Utilization of poly(ethylene terephthalate) waste in the synthesis of air-drying polyester alkyd resins and aliphatic-aromatic poly(ester-carbonate)s*)

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Abstract: Two methods of chemical recycling of poly(ethylene terephthalate) (PET) waste with simultaneous recovery of ethylene glycol were described. In the synthesis of the air-drying alkyd polyester resin phthalic anhydride was replaced with phthalic acid. The resin was obtained in one pot process in which PET waste was reacted with incomplete esters of pentaerythritol and glycerol with unsaturated fatty acids. The side product – ethylene glycol was removed from the reaction mixture by azeotropic distillation. To reduce amounts of volatile organic compounds (VOC) in the lacquers the obtained resins were modified with dibutyl sulfosuccinate sodium salt, and aqueous dispersions were prepared. Drying times and hardness of coatings prepared on the basis of alkyd polyester resins were examined. The second method of recycling consisted in PET reaction with 1,4-butanediol afforded oligo(tetramethylene terephthalate) (OTMT). This oligomer was subjected to a transesterification reaction with oligo(tetramethylene carbonate) (OTMC) to form a high molar mass poly(tetramethylene terephthalate-*co*-tetramethylene carbonate)s (PTMTC). The resulting copolyesters were characterized with NMR and FT-IR spectroscopies, mass spectrometry MALDI-TOF, DSC and mechanical testing. The effect of carbonate unit content on tensile strength and elongation at break, as well as thermal properties was also evaluated.

Keywords: poly(ethylene terephthalate) waste, air-drying polyester alkyd resin, water-thinnable resin, oligo(tetramethylene carbonate), poly(ester-carbonate).

Wykorzystanie odpadowego poli(tereftalanu etylenu) w syntezie poliestrowych żywic alkidowych schnących na powietrzu i alifatyczno-aromatycznych poli(estro-węglanów)

Streszczenie: Opisano dwie metody chemicznego recyklingu odpadowego poli(tereftalanu etylenu) (PET) z jednoczesnym odzyskiem glikolu etylenowego. W syntezie alkidowej żywicy poliestrowej schnącej na powietrzu zamiast bezwodnika ftalowego zastosowano kwas ftalowy pozyskiwany w jednym etapie reakcyjnym z niepełnymi estrami pentaerytrytolu i glicerolu z nienasyconymi kwasami tłuszczowymi oddestylowując azeotropowo glikol etylenowy. Otrzymane żywice modyfikowano za pomocą soli sodowej sulfobursztynianu dibutylu i na ich bazie sporządzano dyspersje wodne. Zbadano czasy schnięcia i twardości powłok sporządzonych na podstawie opracowanych alkidowych żywic poliestrowych. Druga metoda recyklingu polegała na alkoholizie PET 1,4-butanodiolem prowadzącej do otrzymania oligo(tereftalanu tetrametylenu) (OTMT). Na drugim etapie oligomer ten poddawano reakcji transestryfikacji z oligo(węglanem tetrametylenu) (OTMC) z wytworzeniem wielkocząsteczkowego poli(tereftalanu tetrametylenu-*co*-węglanu tetrametylenu) (PTMTC). Otrzymany kopoliester scharakteryzowano metodami spektroskopii NMR i FT-IR oraz spektrometrii masowej MALDI-TOF, a także zbadano jego właściwości mechaniczne. Oceniono wpływ zawartości jednostek węglanowych na wytrzymałość na rozciąganie i wydłużenie względne przy zerwaniu.

Słowa kluczowe: odpadowy poli(tereftalan etylenu), alkidowa żywica poliestrowa schnąca na powietrzu, żywica wodorozcieńczalna, oligo(węglan tetrametylenu), poli(estro-węglan).

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Poly(ethylene terephthalate) (PET) is an indispensable polymer with vast applications due to its excellent mechanical and chemical properties. On the other hand, due to its non-biodegradability, PET waste disposal has impacted serious environmental and economic concerns. Thus, utilization of PET waste has become an important problem to be solved. Recycling the remains is the most viable option for the treatment of waste PET. Among the various methods of PET recycling only chemical recycling conforms to the principles of sustainable development, because it leads to the formation of the raw materials from which PET is originally made – terephthalic acid and ethylene glycol as well as other valuable derivatives and polymers of terephthalic acid. Moreover, due to the presence of labile ester linkages chemical recycling can be performed selectively and with high yield.

Chemical recycling, involves the transformation of the PET polymer chain. Usually by means of a chain cleavage, this process can either be a total depolymerization back to its monomers or a partial depolymerization to its oligomers and other industrial chemicals. Since PET is polyester with functional ester groups, it can be cleft by some reagents such as water [1], alcohols [2], glycols [3, 4] and amines [5, 6]. These low molar mass compounds can then be reused as raw materials to produce high quality chemical products [7]. As early as in the 1960s, Ostrysz and co-workers [8–10] proposed using product of PET glycolysis in synthesis of unsaturated polyester resins. To obtain terephthalic acid (TPA) usually hydrolysis of PET is carried out under basic conditions. Karayannidis *et al.* [11] described alkaline hydrolysis of PET flakes with aqueous solution of NaOH as well as non-aqueous solution of KOH in methyl Cellosolve to obtain TPA with purity 98 %. Nikje and Nazari [12] applied microwave radiation to ester bond breaking of PET to TPA in the process performed in glycerol, diethylene glycol or monoethanolamine as solvolytic medium and KOH or NaOH as the catalysts. Very recently Issam [13] synthesized Kevlar-49 from PET waste bottles. Both starting materials: terephthalic acid chloride and *p*-phenylenediamine were obtained from recycled TPA. The same author revealed that recycled terephthalic acid can be applied to synthesis of the new unsaturated poly(ester-urethane) in the reaction of 4,4′-methylenediphenyldiisocyanate (MDI) with bis(4-hydroxy-2-butene)terephthalate. The latter one was prepared in the reaction of *cis*-2-butene-1,4-diol with terephthalic acid [14].

Bis(2-hydroxyethyl)terephthalate (BHET) obtained in the most important method of glycolysis of PET can be used in synthesis of virgin PET [15]. The glycolysis is usually performed in the presence of metal salts [16, 17]. The reaction time can be shortened from 8 h to 35 min when instead of conventional heating a microwave energy is used [18, 19]. The glycolysis of PET waste flakes can be carried out in the presence of new class of catalyst such as ionic liquids [15, 20], hydrotalcites [21, 22] and enzymes [23, 24].

In very few chemical methods of PET recycling ethylene glycol was exchanged with other di- or multifunctional alcohols or amines and removed from the reaction system. Mendes *et al.* [25] described recycling of PET waste in the melt state through alcoholysis with multifunctional alcohol – pentaerythritol in the presence of zinc acetate as a catalyst. Depending on monomers molar ratio applied in the process, the authors observed formation of star-branching copolymer or oligoester – bis(trihydroxyneopentyl)terephthalate. The final products have potential application as an asphalt additive or adhesive [26]. Spychaj *et al.* [27] characterized methods of aminolysis and aminoglycolysis of PET waste. The reaction products with polyamines as well as triethanoloamine were used as hardeners of epoxy resin and polyols for polyurethane foams. Very recently, Dutt and Soni [28] revealed very attractive synthesis method of bis(2-aminoethyl)terephthalamide by the reaction of ethylene diamine with PET waste. The process was carried out in 5 days under ambient conditions – at room temperature and normal pressure. The precipitated white product was isolated by filtration. The resultant diaminodiamide was applied as an epoxy resin hardener. Fukushima *et al.* [29] presented the effective organocatalysis to promote aminolytic depolymerization of waste PET using 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD). The presence of this organocatalyst enables the production of a broad range of terephthalamide compounds that are crystalline with desirable thermal and mechanical properties. The products were isolated by trituration and washing with organic solvents. The diverse set of monomers showed a large potential as a building block of high performance materials due to their physical properties arising from terephthalic moiety and amide hydrogen bonding. Yamaye and coworkers [30] proposed PET waste as a source of aromatic units for preparation of terephthalohydroxamic acid and terephthalohydrazide.

Alkyd resins still offer a very attractive solution for meeting the environmental challenges that the paint industry is facing. The continuing demand to lower volatile organic compounds (VOCs) and reduce carbon has forced scientists to formulate alkyd water dispersions [31, 32].

The aim of this work was the study of two methods of chemical recycling of PET waste. According to the method proposed by us, the process of alcoholysis is combined with removing side product – ethylene glycol by azeotropic distillation. We used the product of vegetable oil alcoholysis, namely incomplete esters of glycerol and pentaerythritol with unsaturated fatty acids as an alcoholic ingredient in the synthesis of air-drying polyester alkyd resin. The synthesis is very similar to the classical one when phthalic anhydride is used as an acidic ingredient and condensation water is removed from the reaction system by azeotropic distillation. According to our approach, origin from PET terephthalic acid is used instead of phthalic anhydride and the reaction by-product

– ethylene glycol is removed by azeotropic distillation. To achieve the water thinnability of alkyd resin we used dibutyl sulfosuccinate sodium salt as an additional hydrophilic acidic ingredient.

The second method of PET chemical recycling based on azeotropic removing of ethylene glycol presented in this article concerns synthesis of copoly(ester-carbonate)s. In this case ethylene glycol was replaced with 1,4-butanediol. The resultant oligo(tetramethylene terephthalate) was reacted with oligo(tetramethylene carbonate) to obtain high molar mass poly(tetramethylene terephthalate-*co*-tetramethylene carbonate). This copoly(ester-carbonate) exhibits similar mechanical properties to the one produced by BASF biodegradable aliphatic-aromatic copolyester Ecoflex®.

EXPERIMENTAL PART

Materials

For synthesis the following materials were used:
- 1,4-butanediol (99 %, Sigma-Aldrich),
- 1-butanol (POCh),
- 1,4-butynediol (99 %, Merck),
- dibutyl maleate (98 %, Sonderahfall-Schluessel),
- dibutyltin oxide (98 %, Merck),
- diethylene glycol monobutyl ether (98 %, Merck),
- *n*-heptane (≥99 %, Roth),
- pentaerythritol (≥95 %, Chemko),
- propylene carbonate (≥99 %, Merck),
- siccative for solvent based paints [Co (10 wt %), Zr (18 wt %), Ca (10 wt %), Chemiglob],
- siccative for water-thinnable paints ADDITOLVXW-4940 [Co (3 wt %), Zr (3 wt %), Ba (5 wt %), RAFIL],
- sodium pyrosulphite (POCh),
- soybean oil (Chemiglob),
- titanium(IV) butoxide [Ti(OBu)$_4$, ≥97 %, Aldrich],
- white spirit (Chemiglob),
- xylene (mixture of isomers, 98 %, POCh).

PET flakes were prepared from used PET bottles. The caps and bottom parts as well as the label and the adhesive had been removed. The bottles were cut and fed to a rotary cutter (Chemiglob).

Synthesis of polyester alkyd resin based on PET waste (SPAR)

The reaction was carried out in a 2 dm^3 four-neck round-bottomed reactor equipped with an anchor shape mechanical stirrer, thermometer and a nitrogen supply system. Reagents in amounts of 791.7 g of soybean oil, 163.2 g (1.20 mol) of pentaerythritol and 0.8 g (0.1 wt %) of dibutyltin oxide were placed in the reactor. The reaction mixture was heated up to 250–255 °C and stirred for next 1 h. Then the reaction mixture was cooled down to 220–230 °C and 360.8 g of PET waste pieces were added stepwise. The reaction was continued for another 6 h. Then a Dean-Stark reflux condenser was installed and around 80 cm^3 of xylene was added to keep the temperature at 220–230 °C. At this temperature azeotropic distillation was continued till 84 g of ethylene glycol was collected (72 % of the theoretical amount).

Synthesis of dibutyl sulfosuccinate sodium salt (DBSSS)

The synthesis was performed in a 250 cm^3 three-neck round-bottomed reactor, equipped with a magnetic stirrer, thermometer, reflux condenser, dropping funnel and nitrogen supply system. Dibutyl maleate in the amount of 79.8 g (0.35 mol) was placed in the reactor and heated up to 90–95 °C. Then 96 g of 40 wt % of sodium pyrosulphite aqueous solution was added within 3 h and then reaction mixture was stirred for next 4–6 h. The product was isolated by crystallization from an aqueous solution at 2 °C, followed by vacuum filtration at room temperature. After drying under reduced pressure 108.8 g of the dibutyl sulfosuccinate sodium salt in the form of white crystals was obtained.

Synthesis of water-thinnable air-drying polyester alkyd resin (WPAR) based on PET waste and dibutyl sulfosuccinate sodium salt

In a 250 cm^3 three-neck round-bottomed reactor, equipped with a mechanical stirrer, thermometer and set for vacuum distillation 221.0 g of SPAR and 46.1 g of DBSSS (6 wt %) were placed. The reaction mixture was heated up to 166–165 °C and distillation under reduced pressure (13–27 hPa) was carried on for 8 h. As a result 226.5 g of light-brown resin of high viscosity was obtained.

Dispersion preparation

To prepare water-dispersions of WPAR the coalescent solvent (diethylene glycol monobutyl ether) was added. Next distilled water was added stepwise and the mixture was homogenized using a high speed mechanical stirrer.

Synthesis of oligo(tetramethylene terephthalate) (OTMT) from PET waste and 1,4-butanediol

In a 250 cm^3 three-neck round-bottomed flask, equipped with a magnetic stirrer, thermometer, Dean-Stark distillation trap, and reflux condenser, 47.16 g (0.52 mol) of 1,4-butanediol, 50.00 g (0.26 mol of a repeated units) of PET waste, 0.13 g (0.4 mmol) of Ti(OBu)$_4$ as a catalyst and 50 cm^3 of xylene were placed. The reaction was carried out at the boiling point of the reaction mixture (180–210 °C) with continuously removal of ethylene glycol by azeotropic distillation with xylene. The reaction was continued till no ethylene glycol droplets were observed in the distillate. The product was filtered and solvent distilled off under reduced pressure. 66.70 g of OTMT with molar mass of 3360 g/mol was obtained as a white solid.

Synthesis of oligo(tetramethylene carbonate) (OTMC) from propylene carbonate and 1,4-butanediol [33]

In a 250 cm^3 three-neck round-bottomed flask, equipped with magnetic stirrer, thermometer Dean-Stark distillation trap, and reflux condenser 60.00 g (0.6658 mol) of 1,4-butanediol, 135.94 g (0.6356 mol) of propylene carbonate, 0.6 g (0.0018 mol) of $Ti(OBu)_4$ as a catalyst and 80 cm^3 of *n*-heptane (azeotropic solvent) were placed. Reaction was carried out at the boiling point (165–170 °C) of the reaction mixture with continuously removal of propylene glycol by codistillation with *n*-heptane for 6 h under atmospheric pressure. The second step – polycondensation was performed under reduced pressure of 0.5 mbar at 200 °C for 2 h. The obtained product was dissolved in chloroform and washed with 3 % water solution of HCl, and then with demineralized water until the conductivity of the aqueous phase was lower than 30 μS. The precipitated catalyst residue was filtrated off and organic solvent was evaporated under reduced pressure. 55.47 g of OTMC with molar mass of 1090 g/mol was obtained as a white solid.

Synthesis of poly(tetramethylene terephthalate-*co*-tetramethylene carbonate) (PTMTC)

In a 250 cm^3 three-neck round-bottomed reactor, equipped with a mechanic stirrer, thermometer, set for vacuum distillation 50.0 g (0.22 mol of repeating unit) of OTMT and 32.86 g (0.28 mol of repeating unit) of OTMC and $Ti(OBu)_4$ (0.01 mol %) as a catalyst were placed. The reaction mixture was heated up to 160–180 °C and the reaction was continued for 2 h. Next the temperature was increased up to 200–220 °C and distillation under reduced pressure (0.13–13 hPa) was carried on for next 6 h. As a result 75.7 g of the product (PTMTC) in a form of white solid was obtained.

Methods of testing

FT-IR spectra recordings on BIORADFTS-165 were carried out in the wavenumber range between 400 and 4000 cm^{-1} with sample films applied to KBr pellets. The number of scans per one recording was 16 and the resolution was 2 cm^{-1}.

The ^{1}H NMR spectra were recorded on a Varian Mercury VXR 400 MHz spectrometer using tetramethylsilane as an internal reference and D_2O or $CDCl_3$ as a solvent. Spectra were analyzed with MestReNova v. 6.2.0-7238 software.

Matrix-assisted laser desorption/ionization time-of--flight mass spectroscopy (MALDI-TOF/MS) measurements were performed on a Bruker Ultra Flex MALDI--TOF/TOF spectrometer (Bremen, Germany) in a linear mode using MwCNt (multiwalled carbon nanotubes) matrix and Bruker Peptide Calibration Standard (molecular weights range 1047.19–3149.57) as a calibrant and analyzed with flexAnalysis v.3.3 (Bruker Daltonik GmbH) and Polymerix v. 2.0 (Sierra Analytics Inc.) software.

Measurements of viscosity were conducted using Mettler RM180 rheometer. Studies of samples were performed at 25 °C. Prior to measurement the sample was thermostated for 15 min in the thermostat Horyzont MT-1. Measurements were performed over the shear rate range from 6.5 to 1291 s^{-1}.

Hardness of polymer films was measured with Persoz pendulum (number of oscillations of a pendulum) according to DIN EN ISO 1522:2006 standard.

Mechanical properties of poly(ester-carbonate)s were determined using a testing machine Instron 5566 with head speed 50 mm/min. Samples were dog-bone shaped with 30 mm length, 0.1 mm thickness and 4 mm width of the measuring section.

DSC studies were carried out using a TA Instruments DSC Q200 apparatus. Samples of poly(ester-carbonate)s were heated in the temperature range between -80 and 200 °C, then cooled back to -80 °C and if the sample had a crystalline phase, heated again to 200 °C. Heating and cooling rate was 10 °C/min in all measurements.

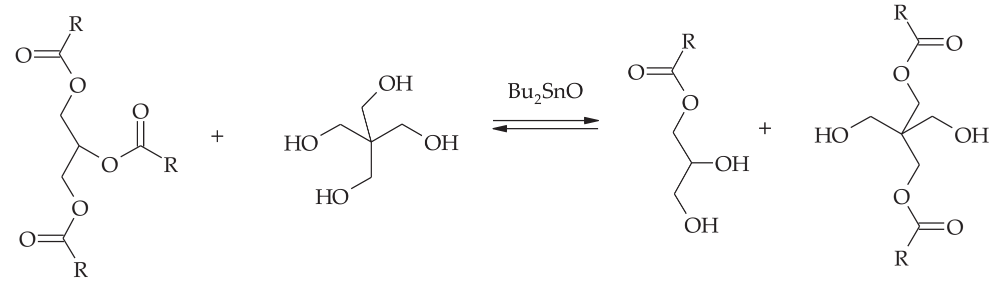
The polymer films were prepared on a glass plate. Polyester alkyd resins 60 wt % solutions in white spirit were prepared and applied on glass plates (10 x 10 cm) using a metal applicator with the gap width of 45 mm and a depth of 120 and 90 μm. Then a siccative for solvent-based paints was added in amounts of 0.3 wt % of Zr, 0.1 wt % of Ca and 0.05 wt % of Co (in relation to the weight of dry resin). Then coatings were kept in air at 25 °C.

Water dispersion with addition of siccative was applied on the glass plates (10 x 10 cm) using a metal applicator with the gap width of 45 mm and a depth of 120 and 90 μm. Then a siccative was applied. Siccative for solvent-based paints was added in amounts of 0.3 wt % of Zr, 0.1 wt % of Ca and 0.05 wt % of Co, and siccative for water-thinnable paints in amount of 4.0 wt % (corresponding to 0.12 wt % of Co) (in relation to the weight of dry resin). Then coatings were kept in air at 25 °C. Dryness degrees *T*1 and *T*3 were measured according to PN-C-81519:1979 standard.

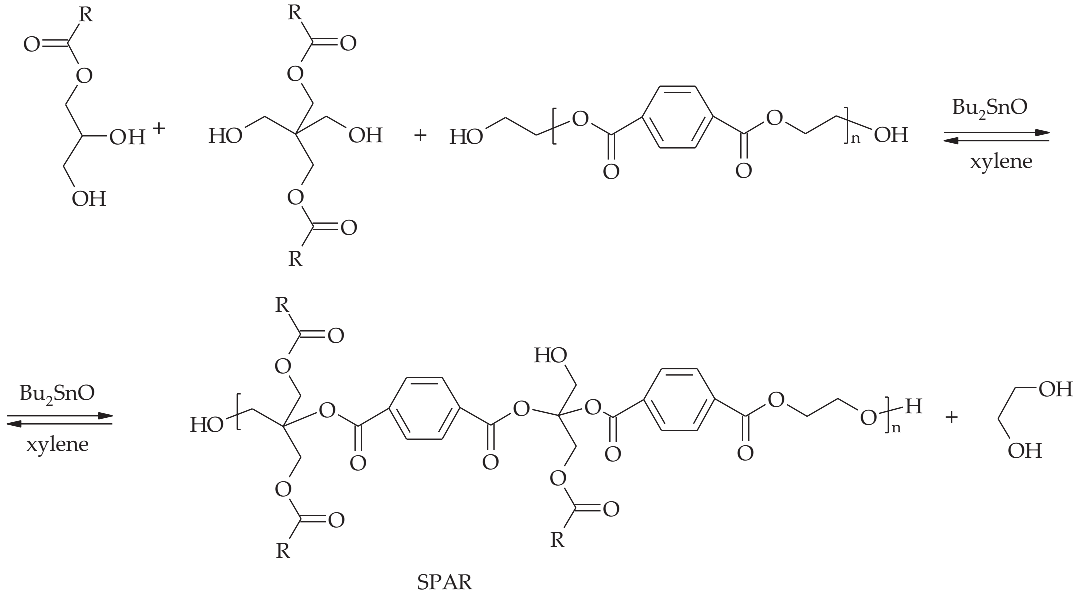
RESULTS AND DISCUSSION

Air-drying polyester alkyd resins based on soybean oil, pentaerythritol and PET waste

Origin from PET waste terephthalic acid was used as an alternative to phthalic anhydride or isophthalic acid for synthesis of air-drying polyester alkyd resins. Instead of esterification, two step transesterification of PET using incomplete esters of pentaerythritol and glycerol with soybean unsaturated fatty acids was used. At the



Scheme A



Scheme B

first step, presented in Scheme A, soybean oil was subjected to alcoholysis with pentaerythritol in the molar ratio leading to the average number of hydroxyl groups in a molecule in the range of f_{OH} = 2.0–2.2.

In the next step, shown in Scheme B, transesterification of PET with incomplete esters of pentaerythritol and glycerol with soybean fatty acids was performed. The reaction mixture from the first step was cooled down to 220–230 °C and PET flakes were added. Under those conditions degradation of polymer chains took place, resulting in oligomerols terminated with hydroxyl groups. Then, reaction mixture was cooled down and xylene was added. To shift the transesterification equilibrium towards the polymer, distillation of a side product – ethylene glycol was applied. Xylene was found to be the best azeotropic solvent for selective removal of ethylene glycol from the reaction mixture. Characteristics of the resins syntheses are presented in Table 1. Experiments were performed using 25, 30 or 35 wt % of PET flakes.

Table 1. Characteristics of performed syntheses of air-drying polyester alkyd resins, based on soybean oil, pentaerythritol and PET waste (SPAR)

Run	f_{OH} [a]	PET amount, wt %	Soybean oil amount, wt %	Ethylene glycol amount [b], %
1	2.0	25	69.5	92
2	2.1	25	67.3	79
3	2.2	25	65.1	69
4	2.0	30	65.7	68
5	2.1	30	63.4	81
6	2.2	30	61.1	74
7	2.0	35	61.9	62
8	2.1	35	59.5	57
9	2.2	35	57.1	84

[a] f_{OH} – average functionality of the alcoholysis product.

[b] Amount of ethylene glycol distilled off in comparison to theoretical one.

Table 2. Characteristics of the obtained air-drying polyester alkyd resins, based on soybean oil, pentaerythritol and PET waste (SPAR)

Run	f_{OH}[a]	PET amount wt %	η[b] Pa · s	1st degree of dryness min	3th degree of dryness min	Hardness[c]
1	2.0	25	0.075	515	825	59
2	2.1	25	0.094	480	760	60
3	2.2	25	0.090	470	695	63
4	2.0	30	0.572	500	700	65
5	2.1	30	0.679	435	640	77
6	2.2	30	1.510	425	575	95
7	2.0	35	0.671	350	660	65
8	2.1	35	1.420	300	565	95
9	2.2	35	5.950	280	495	136

[a] f_{OH} – functionality of the alcoholysis product of soybean oil with pentaerythritol.

[b] η – viscosity.

[c] Persoz hardness (oscillation number).

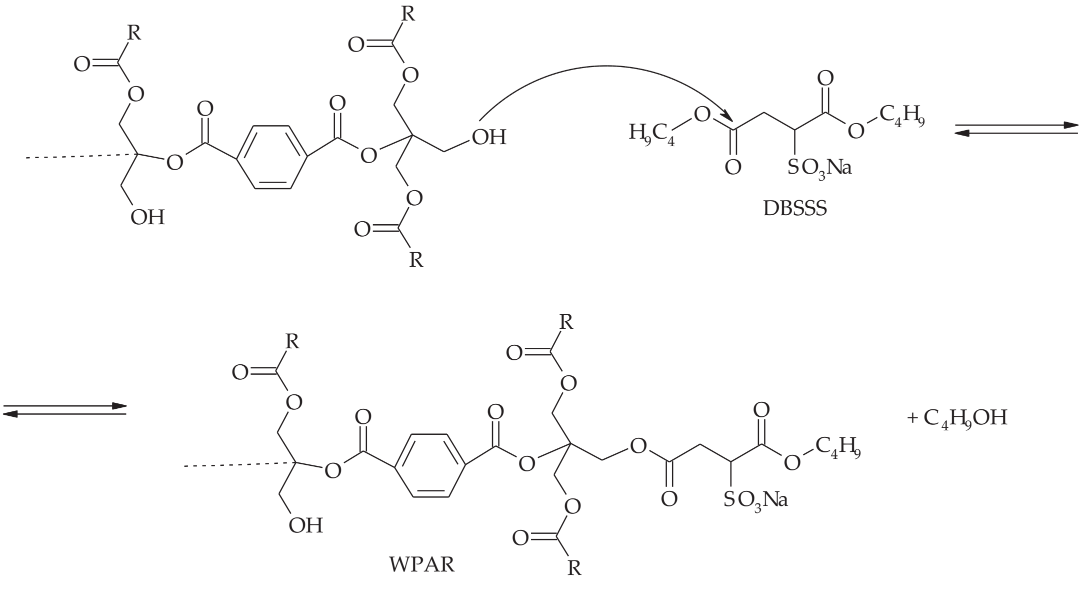
In the next step the lacquers based on the obtained resins were applied on glass plates and the time of drying (1st and 3rd degree of dryness) and hardness were examined. The results are listed in Table 2. With the increasing amount of PET [so with decreasing excess of hydroxyl groups and increasing functionality of the alcoholysis product (f_{OH})] the viscosity (η) of resins increased. In the case of f_{OH} = 2.1 and 2.2 maximum amount of PET which can be incorporated to the structure of resin was *ca.* 30 %; above that amount the system was prone to crosslink. For f_{OH} = 2.0 it was possible to incorporate 35 % of terephthalate units, but the viscosity of the resultant resin was too low (according to PN-EN ISO 2431:1999 standard). With the increasing content of PET in the resins drying time shortened. The optimal properties were achieved when f_{OH} = 2.2 and PET content was 30 wt %. 1st degree of dryness of lacquer layer was achieved after 8 h and 3rd degree of dryness after 12 h, resulting in Persoz hardness of 95 (number of oscillations) (Table 2, run 6).

Water-thinnable air-drying polyester alkyd resins

To reduce amount of VOC used for preparation of lacquers based on the polyester alkyd resins we propose modification of the resin by incorporation of a hydrophilic agent – dibutyl sulfosuccinate sodium salt (DBSSS). Due to the presence of butyl ester groups DBSSS can be incorporated into the resin structure by transesterification reaction. DBSSS was easily prepared in the reaction of dibutyl maleate with molar excess of $NaHSO_3$ ($NaHSO_3$:dibutyl maleate molar ratio was 1.1:1). Usage of small excess of $NaHSO_3$ led to the product yield over 94 %. It was observed, that addition of 15 wt % of the product to the reaction mixture shortened the reaction time of 2–4 h. FT-IR and ^{1}H NMR characteristic of the obtained product was as follows:

– FT-IR (KBr): 3579, 3446, 2850–3000, 1732, 1705, 1600––1650, 1350–1450, 1256, 1218, 1179, 1056, 400–800 cm^{-1}.

– ^{1}H NMR (400 MHz, D_2O): δ (ppm) = 4.20 (m, 3H, H_i, H_d), 4.10 (t, 2H, H_e, $J_{He,Hc}$ = 6 Hz), 3.13 (dd, 1H, H_h,



Scheme C

T a b l e 3. Characteristics of water thinnable air-drying polyester resins (WPARs) preparation

Run	DBSSS amount wt %	SPAR amount wt %	Water amount wt %	White spirit amount[a)], wt %	Coalescent amount, wt %	η, Pa · s	1st degree of dryness	Hardness[b)]
R-S1-ws[c)] R-S2-os[d)]	6	42	28	17	12	1.06	600 660	37 35
R-S3-ws R-S4-os	6	48	33	12	7	1.66	420 630	34 35
R-S1-ws R-S2-os	3	41	30	17	12	0.28	420 510	26 30
R-S3-ws R-S4-os	3	48	34	12	6	0.25	420 450	24 25

[a)] Diethylene glycol monobutyl ether; [b)] measured after 1 day, using Persoz pendulum (oscillation number); [c)] water-based siccative; [d)] organic solvent-based siccative.

$J_{Hh,Hf}$ = 8 Hz, $J_{Hi,Hh}$ = 17 Hz), 3.04 (dd, 1H, H_f, $J_{Hi,Hf}$ = 17 Hz), 1.6 (m, 2H, H_c), 1.33 (m, 2H, H_b), 0.87 (m, 3H, H_a).

In the next step sulfate derivative was introduced to PET-based resin, according to Scheme C. Progress of the incorporation of the sulfosuccinic acid derivative was monitored by amount of butanol distilled off. Two resins containing 3 or 6 wt % of DBSSS modifier were obtained. They were characterized by viscosity around 1 Pa · s and light brown color.

To prepare water dispersions from the obtained modified resins, first coalescent solvent (diethylene glycol monobutyl ether), which improved stability of the resin, wettability and the spreading ability on the glass surface, was added. Next, water in small portions was dosed and mixed using mechanical stirrer with high rotation speed. The stability of obtained resins did not exceed several hours, so small amount of white spirit (10–20 wt %) was added. Two kinds of siccative were also utilized in the system: one dedicated to organic solvent-based systems (os), and the other one to water-based ones (ws). Both were used in amount of 4 wt % in relation to dry resin which corresponds to 0.12 wt % and 0.05 wt % of Co ions in water- and solvent-based siccative, respectively (Table 3).

Coatings were applied on glass plates using metallic applicator with the depth of slot of 90 μm. As can be seen in Table 3 water-thinnable compositions dry faster when the water-based siccatives were used. This can be a result of over two-times higher concentration of Co ions, which are responsible for the speed of drying. Resins containing 6 wt % of DBSSS were much more stable than those containing only 3 wt %. They were opalescent, formed a homogeneous surface on the glass surface and did not delaminate. Addition of the sulfosuccinic acid derivative (DBSSS) and water resulted in a decrease of hardness and increased the time to reach the 1st degree of dryness.

Synthesis of aromatic-aliphatic poly(ester-carbonate)s

Transesterification of PET waste using 1,4-butanediol to replace ethylene glycol can be used to obtain OTMT. This hydroxyl groups terminated compound can be used in the synthesis of aliphatic-aromatic poly(ester-carbonate)s as a monomer introducing the aromatic units to the macromolecules.

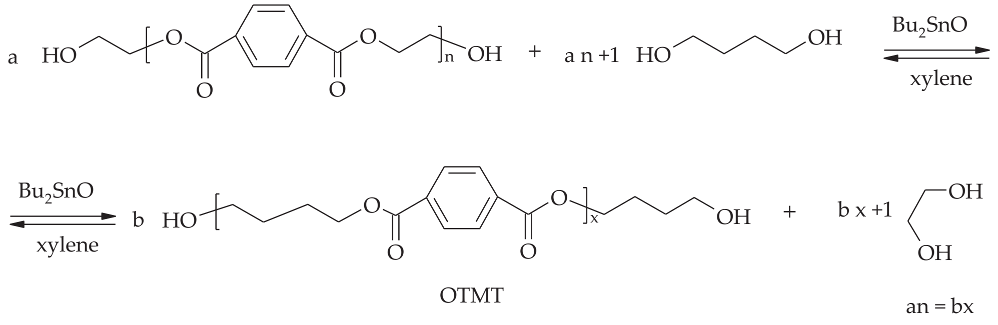
The first step of the process – alcoholysis of PET with 1,4-butanediol presented in Scheme D – was carried in the analogous way as previously. As a result OTMT containing no ethylene glycol units was obtained.

^{1}H NMR (400 MHz, *d*-$CHCl_3$ + *d*-CF_3COOH) characteristic of product can be given by: δ (ppm) = 8.14 (s, 4H), 4.51 (4H, t), 3.90 (4H, t), 2.06 (4H, t), 1.99 (4H, t), 1.92 (4H, t).

MALDI-TOF mass spectrum of OTMT is shown in Fig. 1.

In the next step transesterification of OTMT with OTMC was performed, resulting in poly(ester-carbonate), as it is shown in Scheme E. Depending on the molar ratio of OTMT and OTMC (repeating unit), products containing various carbonate units amount were obtained as it is shown in Table 4. OTMC was obtained according to the procedure already reported, using propylene carbonate as a source of carbonate units [33].

^{1}H NMR (400 MHz, $CDCl_3$) characteristic of OTMC is as follows: δ (ppm) = 4.15 [4H, t, C(O)OCH_2], 3.68 (4H, t, CH_2OH), 1.77 (4H, m, OCH_2CH_2).



Scheme D

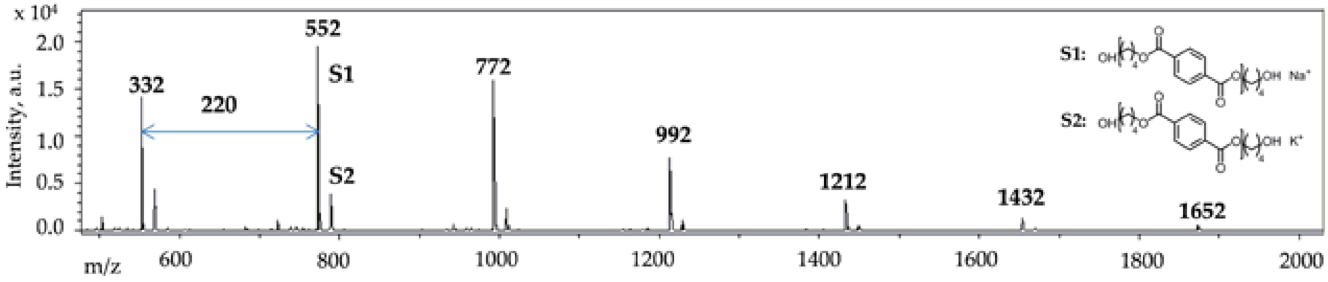


Fig. 1. MALDI-TOF mass spectrum of oligo(tetramethylene terephthalate) (OTMT) – no ethylene glycol units are in the product

The last step was performed under reduced pressure, while an excess of 1,4-butanediol was distilled off from the system and the required molecular mass of the final product was obtained. As a result, PTMTC is formed as a white solid. FT-IR and ^{1}H NMR characteristic of PTMTC is given by:

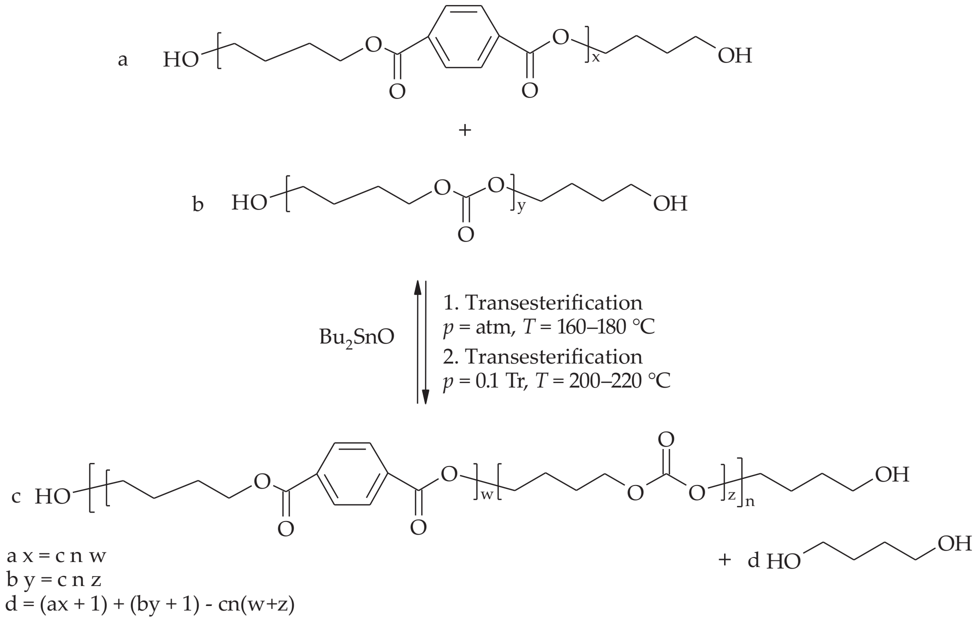
– FT-IR (KBr): 3550, 2965, 2905, 1746, 1713, 1248, 1121, 930, 727 cm^{-1}.

– ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.09 (s, 4H), 4.43 (t, 4H), 4.38 (t, 4H), 4.21 (t, 4H), 4.16 (t, 4H), 3.73 (t, 4H), 3.68 (t, 4H), 1.97 (m, 4H), 1.84 (m, 4H), 1.78–1.58 (m, 8H).

Based on ^{1}H NMR spectra (exemplary spectrum is shown in Fig. 2), the amount of each units (aliphatic/aromatic) content were estimated. Average molar mass was measured using GPC with triple detection system.

Based on relative areas of the signals of the OCH_2 protons of the terephthalate units located at 4.36–4.46 ppm (TT+TC) and the OCH_2 protons of the carbonate units at 4.12–4.24 ppm (CC+CT), the degree of randomness (*R*) was calculated and it was very close to 1, indicating the random nature of the prepared poly(ester-carbonate)s [34]. According to Yamadera and Murano, the number-average sequence length for terephthalate (*LnT*) and carbonate (*LnC*) units, also known as the corresponding block length, can be calculated using the same equations. In case of obtained poly(ester-carbonate)s *LnT* and *LnC* were in the range of 1–3.

Mechanical as well as thermal properties of the products were investigated and are listed in Table 4. It was found that within increase of carbonate units content, tensile strength as well as elongation at break decreased. For PTMTC3 and PTMTC4, containing 45 and 75 mol % of carbonate units, respectively, values of $\overline{M}_n$ were *ca.* 11 000 g/mol, tensile strength decreased from 37 to 6 MPa, and elongation at break decreased from 700 to 220 %. The values of Young modulus (*E*) were higher in case of samples with higher content of terephthalic units, especially when the molar mass of the sample was relatively high – 670 and 1180 MPa (PTMTC3 and PTMTC4), respectively. Samples did not show elastomeric properties. The content of carbonate units in the range of 40–55 mol % led to the structures exhibiting two melting points, which suggest strong phase separation of two kinds of polymer chain components – with melting temperatures T_{m1} around 40–50 °C related to the aliphatic carbonate units and T_{m2} in the range of 124–176 °C related to aliphatic-aromatic units. In case of the sample with 75 mol % of carbonate units only one melting point was observed. An increase of aromatic units in the polymer chain increases the stiffness of the structure and causes increase of glass transition



Scheme E

Table 4. Thermal and mechanical properties of poly(tetramethylene terephthalate-*co*-tetramethylene carbonate)

Sample	Carbonate unit content, mol %	$\overline{M}_n$ g/mol	$\overline{M}_w$ g/mol	DI[a)]	σ[b)] MPa	ε[c)] %	E[d)] MPa	T_{m1}[e)] °C	T_{m2}[e)] °C	T_g[f)] °C
PTMTC1	40	6580	18 100	2.7	27 ± 2	610 ± 32	740 ± 80	41	176	4
PTMTC2	55	7100	18 600	2.6	9 ± 1	180 ± 20	750 ± 110	49	124	-2
PTMTC3	45	12 300	32 000	2.6	37 ± 2	700 ± 15	670 ± 170	44	144	3
PTMTC4	75	10 700	27 400	2.6	6 ± 1	220 ± 25	1180 ± 20	50	–	-14

a) DI – dispersity; b) σ – tensile strength; c) ε – elongation at break; d) E – Young modulus; e) T_{m1}, T_{m2} – melting points (based on DSC measurement); f) T_g – glass transition temperature.

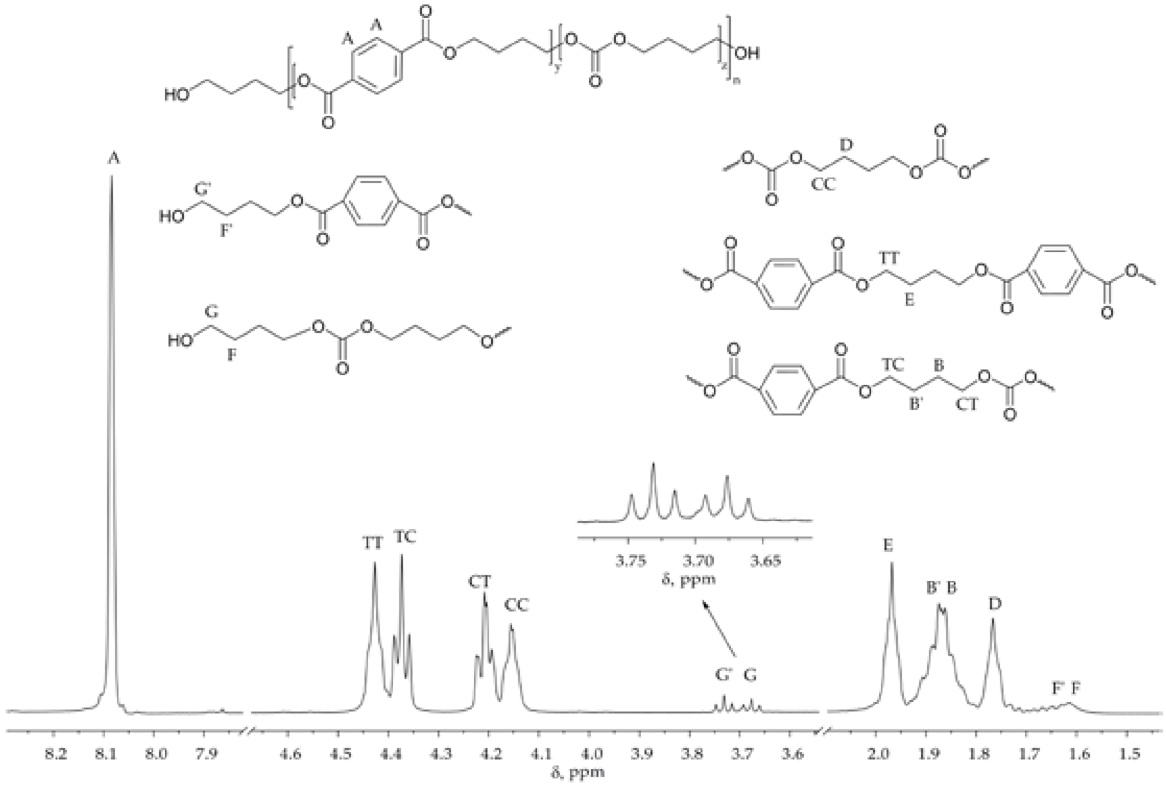


Fig. 2. ^{1}H NMR (400 Hz, $CDCl_3$) spectrum of poly(tetramethylene terephthalate-*co*-tetramethylene carbonate) (PTMTC3)

temperature (T_g > 3 °C and -14 °C for PTMTC3 and PTMTC4, respectively).

CONCLUSIONS

A new versatile method of chemical recycling of PET waste, in which ethylene glycol is removed from the reaction system, was elaborated. Polycondensation with PET proceeds similarly to classical polycondensation with usage of terephthalic acid, but instead of water, ethylene glycol is removed by azeotropic distillation. According to the developed method, incomplete esters of pentaerythritol and glycerol with unsaturated fatty acids were used in the reaction with PET waste to afford alkyd polyester resin. The lacquers prepared from the obtained resin exhibited similar properties, such as the degree of dryness and pendulum hardness to those based on a typical resin. The alkyd polyester based on PET waste was easily modified with dibutyl sulfosuccinate sodium salt to obtain water-thinnable resin.

PET waste can also be used for preparation of high molar mass aliphatic-aromatic poly(ester-carbonate)s. In this case PET flakes reacted with 1,4-butanediol and the resultant oligo(tetramethylene terephthalate) was subjected to transesterification with oligo(tetramethylene carbonate). The resultant poly(tetramethylene terephthalate-*co*-tetramethylene carbonate)s exhibited very good mechanical properties – tensile strength of 37 MPa and 650 % of elongation at break.

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Instytut Chemii Przemysłowej im. prof. I. Mościckiego w Warszawie

opracował ogólnokrajową

BAZĘ APARATURY DO OKREŚLANIA CHARAKTERYSTYKI I PRZETWÓRSTWA POLIMERÓW

będącej w posiadaniu uczelni, instytutów PAN i instytutów badawczych.

Baza jest wyposażona w funkcje umożliwiające wyszukiwanie wg zadanych parametrów: nazwy, typu lub modelu aparatu, roku produkcji, producenta, charakterystyki parametrów technicznych, zastosowania do badań, lokalizacji, słów kluczowych, sposobu wykonywania badań, numerów norm, wg których prowadzi się badania, oraz adresu i kontaktu z osobą odpowiedzialną za dany aparat. Baza jest ciągle uaktualniana.

Dostęp do danych i wyszukiwanie informacji w bazie jest bezpłatne.

Instytucje i firmy zainteresowane zamieszczeniem w bazie informacji o posiadanej aparaturze prosimy o przesłanie danych na adres polimery@ichp.pl

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