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Thermal Properties of Polyurethane-Polyisocyanurate Foams Based on Poly(ethylene terephthalate) Waste

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A series of polyurethane-polyisocyanurate (PU-PIR) foams synthesized from PET-waste-derived aromatic polyester polyols (APP) was studied using thermogravimetric analysis, Cone calorimeter and burning tests. The effect of chemical structure of the APP containing fragments of glycerol, adipic acid, poly(propylene glycol) or hexanediol on thermal stability and flame resistance of the PU-PIR foams was elucidated. PU-PIR foams prepared from APP containing fragments of glycerol and/or adipic acid had higher thermal stability and lower weight loss at 330 °C. The foams based on APP derived from industrial PET waste were characterized by relatively low heat release and low smoke production. The presence of the fragments of the functional additives glycerol and/or adipic acid in the structure of APP used for production of PU-PIR foams, marginally decreased the heat release and slightly increased the smoke production.

Keywords: polyurethane, polyisocyanurate, thermal properties, flame resistance, aromatic polyester polyol, PET.

1. INTRODUCTION

Recently, the consumption of poly(ethylene terephthalate) (PET) has tremendously increased resulting in greater quantities of postconsumed and industrial PET waste. The problem of PET utilization is presently being solved mainly by physical (bottle to bottle process) and chemical (receiving raw materials or polyols) recycling. One important trend of chemical recycling of PET waste is production of aromatic polyester polyols (APP), which may be used for formation of an insulation material – rigid polyurethane foams.

Rigid polyurethane (PU) foam, based on petrochemical raw materials, is not applied in construction industry on a large scale due to its high price; its price is higher than that of foamed polystyrene or mineral wool. If the cost of the rigid PU foam production is reduced, it will be competitive to other materials commonly used for insulating, e. g., foamed polystyrene, mineral wool and others [1]. Thermal conductivity of polyurethane foam varies from 0.018 W/(mK) up to 0.028 W/(mK), i. e. it is about two times lower than that of polystyrene, an alternative material for insulation. Moreover, fire resistance and physical-mechanical properties of polyurethane foam are superior to those of polystyrene [2].

Reduction in price of rigid polyurethane foam becomes possible, among others, by the use of PET-waste-derived APP as raw materials. Thermal stability of the foam depends on the polyol structure, and aromatic polyols are superior over aliphatic polyols from this point of view. Major commercial APP based on terephthalic acid or phthalic anhydride have high content of aromatic fragments, around 20 %. The presence of aromatic fragments in the structure of polyols enhances many properties of polyurethane foam enabling to achieve good mechanical characteristics, high thermal stability, resistance to major chemical solvents, and low flammability [3 – 6]. It is well known that a considerable improvement of thermal stability and fire resistance behavior of polyurethane foams may be achieved through the introduction of isocyanurate structures into polyurethane matrix, as these are more stable than urethane bonds [7].

The modified polyurethane-polyisocyanurate (PU-PIR) foam has been widely used as an insulation material in construction, transportation and industrial applications, e. g., for insulation of floor panels, roofing materials, cavity walls, refrigerators and freezers. Recently, the demand of PU-PIR foam has been increased markedly because of its high flame resistance, effectiveness of insulation and structural properties [6 – 11]. Flammability of polyurethane foams is successfully reduced by halogenated flame retardants or phosphorus containing polyols used as reactive hydroxyl-containing compounds. However, during combustion of polyurethane foams containing flame retardants, besides usual smoke and environmentally unfriendly toxic gases like carbon dioxide, carbon monoxide, nitrogen oxides, ammonia, benzene, toluene, acetaldehyde, alkenes and trace hydrogen cyanide, halide compounds like hydrogen fluoride, hydrogen chloride, hydrogen bromide and phosgene are produced. The use of flame retardants can be reduced by employing aromatic polyols as raw materials for production of PU-PIR foams, since polyisocyanurate fragments improve flame resistance. Thermal stability of isocyanurate linkages is inherently higher than that of urethane linkages – the latter dissociate at approx. 200 °C compared to 350 °C, characteristic for polyisocyanurates. However, being preferable because of higher flame resistance, polyisocyanurate foams suffer from excessive friability limiting their practical utility. Combining urethane and isocyanurate linkages in the foam composition addresses the above problems simultaneously – the urethane component provides the desired physical characteristics while the isocyanurate moieties improve flame retardancy [9].

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The present paper describes thermal properties of PU-PIR foam based on APP synthesized by transesterification of industrial PET waste with diethylene glycol in the presence of glycerol, adipic acid, poly(propylene glycol) or hexanediol as functional additives. Thermal and fire resistance properties of PU-PIR foam prepared from PET-waste-derived APP of various chemical structure and from commercial APP Lupraphen 8007 based on terephthalic acid were evaluated and compared that enabled to demonstrate valuable properties of the materials made from PET waste.

2. MATERIALS AND METHODOLOGY

2.1. Materials

Diethylene glycol (DEG), glycerol (Gl), adipic acid (ADA), poly(propylene glycol) (PPG) (M_n 425), 1,6-hexanediol (HD), terephthalic acid (TPA) and potassium acetate were purchased from SIGMA-ALDRICH and used without further purification. Industrial PET waste (dust) (T_m – 246.3 °C, intrinsic viscosity (IV) – 0.78 dl/g) was obtained from bottle grade PET plant of Neo Group (Lithuania). Diphenylmethane diisocyanate (MDI), containing oligomers of high functionality, was supplied by BASF AG as Lupranat M20R, amount of isocyanate groups 31.5 %, average functionality 2.7. Aromatic polyester polyol Lupraphen 8007 (Lup) was from ELASTOGRAN, dynamic viscosity 12 Pa·s, hydroxyl number 240 mg KOH/g, functionality 2.0.

The catalyst employed for cyclotrimerization of isocyanate was 30 % solution of potassium acetate in diethylene glycol. The catalyst employed for polyurethane production was 1,1,4,7,7-pentamethyldiethylenetriamine supplied as Polycat 5 by AIR PRODUCTS. The blowing agent was a blend of 1,1,1,3,3-pentafluorobutane and 1,1,1,2,3,3,3-heptafluoropropane and was supplied as Solkane 365mfc/227ea by SOLVAY FLUOR GmbH. Flame retardant *tris*-β-chloropropyl phosphate (TCPP) was produced by ALBEMARLE, and silicone surfactant Niax silicone L-6915 was produced by MOMENTIVE PERFORMANCE MATERIALS.

2.2. Methods

2.2.1. Preparation of polyurethane-polyisocyanurate foam

Aromatic polyester polyols were synthesized by transesterification of industrial PET waste by DEG without additives or in the presence of functional additives glycerol, adipic acid, poly(propylene glycol) or hexanediol according to the procedure reported earlier [12 – 13]. Functional additives used for the synthesis of APP are listed in Table 1. The obtained APP were characterized by relatively low functionality (slightly above 2), low acid number (from 0.63 mg KOH/g to 1.95 mg KOH/g), moderate hydroxyl number (from 171 mg KOH/g to 472 mg KOH/g), and varying viscosity (from 0.8 Pa·s to 51.6 Pa·s) [13].

Preparation of polyurethane-polyisocyanurate foam was carried out by hand mixing method. An APP, MDI and other components of the formulation were vigorously mixed for 5 s at room temperature, and a viscous mass was immediately poured into an open box mould with sizes (200×200×100) mm. Formulations for the production of PU-PIR foams contained fixed amounts of the components: 100 g APP, 2.0 g silicone surfactant Niax silicone L-6915, 2.0 g 30 % potassium acetate solution in diethylene glycol, 0.8 g Polycat 5, 25.0 g flame retardant TCPP and 25.0 g blowing agent Solkane 365mfc/227ea. The amount of MDI was varying to keep the isocyanurate index (II) equal to 250 (the isocyanate index indicates molar ratio of isocyanate groups to hydroxyl groups multiplied by 100). Characteristics of the foam formation process and physical-mechanical properties of PU-PIR foams are described in our previous publication [13].

Table 1. Functional additives used for the synthesis of APPs

APP	DEG:PET, mol / mol	ADA, %	Gl, %	Other, %
LP-1	1.8	–	–	–
LP-2	1.8	1	–	–
LP-3	1.8	–	1	–
LP-4	1.8	1	1	–
LPT	1.9	11	2.5	–
LHD	1.3	16	1	18 (HD)
LPPG	1.3	4.1	1	33 (PPG)
LTPA	2.6*	5	–	–

*molar ratio DEG : TPA.

2.2.2. Thermogravimetric analysis

Thermal stability of PU-PIR foam was studied using Mettler Toledo TGA/SDTA 851^e instrument. About 10 mg of granulated PU-PIR foam was used to obtain the TGA and DTG profiles. The heating rate was set to 10 °C/min under flow of 20 ml/min nitrogen, and the temperature range was from 30 °C to 1000 °C. The results were obtained as weight loss versus temperature.

2.2.3. Flammability measurements

Flammability of the prepared foam samples was measured by burning test [14] and Cone calorimetry [15] (Fire Testing Technology). For the burning test, (160×60×30) mm samples were cut from the block foam. The sample was hung vertically in burning chamber, and the burner was positioned at a distance of 16 mm from the foam. The sample burned for 30 s. At the end of the test, the length of the damaged part of the sample (in cm) was measured. For Cone calorimeter test, (100×100×35) mm samples were cut. The radiant heat flux was set at 50 kW/m^2, and the measuring time was set at 600 seconds. Peak heat release rate, smoke release rate, total heat release and total smoke release were measured.

3. RESULTS AND DISCUSSIONS

3.1. Thermal stability

A series of PU-PIR foams formulated from APP derived by transesterification of industrial PET waste in the presence of various additives was prepared [13]. PU foams contained isocyanurate rings formed as a result of cyclotrimerization of isocyanate groups (Fig. 1), which are common for polyurethane formulations containing high

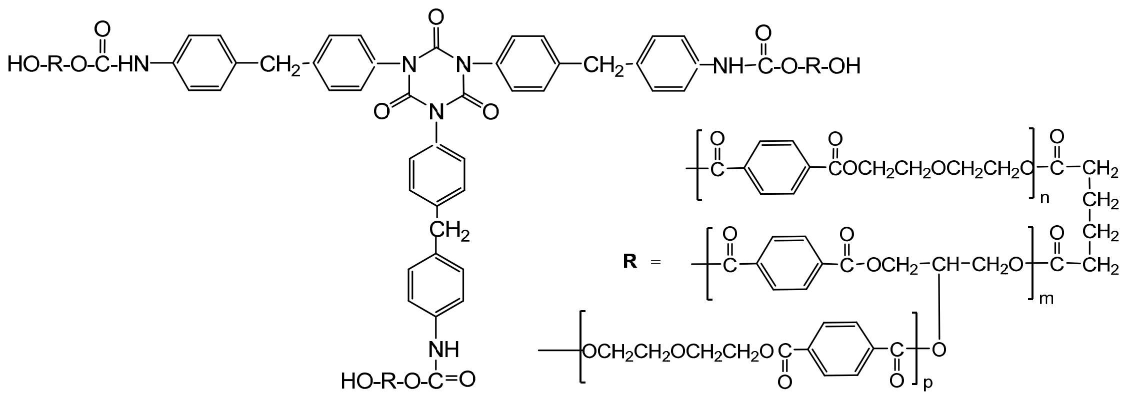

Fig. 1. Structural formula of PU-PIR foams obtained from PET-waste-derived APP containing fragments of glycerol and adipic acid. Subscripts m, n and p are whole number (1, 2, 3, …) and denote degree of polymerization of the structural units

isocyanate index [16].

PU-PIR foams prepared using PET-waste-derived APP were characterized by high closed cell content (more than 94 %) and apparent density varying from 37 kg/m^3 to 87 kg/m^3.

Typical TGA and DTG curves of PU-PIR foam prepared using PET-waste-derived APP are presented in Fig. 2. 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.

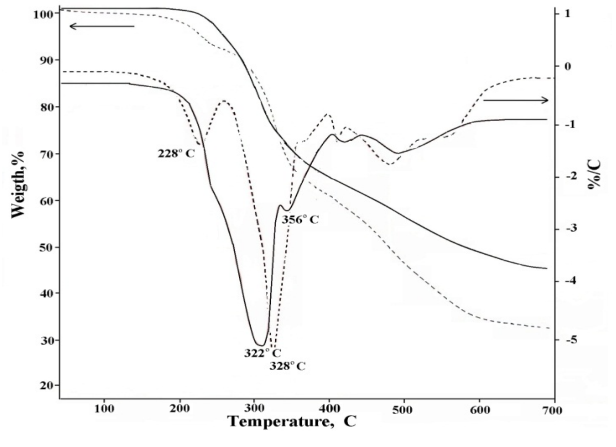

Fig. 2. TGA/DTG curves of PU-PIR foam prepared using APP LP-4 (-----) and LPT (—); no flame retardant was added to the formulation of LPT

The formulation of LPT was without flame retardant, while the formulation of LP-4 contained TCPP (Fig. 2). The difference between TGA profiles of these two foams is the absence of weight loss at 190 °C – 240 °C for the PU-PIR foam prepared from LPT. Apparently, the first step of the weight loss (about 8 % – 10 % of the weight) during thermogravimetric analysis of the PU-PIR foams is related to evaporation of the flame retardant TCPP, whose flash point is at 218 °C and the decomposition temperature at 244 °C [10, 19, 20]. During the most intense degradation step with the DTG peak maximum at 320 °C – 340 °C, the weight loss was in the range from 27 % to 46 %. The weight residues at 610 °C for PU-PIR foams from different polyols varied between 30 % and 51 % (Table 2); the largest weight residue was characteristic for the foam prepared from the branched polyol LPT. Usually, polyurethane structure decomposes at around 200 °C giving a char yield about 20 % [4]. The obtained foams containing isocyanurate rings are much more thermostable and decompose at about 320 °C, with a char yield of around 30 % – 50 %. Dominguez-Rosado et. all [9] reported similar thermal profiles of polyisocyanurate foams based on APP with similar weight residue at around 44 %.

Thermal resistance of a compound is related to the breakdown of the weakest bonds at a certain temperature. This phenomenon involves degradation of a polymer that is manifested by reduction of molecular weight. Thermal resistance of the PU-PIR foams is related to the temperature of the thermal dissociation of the bonds present in the rigid structure of the foams. Urethane bonds formed under the reaction of aromatic diisocyanates with polyols are characterized by the temperature of thermal dissociation of about 200 °C [1]. The temperature of thermal dissociation of ether and ester bonds is about 350 °C and 260 °C, respectively. It is known that the major rigid polyurethane foams based on polyester polyols are characterized by three-step TGA curves: the first one at 120 °C – 140 °C is assigned to the moisture absorbed by the foam and evaporation of a foaming agent and low molecular weight compounds; the second one at 270 °C – 280 °C is due to thermolysis processes disrupting the weakest bonds; at the third stage occurring at 300 °C – 350 °C, destruction of isocyanurate and diphenylmethane structures of the foam takes place [14, 21]. The weight loss at 270 °C – 280 °C is absent during degradation of PU-PIR foams prepared from PET-waste-derived APP which can be explained by high isocyanurate yield.

Beyond a doubt, thermal stability and char yield depend on polyol structure. The PU-PIR foams prepared from APP containing fragments of glycerol and/or adipic acid, had higher thermal stability and lower weight loss at 330 °C (Table 2). Thermal stability of PU-PIR foams based on Lup and APP containing fragments of hexandiol or poly(propylene glycol) was lower than that of the foams based on the branched polyols containing fragments of both adipic acid and glycerol (LP-4, LPT).

The temperature characterizing the highest decomposition rate of the PU-PIR foams (the main peak of

Table 2. Thermal stability of PU-PIR foams based on PET-waste-derived APP

APP	1 step		2 step		Weight residue at 610 °C, %
	T, °C at DTG$_{min}$ (temp. interval, °C)	Weight loss, Δ*m*, %	*T*, °C at DTG$_{min}$ (temp. interval, °C)	Weight loss, Δ*m*, %	
Lup	193 (110 – 246)	10	320 (244 – 420)	46	30
LP-1	219 (140 – 252	8	324 (251 – 412)	32	47
LP-2	236 (192 – 266)	8	332 (265 – 382)	28	35
LP-3	201 (106 – 245)	9	322 (243 – 431)	34	45
LP-4	228 (159 – 260)	8	328 (258 – 362)	27	35
LPT	–	–	322 (208 – 347); 356	35	51
LHD	195 (142 – 243)	9	331 (242 – 446)	37	32
LPPG	195 (121 – 238)	11	336 (237 – 418)	44	28
LTPA	229 (151 – 261)	8	330 (260 – 386)	33	47

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.

3.2. Heat release and smoke production

Reaction of foam to direct impingement of flame was tested by the burning test for building insulation products. Fig. 3 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.

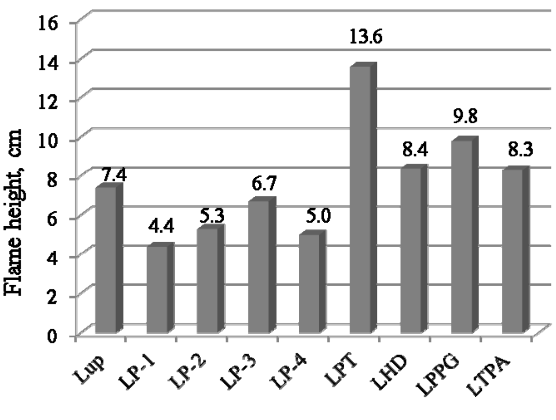

Fig. 3. Flamability of PU-PIR foams based on various polyols

The Cone calorimeter test provides ingnition time, total heat release, peak heat release rate and smoke generation, which can be measured at various stages of a process. The values of ignition of the foam are given in the Table 3. It is evident that low ignition time is characteristic for the foam based on polyols containing fragments of glycerol, hexanediol and poly(propylene glycol). Longer ingnition time is related to better foam flame retandacy since in a fire accident the escape-time plays an important role in the survival of people [15].

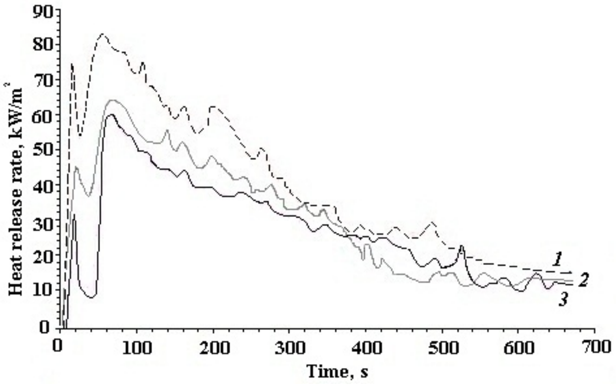

Fig. 4. Heat release rate curves of the PU-PIR foams based on polyols: 1 – Lup; 2 – LP-1; 3 – LP-4

Decomposition of the PU-PIR foam appears to occur in two steps (Fig. 4). The initial peak in heat release rate curves may be attributed to the surface pyrolysis of the foam and the plug associated with the char formation. Subsequent peak is associated with the burning of the surface caused by cracking of the initially formed char that was visually observed, and an increase in the bulk temperature of the foam. The two-step decomposition is explained [15] by a shrinkage and melting of the foam exposed to the heat giving a carbonaceous material and a tar, which burns on subsequent heating leading to higher amount of the heat production.

The peak heat release rate for the foams prepared from LP series is about 60 kW/m^2 – 73 kW/m^2, compared to 83 kW/m^2 for the foams obtained from Lup. The presence of aliphatic fragments of adipic acid 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 glycerol and adipic acid 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 3). 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).

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.

Table 3. Results of Cone calorimeter test of the PU-PIR foams based on PET-waste-derived APP. The heat flux was 50 kW/m^2

APP	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

4. CONCLUSIONS

PU-PIR foams based on PET-waste-derived aromatic polyester polyols (APP) are thermally stable materials giving large weight residues (28 % to 47 %) at 610 °C. PU-PIR foams prepared from APP containing fragments of glycerol and/or adipic acid had higher thermal stability and lower weight loss at 330 °C. Thermal stability of PU-PIR foams based on Lupraphen and APP containing fragments of hexanediol or poly(propylene glycol) was lower.

PU-PIR foams based on APP derived from industrial PET waste are characterized by relatively low heat release and low smoke production, <19 MJ/m^2 and <1.0 m^2, respectively. The presence of the fragments of the functional additives glycerol and/or adipic acid in the structure of APP used for production of PU-PIR foams, marginally decrease the heat release and slightly increase the smoke production.

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