E, F) and plastified by starch with 20 wt. % of glycerol are significantly lower compared to SE values of TPS itself. From the comparison with the values referred to PET it can be concluded that the wettability of the tested blends would not markedly limit their possible use for packaging.

Two blends — G and H containing 75 and 65 wt. % of the copolyester PET/PLA, respectively and 25 and 35 wt. % of TPS plasticized by 15 wt. % of glycerol (Table 1), respectively — were exposed to a mixed culture of microorganisms of digested sludge from wastewater treatment plant under thermophilic conditions (55 °C). Films of tested blends (thickness of 0.45 mm) swelled extremely during the first week of exposition and within

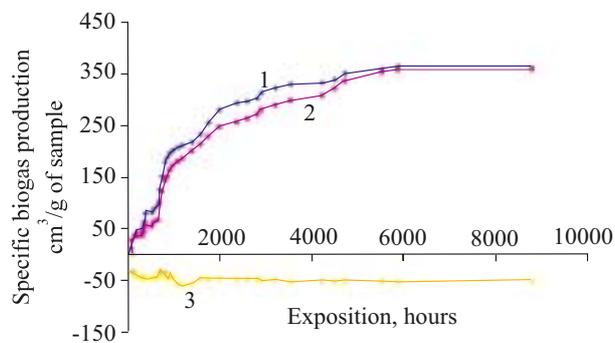


Fig. 5 Specific biogas production during the anaerobic biodegradation of copolyester/starch blends (1 — G, 2 — H) and PET (3) under thermophilic conditions at 55 °C (symbols of blends — see Table 1)

4 months they were completely disintegrated. Decomposition of the blends was accompanied by an intensive biogas production (Fig. 5). The biogas contained 61–65 % of methane as a product of copolyester/starch blends mineralization beside carbon dioxide, water vapor and other minor gases. Under the same conditions PET shows no signs of degradation — no biogas production even at exposition time over 4000 hours. The initial slump to the negative values of biogas production in this case is caused by adaptation of biomass to the strange material. The biomass was not prevented from degradation of other available materials by presence of PET.

Table 2. Changes of reduced viscosity (η_{red}) values for copolyester/starch blends exposed to anaerobic biodegradation

Blends copolyester/TPS ^{*)}	$\eta_{\text{red}}, \text{cm}^3/\text{g}$		
	original copolyester	samples after degradation for	
		1 month	4 months
G	60	22	12
H	60	26	12

^{*)} Samples symbols — see Table 1.

Biodegradation of the copolyester PET/PLA fraction of the blends is demonstrated also by a strong decrease in reduced viscosity of its cresole solutions compared to the corresponding value of the original copolyester used for blending with TPS (Table 2). According to the preliminary ecotoxicity tests the sludge in which copolyester PET/PLA degraded was not contaminated by eventual toxic products of the biodegradation [7].

CONCLUSION

The blending of an aromatic-aliphatic copolyester based on PET from disposed beverage bottles and lactic acid containing 35 mol. % of aromatic ester units with thermoplastic wheat starch (TPS) yields a biodegradable product potentially applicable as packaging material. Blends prepared from copolyester and native starch, plasticized by 15, 20 or 30 wt. % of glycerol, at copolyester: TPS ratios 55:45, 65:35 or 75:25 by weight are characterized by tensile strength 9–30 MPa, depending on the blend composition. Elongation at break of these blends is very low and is close to those of polystyrene.

Free surface energy and critical surface tension values calculated according to the commonly used methods show that the wettability of the tested blends would not limit possible use of them for packaging. Water sorption of prepared blends, determined gravimetrically, does not exceed 8.1 wt. % at RH 66 % and temperature 23 °C. Blends containing 65 or 75 wt. % of copolyester have been succumbed to a relatively fast biodegradation under action of thermophilic (55 °C) mixed culture of microorganisms of digested sludge from wastewater treatment plant. Decomposition of the blends is indicated by massive biogas production. Degradation of the copolyester fraction in the blends is demonstrated by a dramatic decrease in reduced viscosity of their cresol solutions.

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