VILNIUS UNIVERSITY

CPST, INSTITUTE OF CHEMISTRY

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CHEMICAL RECYCLING OF INDUSTRIAL POLY(ETHYLENE TEREPHTHALATE) WASTE: SYNTHESIS OF AROMATIC POLYESTER POLYOLS, THEIR PROPERTIES AND USE

Summary of doctoral dissertation

Physical Sciences, Chemistry (03P)

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The scientific work was carried out in 2005-2011 at Vilnius University, Faculty of Chemistry, Department of Polymer Chemistry.

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VILNIAUS UNIVERSITETAS

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POLIETILENTEREFTALATO GAMYBINIŲ ATLIEKŲ CHEMINIS PERDIRBIMAS: AROMATINIŲ POLIESTERPOLIOLIŲ SINTEZĖ, SAVYBĖS IR PANAUDOJIMAS

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1. INTRODUCTION

Relevance of the work. Poly(ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. PET is one of the versatile engineering plastics which is used to manufacture mainly textiles and bottles, as well as used for packaging, photographic films, video and audio tapes. Rapid development of PET production industry in Lithuania inevitably causes continuously growing stream of post consumed and industrial PET waste. The main post-consumed PET waste source today is PET bottles which are mechanically recycled (grinded, washed, separated from other plastics and impurities) and re-used in the PET packaging production. The industrial PET waste is generated at various stages of the production of bottle grade PET and includes oligomers, prepolymers, polymer lumps, dust and etc. Because of different physical properties and composition, recycling and recovery of industrial PET waste is much more complicated and difficult to implement compared to post-consumed PET waste.

One important trend of chemical recycling of PET waste is glycolysis. PET waste can be glycolysed by ethylene glycol (EG) into constitutional repeating unit of PET bis(2-hydroxyethylene) terephthalate (BHET) and mixture of its oligomers which can be returned back to PET production process. As an alternative, PET waste can be transesterificated by diethylene glycol (DEG) obtaining oligomeric diols and aromatic polyester polyols (APP) which can be used as starting materials in the production of polyurethane (PU) or polyisocyanurate (PIR) foam.

Chemical recycling of PET is under continuous development and depends on source and type of PET waste, and on its characteristics. APP obtained by transesterification of PET with an excess of DEG are usually very viscous liquids with apparent tendency to crystallization; they are insoluble in blowing agents which makes difficult their use in the PU production. These disadvantages can be solved out introducing flexible fragments by the use of aliphatic acids such as adipic, sebacic or glutaric acid, or by addition of glycols with higher functionality followed by polycondensation reaction resulting in oligoester polyols with increased functionality. Unfortunately, these additives do not always provide the necessary properties of the final products – PU and PIR foams and coatings.

Characteristics of APP have considerable effect on physical-mechanical and thermal properties of the PU foam. Nature of a polyol determines whether the foam will be rigid or flexible, whether it will be brittle or not, and whether it will be flame retardant or not.

The main aim of the present work was transesterification of industrial PET waste in the presence of glycerol, adipic acid and other functional additives, directed to the synthesis of aromatic polyester polyols suitable for production of rigid polyurethane-polyisocyanurate foam.

The objectives of the research are the following:

1. determination of properties and chemical composition of industrial PET waste generated at various stages of PET production;
2. synthesis of bis(2-hidroxyethylene) terephthalate by glycolysis of PET waste with ethylene glycol and determination of the optimal conditions of glycolysis reaction;
3. synthesis of aromatic polyester polyols (APP) by transesterification of industrial PET waste with diethylene glycol in the presence of glycerol, adipic acid or other functional additives, and study of their properties in respect to transesterification recipe and type of catalyst;
4. synthesis of polyurethane-polyisocyanurate (PU-PIR) foam using APP derived from industrial PET waste, and study the effect of chemical structure of APP on physical-mechanical, thermal and flame retardant properties of PU-PIR foam.

Scientific novelty and practical value of the work. Different chemical recycling ways were suggested for each kind of industrial PET waste. The effect of functional additives on transesterification process and viscosity of APP was thoroughly studied and mathematically described for the first time. The influence of the structure of APP containing fragments of glycerol, adipic acid and other additives, on physical-mechanical, thermal and flame resistant properties of the synthesized polyurethane-polyisocyanurate foam were evaluated. PU-PIR foams synthesized from PET-waste-derived APP are promising materials for production of PU insulation building panels.

The results presented in the dissertation enable to defend the following most important ***statements***:

- Aromatic polyester polyols synthesized by transesterification of industrial PET waste with diethylene glycol in the presence of functional additives adipic acid and/or glycerol have lower crystallinity and are much more stable during storage at room temperature.
- Polyurethane-polyisocyanurate foam based on PET-waste-derived APP containing fragments of glycerol and/or adipic acid is characterized by good physical-mechanical properties, high thermal stability, and low heat release and smoke production.

Approbation of the research results. The results of the research have been presented in 10 scientific publications including 3 papers in the journals from the ISI Web of Science list. The results of the work have also been reported in 7 international conferences.

Structure of the dissertation. The dissertation consists of introduction, three chapters, conclusions, list of references (120 entries) and the list of original scientific publications. The material of the dissertation is presented in 136 pages including 25 figures, 30 schemes and 34 tables.

2. EXPERIMENTAL

Main materials. Diethylene glycol (DEG), glycerol (GL), adipic acid (ADA), poly(propylene glycol) (PPG) (M_n 425), 1,6-hexanediol (HD), terephthalic acid (TPA), dibutyltin dilaurate (DBTL), tin 2-ethylhexanoate ($Sn(Oct)_2$), tetrabutyltitanate ($Ti(OBu)_4$), cobalt acetate were purchased from SIGMA-ALDRICH and used without further purification. Industrial PET waste (oligomers, prepolymers, polymer lumps and dusts) was obtained from bottle grade PET plant of Neo Group (Lithuania). Diphenylmethane diisocyanate (MDI) was supplied by BASF AG as Lupranat M20R, NCO = 31.5%, average functionality 2.7.

Methods. Melting point (T_m) of polyester and polyols was determined by DSC method using *Mettler Toledo 822e* apparatus calibrated with indium. Intrinsic viscosity (IV) of PET and its oligomers was measured in the mixture of phenol and 1,2-dichlorobenzene (3:2, w/w) at 25 °C using Ubbelohde viscometer in automatic viscosity measuring system *PVS LAUDA*. The content of end-carboxylic groups (N_{COOH}) of PET waste was determined by potentiometric titration with 0.05 M KOH solution in ethanol using *Metrohm Titrino 719* apparatus. Acetaldehyde (AA), methyldioxane (MDO), dioxane (DO), diethylene glycol (DEG) and ethylene glycol in PET waste and transesterification side products (distillate) was tested by Gas chromatography (GC) and GC-MS. Water content was measured by culonometric titration using *Metrohm 832 KF Termoprep* apparatus. Dynamic viscosity of polyester polyols was measured by a *Haake Rheostress 300* and *Brookfield* apparatus. Preparation of polyurethane-polyisocyanurate foam was carried out by hand mixing method. FT-IR spectra of solid PU-PIR foam samples obtained by a KBr pellet method were registered with a *Perkin Elmer Spectrum One* FT-IR spectrometer. Mechanical testing of PU-PIR foam was performed on testing machine *Zwick/Roell 500 N.* Thermal stability of PU-PIR foam was studied using *Mettler Toledo TGA/SDTA 851e* instrument. Flammability of the prepared foam samples was measured by burning test and Cone Calorimetry (produced by *Fire Testing Technology*).

3. RESULTS AND DISCUSSION

3.1. Industrial PET waste: generation, composition and properties

Industrial PET waste is generated at various stages of the production of PET and includes PET oligomers, prepolymers, polymer lumps, dusts, etc. In an efficient bottle grade PET manufacturing (Neo Group, Lithuania), the amount of industrial PET waste is approximately 1 000 t per year (about 0.3 % from the total PET production). Formation of industrial PET waste is inevitable part of the production process and is caused by several reasons: deviation from a technological mode, periodic maintenance, service and cleaning of equipment, unexpected repair of equipment, and waste in a place of sampling.

Industrial PET waste differing in morphology and physical properties was collected and analyzed. Industrial PET waste was characterized by the content of acetaldehyde (AA), EG and water, melting point (T_m), intrinsic viscosity (IV), content of end-carboxylic groups (N_{COOH}) and acid number (N_A). Characteristics of industrial PET waste are presented in Table 1.

Table 1. Characteristics of industrial PET waste

No	Waste type	IV, dl/g (±0.02)	AA, ppm	H_2O, %	EG, %	T_m, °C	N_{COOH}, mmol/kg	N_A, mg KOH/g
1.	Oligomers	0.10	33	0.20	40-60	160-300	150	8.4
2.	Prepolymers	0.10-0.25	100	0.20	1.63	110	110	6.2
3.	Amorphous polymer lumps	0.60	< 60	0.20	0.02	250	30-45	1.7-2.5
4.	Wet dust of amorphous PET	0.60[*]	< 60	90	0.02[*]	249	30-45[*]	1.7-2.5[*]
5.	Mix of PET dust and chips (No 1)	0.60	4.0	0.05	0.02	252	39	2.2
6.	Mix of PET dust and chips (No 2)	0.78	1.0	0.10	0.02	248	32	1.8
7.	Mix of PET dust and chips (No 3)	1.04	0.5	0.20	0.02	246	25	1.4

[*] the sample was analyzed after draying

The largest part of industrial PET waste (about 80 %) is amorphous polymer lumps. The amorphous polymer lumps are produced during cleaning or under repair of granulators. Recycling of amorphous polymer lumps is relatively complicated since they have to be crashed before the main process. Mixture of PET dust and chips (about 9 %) is produced during cooling and dedusting processes followed by solid state polycondensation. The ratio of dust to chips depends on technological parameters of PET production and has an effect on recycling time. Wet dust of amorphous PET amounts 9 % of the total waste but because of high water content PET concentration in it is about 10 % only. Oligomers and prepolymers (about 3 %) is a mixture of the products of the reaction between ethylene glycol and terephthalic acid; they are constituted of one, two, three, etc. repeating units of PET.

Before analysis, oligomers and prepolymers were separated into water-soluble (soluble in boiling water) and water-insoluble fractions (WSF and WIF, respectively). It was determined that the amount of WIF in oligomers ranged from 47 to 62 %, and the amount of WSF was up to 2 %; the residual was EG and water. According to DSC measurements, both WIF and WSF contained aliphatic oligomers as well as cyclic dimers, trimers and tetramers.

During production of PET, in parallel to linear polyesters, cyclic oligomers can be produced in small amount (1–3 %). They are characterized by high crystallinity and poor solubility in hot water. It was determined that the content of cyclic oligomers in the intermediate PET products separated after first and second stage of esterification varied from 5 to 7 %. According to the data of thin layer chromatography, intermediate PET products contained various cyclic oligomers.

Analysis of industrial PET waste revealed that the most suitable for the synthesis of aromatic polyester polyols were amorphous polymer lumps and mixes of PET dust and chips collected from different places. Prepolymers and oligomers is a mixture of cyclic and acyclic oligomers; because of high content of EG and water, their use in transesterification processes is rather complicated. This kind of waste could be glycolysed to BHET.

3.2. Glycolysis of industrial PET waste towards monomeric structures: production of bis(2-hydroxyethylene) terephthalate

Glycolysis is the most cost-effective viable process of chemical recycling of PET waste. During glycolysis, ester linkages are broken and replaced by hydroxyl terminals (Fig. 1).

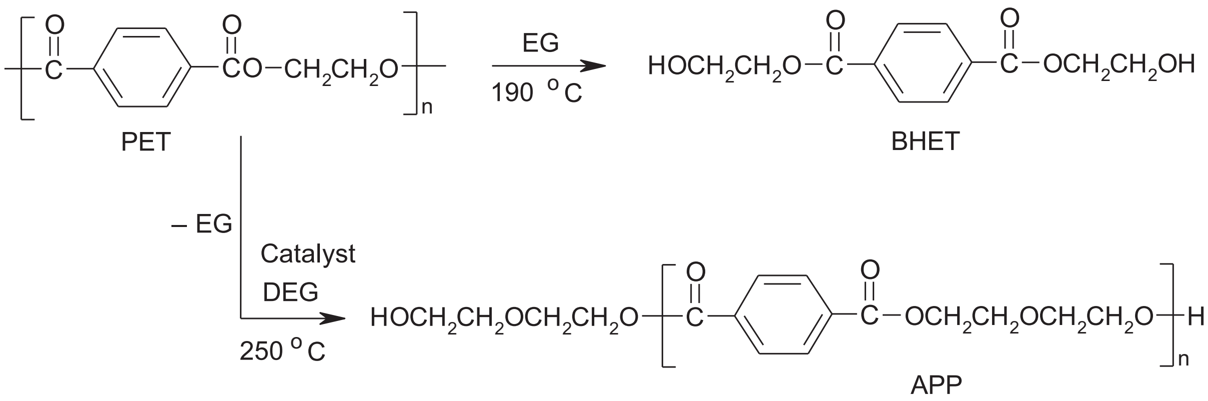

Fig. 1. Glycolysis of PET with EG and DEG

Glycolysis of PET dust and chips No 2 (IV = 0.78 dl/g) by EG in the presence of cobalt acetate catalyst was carried out at 190 °C under reflux. Characteristics of primary glycolysed products (GP) as well as oligomers and BHET derived thereof are presented in Table 2.

Analysis of GP characteristics evidenced that the glycolysis of industrial PET waste (IV = 0.78 dl/g) was almost complete within 3 h of the process, the yield of BHET being achieved 81–82 %. Separation of BHET from GP during crystallization from hot aqueous solution was found to be relatively simple and complete. According to DSC data, the glycolysed products contained mainly BHET; main part of oligomers was dimmers of BHET.

Because of lower crystallization rate and intrinsic viscosity (0.60 dl/g), glycolysis of amorphous polymer lumps was carried out at lower temperature (170 °C) and lower PET:EG weight ratio (1:2) in the presence ($GP_{0.25\%}$) or absence ($GP_{0\%}$) of transesterification catalyst (cobalt acetate).

Table 3. Characteristics of GP derived from amorphous polymer lumps

Sample	GP		Oligomers (WIF)		BHET (WSF)	
	EG, %	T_m, °C	Yield, %	T_m, °C	Yield, %	T_m, °C
$GP_{0,25\%}$	51.2	64.9	13.3	109.6; 156.4; 235.5;	91.5	110.3; 271.6
$GP_{0\%}$	-	-	20.1	-	0.5	-

Glycolysis of amorphous polymer lumps without catalyst was not proceeding, and the yield of BHET did not exceed 0.5 %. In the presence of a catalyst, glycolysis was effective, even at lower excess of EG and catalyst amount giving over 90 % BHET yield within 3 h. Glycolysis of PET oligomers was 2–3 times slower compared to that of amorphous polymer lumps, and the yield of BHET was < 85 %. Glycolysation of oligomeric PET waste was impeded by cyclic oligomers which were stable against glycolysis. BHET yield under glycolysis of oligomeric PET waste at various PET and EG weight ratio is presented in Fig. 2. According to the results of the experiments, the optimal conditions of glycolysis of oligomeric PET waste towards intermediate products intended to be used in direct PET production are as follow: the reaction time 6 h, weight ratio PET:EG = 1:1, concentration of the catalyst 0.25 %.

BHET produced this way may be used by itself or together with other monomers for production of PET or other aromatic copolyesters. BHET obtained from industrial PET waste can be used for various products including food applications which is obvious advantage; GP obtained from post-consumed PET is not suitable for food applications because of impurities and contamination.

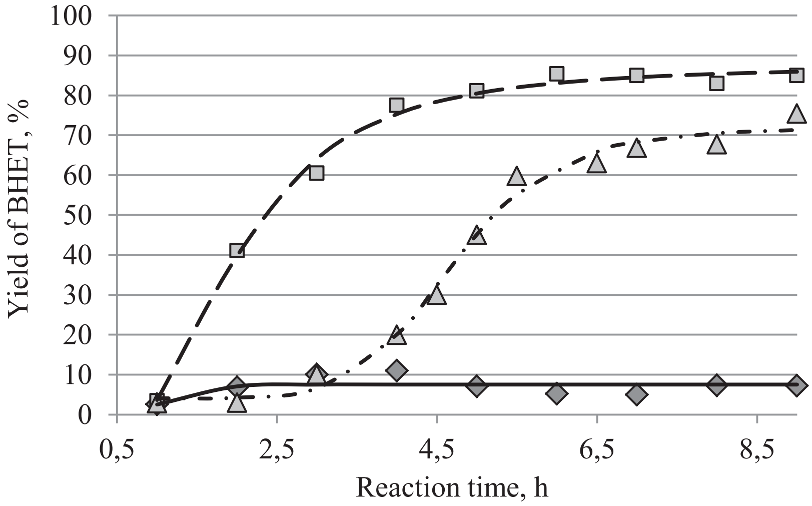

Fig. 2. Dependence of BHET yield on reaction time: (- - - - -) – PET:EG 1:1, Co(Ac)$_2$; (– · – · –) – PET:EG 1:0.5, Co(Ac)$_2$; (——) – PET:EG 1:1, whithout catalyst

3.3. Synthesis of APP by transesterification of industrial PET waste

Transesterification of PET waste with an excess of EG or DEG resulted in polyols susceptible to crystallization which made difficult their use after certain storage. The effect of functional additives glycerol (GL), adipic acid (ADA) and others present in transesterification formulations on properties of APP was evaluated. Possible structure of slightly branched APP containing segments of ADA and GL are shown in Figure 3.

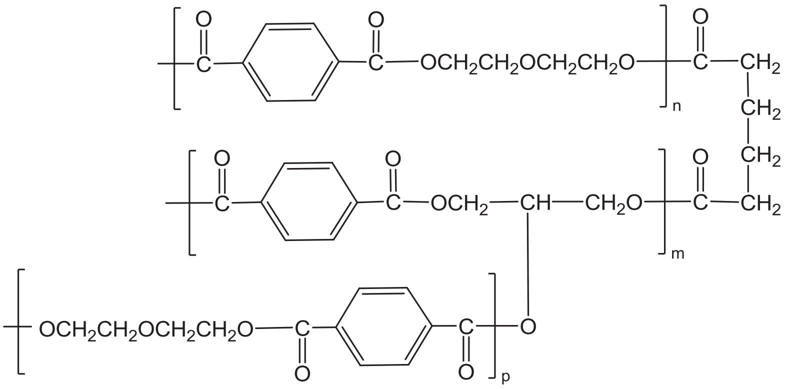

Fig. 3. Fragment of the structure of slightly branched APP containing segments of ADA and GL

The effect of ADA and GL on viscosity of APP and stability against crystallization was investigated. APP were synthesized using the same molar ratio of DEG to PET (1.83); the sample No 1 (Fig. 4 and 5) was without additives, No 2 contained 1 % ADA, No 3 – 1 % GL and No 4 – 1 % ADA and 1 % GL. Main characteristics of the obtained polyester polyols are as follow: hydroxyl number 242 to 345 mg KOH/g, acid number 0.85 to 1.95 mg KOH/g, and viscosity 21 to 52 Pa·s.

The polyester polyols which were synthesized from DEG and PET without additives or in the presence of 1 % ADA, after 10–14 days of storage at room temperature started to become turbid, and during the following 5–6 days turned to white crystalline paste (Fig. 4). The polyester polyols obtained from the formulations including GL or a mixture of GL and ADA, started to become turbid after 8–13 days of storage, and during the following 13–14 days turned to crystalline paste. It is obvious that introduction of ADA and GL moderate crystallization rate and thus enhance stability of APP against crystallization. Viscosity of APP synthesized in the presence of GL is considerably higher which can be related to higher molecular weight of APP containing GL (Fig. 5).

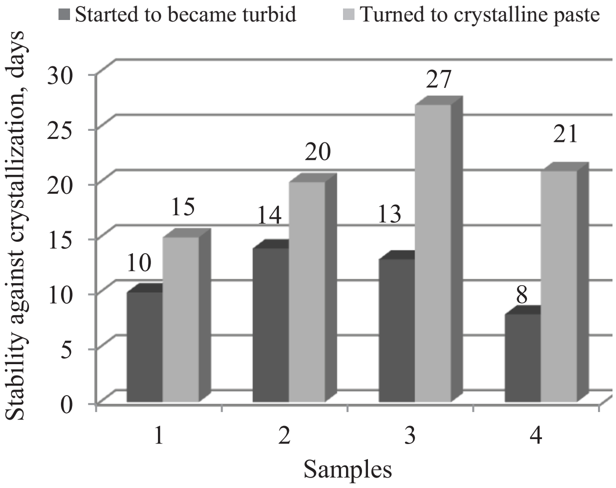

Fig. 4. The effect of ADA and GL on stability of APP against crystallization

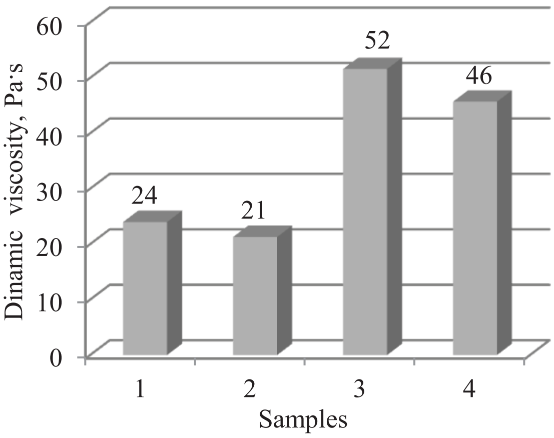

Fig. 5. The effect of ADA and GL on viscosity of APP

In order to decrease crystallinity of the polyester polyols, different amounts of GL and fixed amount of ADA were added to the reaction mixture. Two series of APP were synthesized. In the first series, 6.5 % of ADA and up to 7.5 % of GL were used, while in the second series 2–12 % of GL was used without ADA. Glycolysis using new recipes resulted in APP's which even after long storage had no melting point. The absence of melting as well as different visual appearance suggested that APP from recipes containing ADA and GL were more stable than APP containing only GL, and the stability increased with increasing glycerol amount (Fig. 6). Viscosity of the transesterification products increased with increasing glycerol concentration which suggested noticeable increase in molecular weight and slight branching of APP.

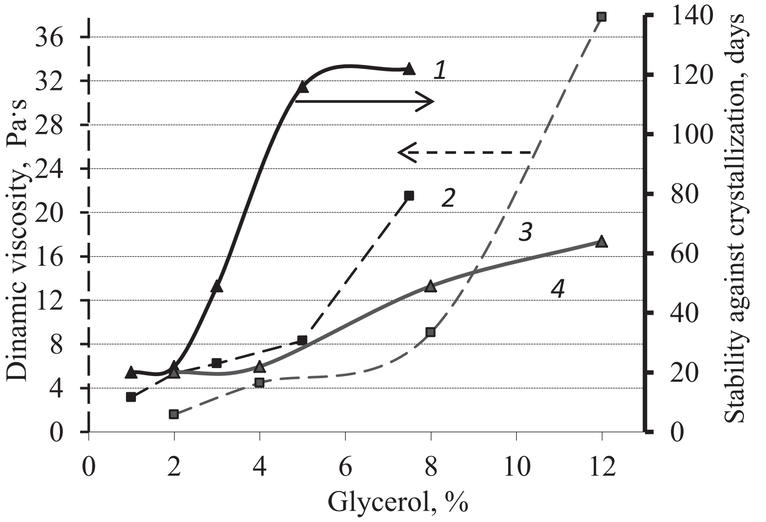

Fig. 6. Effect of GL concentration on stability and viscosity of APP: 1, 2 – polyols were prepared using 6.5 % ADA and up to 7.5 % of GL; 3, 4 – without ADA and using up to 12 % GL

Another series of APP was obtained by transesterification of PET waste with diethylene glycol in the presence of fixed amounts of GL (1 %) and ADA (16 %) and using different amount and type of organometallic catalyst (Fig. 7 and 8). APP with hydroxyl values 250 to 260 mg KOH/g and low acid value (about 0.4 mg KOH/g) were synthesized. Viscosity of APP was in the range 6.0 to 6.5 Pa·s and slightly depended on the type of catalyst used.

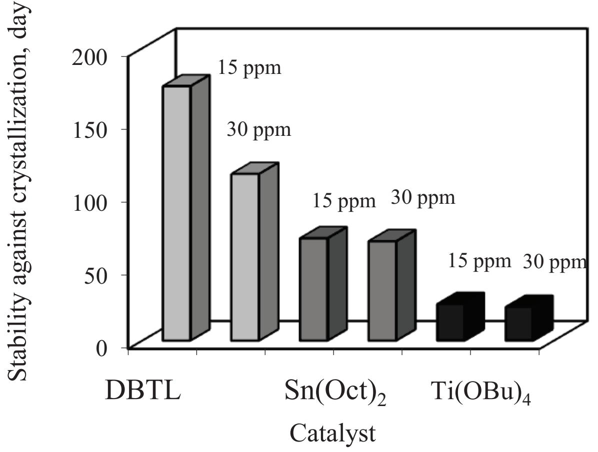

Fig. 7. The effect of catalyst on stability of APP, DEG:PET = 1.83 mol/mol, 16 % ADA and 1 % GL

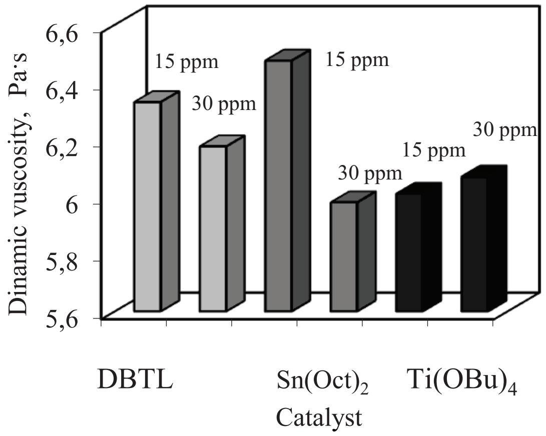

Fig. 8. The effect of catalyst on viscosity of APP DEG:PET = 1.83 mol/mol, 16 % ADA and 1 % GL

Nevertheless all catalysts promoted transesterification of PET waste; polyols synthesized in the presence of DBTL were the most stable. Excess of the catalyst was not suitable because it promoted formation of the products with lower stability.

The aim of statistical analysis was to correlate viscosity of APP with composition of formulations. Statistical 2^3 factorial experiment was realized for a series (LPT) of polyols synthesized from 12 formulations in which as independent variables were molar ratio DEG:PET and the concentrations of the additives GL and ADA. Molar ratio DEG:PET (z_3) was varied from 1.7 to 2.1, and the concentrations of the additives ADA (z_1) and GL (z_2) were varied from 6 to 16 % and from 1 to 4 % of the weight of formulation, respectively. Dynamic viscosity of APP synthesized from all the formulations was measured and qualified as the main parameter (y) outlining quality of APP. Encoding independent variables z_1, z_2 and z_3 by known methods and converting them to dimensionless x_1, x_2 and x_3, respectively, a regression equation was received:

$$y = 44.78 - 12.03 \cdot x_1 + 11.88 \cdot x_2 - 12.98 \cdot x_3 + 3.48 \cdot x_1 \cdot x_2 - 20.78 \cdot x_2 \cdot x_3 + 12.83 \cdot x_1 \cdot x_2 \cdot x_3$$

Qualitative analysis of the equation leads to the conclusion that viscosity of APP directly depends on concentration of glycerol and conversely on concentration of adipic acid as well as molar ratio DEG:PET.

Fig. 9 displays relationship between estimated (calculated by the above equation) and measured viscosity of APP. Experimental data fit to the model very well enabling to use the above equation for predicting dynamic viscosity of APP within the tested range of the variables.

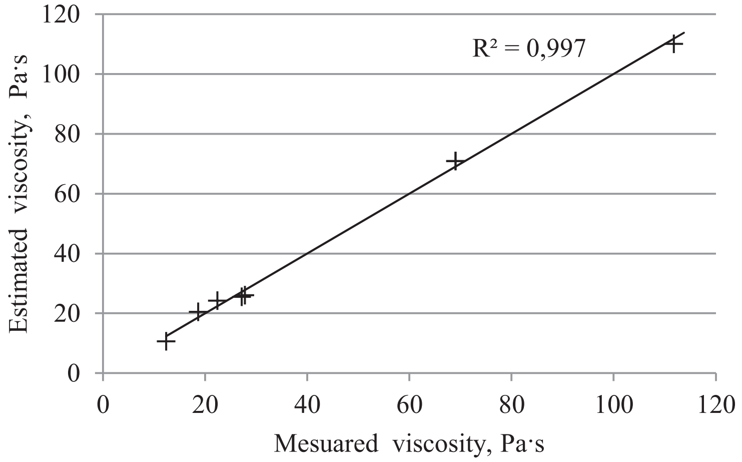

Fig. 9. Relationship between estimated and measured viscosity of APP

A series of APP with other functional additives 1,6-hexanediol (LHD), poly(propylene glycol) (LPPG), succinic acid (LSA), tartaric acid (LTA), terephthalic (LTPA) and isophthalic acid (LIPA) was synthesized and compared to those synthesized by using DEG (LDEG) and ADA (LADA). Polyol LTPA was received by polycondensation of terephthalic acid and DEG in the presence of functional additive ADA. Lower hydroxyl number of LPPG synthesized in the presence of oligomeric additive poly(propylene glycol) is associated with higher molecular weight of that polyol; similarly, high hydroxyl number of LTPA suggests low molecular weight of APP received by different way, i.e. by polycondensation of terephthalic acid resulting in transparent liquid. Viscosity of LTPA was much lower compared to that of other polyols and confirmed the above hypothesis of low molecular weight.

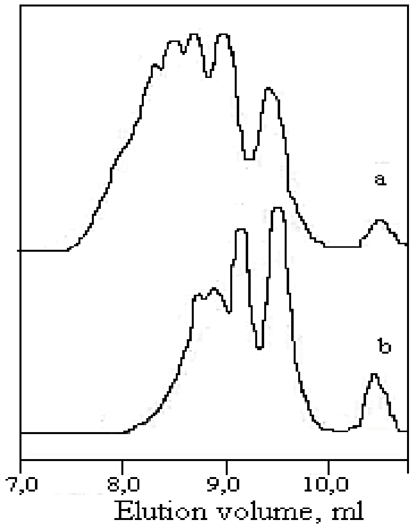

Fig. 10. SEC eluograms of APP: a – L-ADAGL, b – L-GL

Molecular weight (M_n) of APP synthesized by using functional additives GL (L-GL) and GL plus ADA (L-ADAGL) was measured by SEC (Fig. 10). It was determined that molecular weight distribution of the polyols was large, and the number average molecular weight M_n ranged from 107 to 1505 g/mol. According to SEC eluograms, polyols contained unreacted DEG in amount 3 to 8 % of the total weight.

Side product of transesterification reaction (distillate) were analysed by GC-MS. The distillate contained several products of thermal destruction of diethylene glycol and PET – acetaldehyde, dioxane, methyldioxolane, trioxocane and etc. It was determined that up to 10 % of the diol was lost during removal of water and EG from polycondensation and transesterification vessels. The loss of DEG during transesterification in the *mini*-reactor was lower compared to that in the flask.

3.4. Use of APP for the production of rigid PU-PIR foam

PU-PIR foams are produced under the reaction of a polyol with an excess of diisocyanate in the presence of fixed amounts of several additives (catalyst, blowing agent, stabilizer, flame retardant, surfactant). The amount of MDI was varied for each foam formulation and depended on polyol hydroxyl number; isocyanate index (II) was keept constant and equal to 250. The process of the foam formation was monitored measuring duration of its consecutive stages expressed as cream time (τ_0), gel time (τ_G) and tack-free time (τ_T). The main parameters characterizing PU-PIR foam formation process are listed in Table 4.

Gel time and tack-free time of the most formulations were apparently shorter (up to 1.5–2 times) than that of the Lup containing formulation, which served as a comparable commercial polyol. The gel time of the PU-PIR foam formulations based on polyols LP-1, LP-3 is less than 30 s. Low values of this parameter can be explained by hard segments or branched structure of the polyols. A correlation between foaming parameters and the parameters characterizing polyols (hydroxyl number, viscosity) is foreseen: gel time and tack-free time are lower when polyols with higher hydroxyl number and lower viscosity are used.

Table 4. Characteristics of PU-PIR foam formation process

Polyol	τ_0, s	τ_G, s	τ_T, s	T_{exp}, ºC	T_{theor}, ºC	$Y_{isocyanurate}$,%
Lup	14	38	57	147	159	93
LP-1	12	26	30	127	170	75
LP-2	14	34	44	147	180	82
LP-3	14	27	42	105	159	66
LP-4	15	35	52	145	174	83
LHD	7	30	54	128	157	82
LPPG	13	45	143	112	141	79
TPA-5	13	30	30	168	184	91

Fig. 11 shows exothermic profiles of PU-PIR foam formation from several formulations containing various APP. Formation of PU-PIR foams from the formulations containing Lup or LP with ADA fragments provides high exothermal effect (the temperature increases up to 150 °C), whereas formation of the foams from the polyols synthesized without functional additives or with glycerol only provides lower temperature which hardly reaches 100 °C. Relatively low exothermic effect of the formulation containing the polyol LP-3 can be explained by branched structure of that APP containing fragments of glycerol which makes part hydroxyl groups of the APP inaccessible.

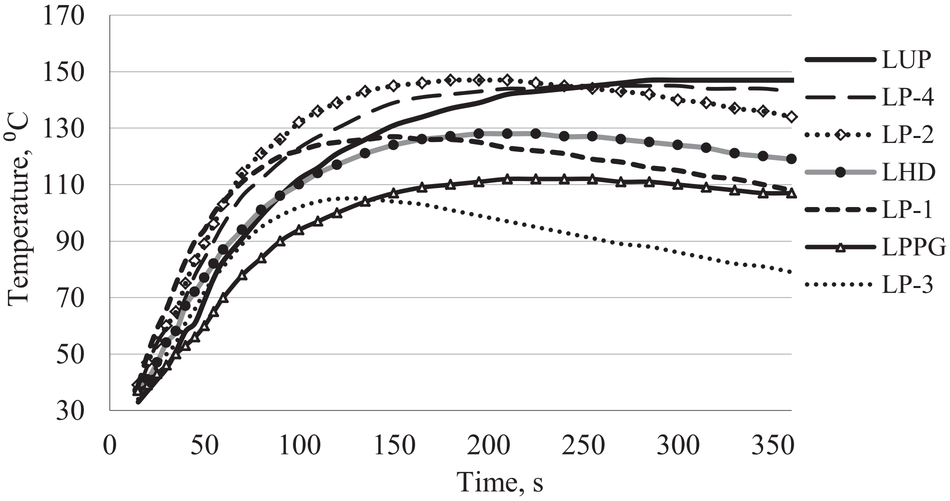

Fig. 11. Dependence of the foam core temperature on the reaction time during PU-PIR foam formation from APP

Structural fragments of PU-PIR foams prepared from the formulations containing polyols obtained by transesterification of PET waste by DEG in the presence of functional additives GL or/and ADA are presented in Fig. 12.

From the FT-IR data, apparent value of isocyanurate yield was estimated by comparing the ratio of intensity of the isocyanurate absorption band at 1412 ± 5 cm^{-1} to intensity of the aromatic absorption band at 1597 ± 5 cm^{-1} or to intensity of the absorption band of ether groups at 1016 ± 5 cm^{-1} present in polyols and diisocyanates.

The isocyanurate yield obtained from FT-IR data correlated well with the data determined by the temperature method. It is obvious that PU-PIR foams obtained from the formulations based on PET-waste-derived polyols containing fragments of ADA or both ADA and GL have high content of isocyanurate moieties.

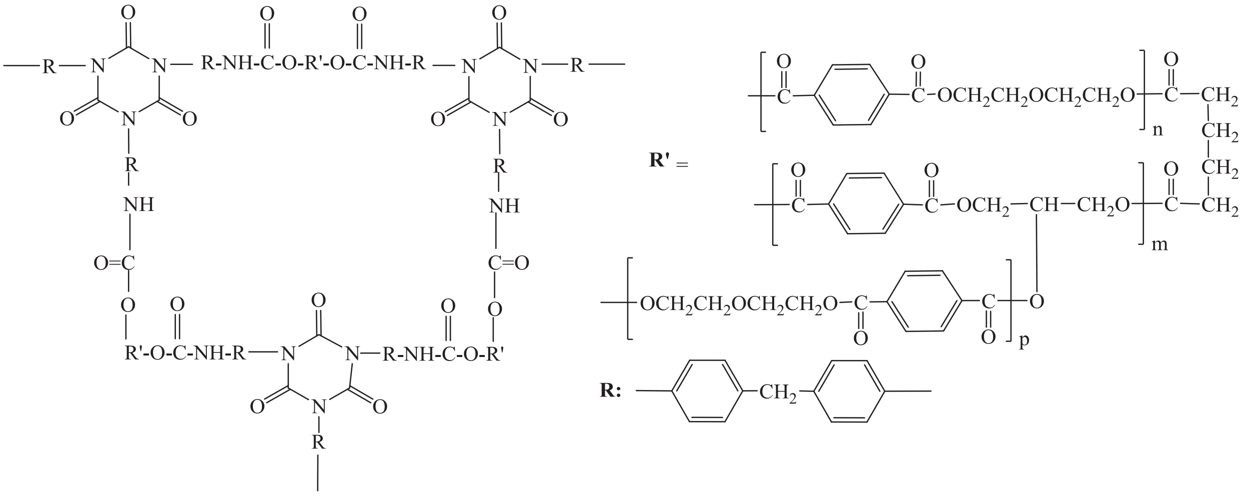

Fig. 12. Structural fragment of PU-PIR foams obtained from PET-waste-derived APP containing fragments of ADA and GL

Physical and tensile properties of the PU-PIR foams are presented in Table 5. PU-PIR foams prepared using PET-waste-derived APP are characterized by high closed cell content (more than 94 %). The presence of ADA fragments in the polyol structure (LP-2) increases core density and tensile strength, while the presence of GL fragments (LP-3) decreases core density and makes PU-PIR foam more elastic.

Table 5. Physical and tensile properties of PU-PIR foams based on PET-waste-derived APP

Polyol	Core density, kg/m^3	Closed cell content, %	Tensile strength, MPa	Tensile modulus, MPa	Elongation at brake, %
Lup	45	97	0.41	7.6	12.2
LP-1	52	96	0.38	8.3	6.7
LP-2	70	96	0.57	13.5	5.4
LP-3	41	94	0.34	5.7	12.2
LP-4	56	95	0.48	8.8	8.8
LHD	37	95	0.23	2.0	14.4
LPPG	87	81	-	-	-
TPA	54	96	0.43	8.4	7.3

The best compromise between satisfactory values of tensile stress and elongation at break was obtained using formulations based on APP containing fragments of both GL and ADA (LP-4). Complement of the APP structure by long alkyl chains (addition of hexanediol) enhances flexibility of the PU-PIR foam. The PU-PIR foams prepared by the use of APP synthesized by transesterification of PET waste with PPG is characterized by poor physical properties, namely, it has high shrinkage, low closed cells content and high core density. Worse physical properties can be a result of low isocyanurate content.

The compression strength is closely related to the dimensional stability of closed cell foams. Minimum compression strength of 0.1 MPa is generally recommended for closed cell foam. As can be seen from the data, PU-PIR foams prepared using PET-waste-derived APP containing fragments of functional additives are characterized by very good physical and mechanical properties. Compression strength increases with increasing isocyanurate yield since the polymer matrix becomes more crosslinked and therefore more resistant. Due to low functionality and the presence of flexible fragments of DEG, GL and ADA, PU-PIR foams are characterized by rather good elastic properties, and this is untypical for major PU-PIR foams.

The presence of aromatic rings in polyester polyols leads to an improvement of mechanical properties, such as tensile strength and compression strength (Tables 5 and 6) which makes such polyols promising for the production of PU sandwich panels.

Table 6. Compression properties of PU-PIR foams based on PET-waste-derived APP (25 °C)

Polyol	Parallel direction to foam rise			Perpendicular direction to foam rise		
	Compressive strength, MPa	Compressive modulus, MPa	↑ Δz, %	Compressive strength, MPa	Compressive modulus, MPa	↔ Δx, %
Lup	0.33	8.2	6.4	0.18	3.6	7.6
LP-1	0.49	11.0	7.0	0.23	4.2	8.2
LP-2	0.60	13.6	6.7	0.39	7.3	10.9
LP-3	0.36	8.7	6.7	0.19	3.6	7.9
LP-4	0.46	11.2	7.1	0.23	4.1	9.8
LHD	0.24	4.5	7.5	0.07	1.4	7.5
LPPG	0.10	1.3	10.9	0.15	2.2	11.0
TPA	0.42	9.3	7.1	0.25	4.2	9.7

An analysis of TGA and DTG curves enabled to determine several characteristics important for elucidation of thermal stability of PU-PIR foams: the temperature of the beginning of the weight loss, the temperature of the beginning of thermal degradation, the temperature of the highest rate of the weight loss, the weight loss during the most intense degradation, the weight residue at 610 °C, and others. It was determined that the obtained foams containing isocyanurate rings are much more thermostable and decompose at about 320–330 °C, with a char yield of around 30–50 %.

Beyond a doubt, thermal stability and char yield depend on polyol structure. The PU-PIR foams prepared from APP containing fragments of GL and/or ADA, had higher thermal stability and lower weight loss at 320–330 °C. Thermal stability of PU-PIR foams based on Lup and APP containing fragments of HD or PPG was lower than that of the foams based on the branched polyols containing fragments of both ADA and GL. The temperature characterizing the highest decomposition rate of the PU-PIR foams (the main peak of DTG curve) was shifted towards higher values (up to 330 °C) for the foams based on LP-4 and other branched polyols, which indicated enhanced thermal stability of these foams.

Reaction of foam to direct impingement of flame was tested by the burning test for building insulation products. Fig. 13 shows the results of this test. As a control, the sample without flame retardant (LPT) was used. According to the test, all foams based on PET-waste-derived APP and Lup provide satisfactory flame retardancy and pass the requirement for insulation foams, which allows maximal flame height of 15 cm and confirms class E according to EN 3501-1. On immediate exposure to the radiant heat, the foam shrinks and melts concomitantly to form a black carbonaceous (coke) residue that does not ignite even after extended period of exposure for almost 30 s.

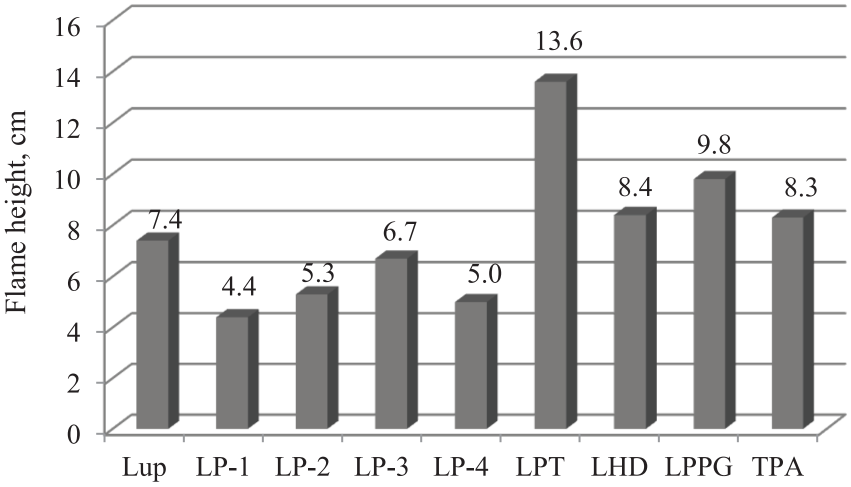

Fig. 13. Flammability of PU-PIR foams based on various polyols

The Cone calorimeter test provides ingnition time, total heat release, peak heat release rate and smoke generation, which were measured at various stages of a process. The values of ignition of the foam are given in the Table 7. It is evident that low ignition time is characteristic for the foam based on polyols containing fragments of GL, HD and PPG. The peak heat release rate for the foams prepared from LP series is about 60–74 kW/m^2, compared to 83 kW/m^2 for the foams obtained from Lup. The presence of aliphatic fragments of ADA in the structure of a polyol increases the peak heat release of foams up to 74 kW/m^2.The presence of the fragments of the both additives GL and ADA in the structure of APP used for production of PU-PIR foams marginally decrease the peak heat release rate and promote the smoke generation (Table 7). The PU-PIR foams based on PET-waste-derived APP exhibit lower total heat release and significantly lower smoke production (19 MJ/m^2 and < 1.0 m^2, respectively) than those based on Lupraphen (25 MJ/m^2 and 2.1 m^2, respectively).

Table 7. Results of Cone calorimeter test of the PU-PIR foams based on PET-waste-derived APP (the heat flux was 50 kW/m^2)

Polyols	Ignition time (s)	Peak heat release rate (kW/m^2)	Total heat release (MJ/m^2)	Total smoke production (m^2)
Lup	5	83	25	2.1
LP-1	10	64	19	0.5
LP-2	26	74	19	0.8
LP-3	4	63	18	1.0
LP-4	7	60	18	0.9
LHD	5	70	19	0.9
LPPG	5	135	45	6.3
LTPA	37	62	17	0.9

Thus PU-PIR foams based on PET-waste-derived APP provide good anti-flammability properties. Obviously, good flameproof properties are provided by high isocyanurate yield and high content of aromatic moieties in the structure of APP used for production of the PU-PIR foams.

CONCLUSIONS

1. Morphology, chemical composition and properties of industrial PET waste were examined in detail. Prepolymers and oligomers consist of a mixture of ethylene glycol, moisture and different acyclic and cyclic oligomers; this type of waste is recommended for glycolysation to monomeric structural units, e.g. BHET. The most suitable for chemical recycling (transesterification) are amorphous PET lumps and mixtures of dust and chips which can be converted to aromatic polyester polyols.
2. During glycolysis of PET oligomers, amorphous polymers lumps and mixtures of dust and chips by ethylene glycol, the yield of bis(2-hidroxyethylene) terephthalate higher than 85 % could be obtained. The optimal conditions for glycolysis of oligomeric PET waste are as follows: equal amounts (by weight) of PET and EG, cobalt acetate as a catalyst (0.25 % from PET weight) and temperature of the reaction 190 °C.
3. Carrying out transesterification of industrial PET waste by diethylene glycol (DEG) in the presence of functional additives glycerol (GL) or/and adipic acid (ADA), a series of aromatic polyester polyols (APP) differing by viscosity and other properties were synthesized. The fragments of adipic acid reduce dynamic viscosity of APP, whereas those of glycerol increase it. Statistical trifactorial experiment made for a panel of polyols revealed that an increase in molar ratio DEG:PET should result in APP with lower viscosity. The fragments of both adipic acid and glycerol moderate crystallization rate of APP and prolong their storage stability at room temperature.
4. Viscosity of APP slightly depended on the catalyst type and its concentration; however, the polyols obtained at higher concentration of a catalyst were less stable. The most stable product (storage time 174 days) was obtained using DBTL (15 ppm) as a catalyst.
5. A series of APP containing fragments of different functional additives – isophthalic, adipic, succinic or tartaric acid, glycerol, hexanediol or polypropylene glycol were synthesized and analyzed. The highest viscosity was characteristic for polyols containing fragments of multifunctional tartaric acid (71.5 Pa·s). APP synthesized in the presence of functional additives tartaric or adipic acid were more stable than

those obtained by the use of succinic or isophthalic acid. The polyol synthesized using hexanediol as an additive was unstable and became turbid during the first day.

6. During transesterification of industrial PET waste in a flask, the DEG loss is up to 10 % while in the *mini*-reactor the DEG loss is lower and amounts to 5–7 %. Under transesterification, a number of thermal destruction processes of PET and DEG take place during which acetaldehyde, dioxane, methyldioxolane and other undefined compounds are produced.
7. PU-PIR foams were produced under the reaction of APP synthesized by transesterification of industrial PET waste and an excess of diisocyanate. It was determined that the fragments of ADA present in the structure of APP increase the cream time, gel time and tack-free time of the foam. Longer cream time is characteristic for viscous polyols containing fragments of glycerol. The foams based on polyols containing fragments of ADA or ADA and GL, are characterized by high isocyanurate yield.
8. PU-PIR foams based on PET-waste-derived APP are characterized by excellent physical-mechanical properties. The foams have high closed cell content. The presence of the fragments of adipic acid in the structure of the foams increases flexibility of the chain which results in higher core density and tensile strength; the presence of the fragments of glycerol acts vice versa and decreases core density.
9. PU-PIR foams based on PET-waste-derived APP containing fragments of GL or/and ADA had high thermal stability and low weight loss at 330 °C. It was determined that the foams provided satisfactory flame retardancy which increased at higher isocyanurate yield. The peak heat release rate of the foams based on the PET-waste-derived APP was up to 74 kW/m^2 what was significantly lower compared to commercial APP. The presence of the fragments of functional additives GL and ADA in the structure of APP used for production of PU-PIR foams marginally decreased the heat release and slightly increased the smoke production. The burning test confirmed that PU-PIR foams satisfied the requirements for class E of construction products and building elements.

LIST OF ORIGINAL PUBLICATIONS

Papers in the journals form the ISI Master Journal list:

1. Vitkauskiene, I., Makuška, R. Glycolysis of industrial poly(ethylene terephthalate) waste directed to bis(hydroxyethylene) terephthalate and aromatic polyesters polyols. *Chemija*, 2008, V. 19 (2), p. 29-34.
2. Vitkauskiene, I., Makuška, R., Stirna, U., Cabulis, U. Synthesis and physical-mechanical properties of polyurethane-polyisocyanurate foams based on PET-waste-derived modified polyols. *Journal of Cellular Plastics*, 2011, V. 47, (accepted), doi: 10.1177/0021955X11409494.
3. Vitkauskiene, I., Makuška, R., Stirna, U., Cabulis, U. Thermal properties of polyurethane-polyisocyanurate foams based on poly(ethylene terephthalate) waste. *Materials Science* (*Medžiagotyra)*, 2011, V. 17 (accepted).

Proceedings of conferences:

1. Vitkauskiene, I., Makuška, R., Useful intermediates from industrial PET waste. *Proceedings of Baltic Polymer Symposium 2007*. Druskininkai, Lithuania, 2007, p. 253-257.
2. Vitkauskiene, I., Makuška, R., Behrendt, G. Synthesis of aromatic polyester polyols by transesterification of industrial PET waste. *Programme and Proceedings of Baltic Polymer Symposium 2009.* Ventspils, Latvia, 2009, p. 5.
3. Vitkauskienė, I., Paltarokaitė, L., Makuška, R. Transesterification of PET waste by a mixture of diethylene glycol, adipic acid and glycerol. *Polymer Chemistry and Technology: Proceedings of Scientific Conference on Chemistry and Chemical Technology.* Kaunas, Lithuania, 2009, p. 78-82.

Abstracts of International Conferences:

1. Vitkauskiene, I., Makuška, R., Useful intermediates from industrial PET waste. *Baltic Polymer Symposium 2007*: *Programme and Book of Abstracts.* Druskininkai, Lithuania, 2007, p. 139.
2. Boyadzhiev, M., Langenstraßen, R., Vitkauskiene, I., Herzog, M., Behrendt, G. Development of a new type of branched polyester polyols based on PET wastes for

rigid polyurethanes. *Baltic Polymer Symposium 2007*: *Programme and Book of Abstracts.* Druskininkai, Lithuania, 2007, p. 104.

3. Vitkauskiene, I., Blaškevičius, E., Makuška, R. Aromatic polyester polyols from industrial PET waste. *Chemija 2007. 8th National Lithuanian Chemist Conference. Book of Abstracts.* Vilnius, Lithuania, 2007, p.76.
4. Vitkauskienė, I., Aštrauskaitė, M., Makuška, R. Glycolysis of industrial PET waste towards bis(2-hydroxyethylene) terephtalate. *Chemija 2009. 9th National Lithuanian Chemist Conference. Book of Abstracts.* Vilnius, Lithuania, 2009, p. 118.
5. Vitkauskienė, I., Makuška, R., Stirna, U., Cabulis, U. Polyisocyanurate foams obtained from aromatic polyester polyols based on PET waste. *Baltic Polymer Symposium 2010*: *Programme and Book of Abstracts*. Palanga, Lithuania, 2010, p. 102.
6. Vitkauskienė, I., Makuška, R., Stirna, U., Cabulis, U. Polyurethane-polyisocyanurate foams based on PET-waste-derived polyols. *Green Chemistry and Nanotechnologies in Polymer Chemistry Workshop 2010, 23-24 September, 2010, SYNPO, Pardubice, Czech Republic.*
7. Vitkauskienė, I., Makuška, R., Stirna, U., Cabulis, U. Thermal and physical-mechanical properties of PU-PIR foam based on poly(ethylene terephthalate) waste. *Green Chemistry and Nanotechnologies in Polymer Chemistry Workshop 2011, 5-6 May, 2011, Latvian state institute of wood chemistry, Riga, Latvia.*

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"*When you want something, the entire universe conspires in helping you to achieve it*"

"The Alchemist" by Paulo Coelho

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POLIETILENTEREFTALATO GAMYBINIŲ ATLIEKŲ CHEMINIS PERDIRBIMAS: AROMATINIŲ POLIESTERPOLIOLIŲ SINTEZĖ, SAVYBĖS IR PANAUDOJIMAS

Santrauka

Visame pasaulyje, taip pat ir Lietuvoje, sparčiai auga polietilentereftalato (PET) poreikis. PET tara užima vis didesnę maisto, gėrimų, farmacijos, kosmetikos ir buitinės chemijos pakuočių rinkos dalį, be to, PET žaliava plačiai naudojama tekstilės, popieriaus pramonėje ir net padangų gamyboje. Didėjant PET gamybai ir jo vartojimui, atsiranda šio polimero atliekų perdirbimo problema. Be buitinių PET atliekų nemažai šio polimero atliekų susidaro PET granulių ir pakuotės gamybos įmonėse.

Pastaruoju metu labai daug dėmesio skiriama cheminiam PET perdirbimui. Svarbiausias cheminio PET perdirbimo produktas – aromatiniai poliesterpolioliai (APP). Tai vienas pagrindinių komponentų gaminant kietus, uždarų porų poliuretano (PU) ar poliizocianurato (PIR) termoizoliacinius putplasčius, kurių panaudojimas pastatų, talpų ir kitų konstrukcijų apšiltinimui sparčiai auga.

Pagrindinis šio darbo tikslas buvo peresterinant gamybines PET atliekas dietilenglikoliu, esant glicerolio, adipo rūgšties ar kitų funkcinių priedų, susintetinti aromatinius poliesterpoliolius, tinkamus poliuretano-poliizocianuratinių putplasčių gavimui.

Svarbiausi šio darbo rezultatai, atspindintys jo naujumą, originalumą ir svarbą:

Pasiūlyti skirtingi cheminio perdirbimo būdai ir sąlygos kiekvienai gamybinių PET atliekų rūšiai. Nuodugniai ištirtos gamybinių PET atliekų susidarymo vietos, priežastys bei jų savybės. PET oligomerai ir prepolimerai yra įvairių aciklinių ir ciklinių oligomerų mišinys, kuriame daug etilenglikolio ir vandens; šios PET atliekos gali būti panaudotos glikolizei iki monomerinių struktūrų. Tinkamiausios gamybinės PET atliekos cheminiam perdirbimui (peresterinimui) iki aromatinių poliesterpoliolių – amorfinio polimero luitai ir PET dulkių bei granulių mišiniai. Vykdant gamybinių PET atliekų glikolizę etilenglikoliu, pasiekta didesnė negu 85 % bis(2-hidroksietilen)tereftalato išeiga. Rastos optimalios oligomerinių PET atliekų glikolizės sąlygos.

Vykdant gamybinių PET atliekų peresterinimą dietilenglikoliu (DEG) ir naudojant funkcinius priedus glicerolį (GL) ir/arba adipo rūgštį (ADR), susintetinta serija

aromatinių poliesterpoliolių, besiskiriančių savo klampa ir kitomis savybėmis. Pirmą kartą nuodugniai ištirta ir matematiškai aprašyta peresterinimo reakcijos mišinyje esančių funkcinių priedų įtaka APP savybėms. Kaip paaiškėjo atlikus trifaktorinį aktyvųjį eksperimentą, mažesnė poliolio dinaminė klampa gaunama esant didesniam DEG:PET moliniam santykiui. Nustatyta, kad tiek adipo rūgšties, tiek glicerolio fragmentai sulėtina APP kristalizacijos greitį ir prailgina jų stabilumą saugant kambario temperatūroje. APP klampa mažai priklauso nuo metaloorganinio katalizatoriaus cheminės sudėties ir jo koncentracijos, tačiau polioliai, gauti esant didesnėms katalizatoriaus koncentracijoms, yra mažiau stabilūs.

Susintetinta ir ištirta serija aromatinių poliesterpoliolių, turinčių įvairių funkcinių priedų – izoftalio, adipo, gintaro arba vyno rūgščių, glicerolio, heksandiolio arba polipropilenglikolio – fragmentų. Nustatyta, kad vykdant gamybinių PET atliekų peresterinimo reakciją kolboje, dietilenglikolio nuostoliai siekia iki 10 %, tuo tarpu peresterinimą vykdant *mini*-reaktoriuje DEG nuostoliai yra mažesni. Peresterinimo metu vyksta nemažai PET terminės destrukcijos procesų, kurių metu susidaro acetaldehidas, dioksanas, metildioksolanas ir kitos neidentifikuotos medžiagos.

Naudojant PET peresterinimo metu gautus APP ir diizocianato perteklių, susintetinti poliuretano-poliizocianurato (PU-PIR) putplasčiai. Ištirta APP, kuriuose yra glicerolio, adipo rūgšties ir kitų priedų fragmentų, cheminės sudėties ir struktūros įtaka sintetinamų poliuretano-poliizocianuratinių putplasčių fizikinėms-mechaninėms, terminėms ir degumo savybėms. Poliuretano-poliizocianuratiniai putplasčiai, gauti naudojant APP, kuriuose yra glicerolio ir/arba adipo rūgšties fragmentų, pasižymi geromis fizikinėmis-mechaninėmis savybėmis ir dideliu terminiu stabilumu, jiems degant išsiskiria mažesnis šilumos ir dūmų kiekis.