

Influence of terephthalic and orthophthalic units on the properties of polyols and polyurethane foams

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Abstract: The effect of aromatic ring substitution in the polyester polyol molecule on its physicochemical properties and on the conditions of synthesis, fire resistance and thermal stability of polyurethane foams was investigated. The greater number of terephthalic units in the polyol results in greater viscosity and reactivity during foam formation. The obtained foams were characterized by higher thermal stability (TGA) and fire resistance (oxygen index, single flame test).

Keywords: aromatic polyester polyol, fire resistance, thermal stability.

Wpływ jednostek tereftalowych i ortoftalowych na właściwości polioli i pianek poliuretanowych

Streszczenie: Zbadano wpływ podstawienia pierścienia aromatycznego w cząsteczce polioli poliesterowego na jego właściwości fizykochemiczne oraz na warunki syntezy, odporność na działanie ognia i stabilność termiczną pianek poliuretanowych. Większa liczba jednostek tereftalowych w polioli skutkuje większą lepkością i reaktywnością podczas tworzenia pianek. Otrzymane pianki charakteryzowały się większą stabilnością termiczną (TGA) i odpornością na działanie ognia (indeks tlenowy, test pojedynczego płomienia).

Słowa kluczowe: aromatyczny polioli poliesterowy, ognioodporność, stabilność termiczna.

Rigid polyurethane foams are a material with a very broad range of applications. They account for 23% of the total production of polyurethane materials [1]. They are mainly used as one of the most effective insulating materials available, to produce sandwich panels with rigid and soft shelling, for insulating tanks and pipelines, for filling spaces in building structures, as insulating material in window and door frame profiles [2–5]. Despite low density, rigid polyurethane foams are characterized by good mechanical strength, good resistance to water and aging [6–8]. The main disadvantage of rigid polyurethane foams, which limits their use, is their flammability with a low oxygen index of approx. 19%, rapid flame spread, rapid heat release and high smoke emission, which has recently become a special research focus [9–12].

The thermal degradation of polyurethane foam does not essentially differ from the degradation of the non-foamed form, with the only exception that the structure of the foam enhances its insulating properties, which means that the material in this form undergoes thermal degradation slower than in the non-foamed form [13]. However, due to low thermal inertia, the foam will ignite within a few seconds when exposed to an external heat

flux [14]. With the rapid heating of the cell walls, the heat radiation-absorbing layer transforms into liquid pyrolysis products, which leads to a fast development of the combustion process [15].

When heated in an inert atmosphere, polyurethanes display a progressive disintegration of bonds. Biuret and allophanate bonds decompose at temperatures between 100 and 125°C. Urethane bonds formed because of the reaction of aromatic diisocyanates with polyols and bonds in urea structures decompose at temperature from 180 to 250°C. Isocyanurate and carbodiimide groups, on the other hand, have a decomposition temperature above 270°C [16]. The thermal degradation of foams can be mitigated by increasing the polyol and isocyanate functionality, which results in higher cross-linking density and charring ability [17]. However, the most significant effect is obtained by increasing the content of isocyanurate groups formed because of cyclotrimerization of isocyanate groups; for more than 30 years, this has been used as the industrial method for making flame retardant polyisocyanurate foams (PIR) [18].

Similarly, when exposed to fire, foams containing carbodiimide groups generate less smoke than conventional polyurethane foams [19]. Compared to polyurethane foams based on aliphatic polyester polyols, foams based on aromatic polyester polyols display a greater thermal

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stability and char formation during thermal degradation, along with lower smoke emissions [11, 20].

Smoke formation begins in the process of thermal degradation in the condensed phase, followed by the char layer phase, to produce smoke particles in the gaseous phase [21]. The resulting smoke contains not only non-toxic products such as carbon dioxide and nitrogen, but also some highly toxic compounds such as carbon monoxide (CO), hydrogen cyanide (HCN), NH₃ and NO_x [22]. In addition, toxic isocyanate is released because of the depolymerization reaction [23]. The toxicity of the resulting combustion products is assessed using the fractional effective dose model (FED). The PN-EN 60695-7-1 standard [24] defines FED as the ratio of the exposure dose of an asphyxiating toxic agent to one at which a specific effect of an exposed subject of average sensitivity can be expected. Compared to other insulation materials (glass wool, rock wool, styrofoam, and phenolic foam), polyurethane foams have higher FED values in both well-ventilated and under-ventilated fire conditions [25].

It is generally known that rigid polyurethane foams undergo charring during combustion. The resulting char, depending on its thickness and tightness, leads to a reduction in the amount of heat released during the combustion of the material and has an influence on the size and type of emissions. Char formation protects the inner layers of the material from the access of flame and temperature, which slows down the process of thermal degradation. At the same time, char reduces the emission of thermal degradation products outside the material, thus reducing the amount of fuel necessary to develop and sustain the fire. However, the thickness of char formed when burning unmodified rigid polyurethane foams is small [26].

Aromatic polyester polyols are mainly used to produce polyurethane and polyisocyanurate foams for the construction industry. Commercial aromatic polyester polyols are obtained by synthesis of glycols, mainly diethylene or ethylene glycols, low molecular weight polyglycols with acid anhydrides, acids, or esters and oligoesters, mainly phthalic anhydride, adipic acid, isophthalic acid, terephthalic acid, or dimethyl terephthalate, as well as recycled poly(ethylene terephthalate) (rPET) [27]. Flame retardancy is one of the main requirements for building foams. Aromatic polyester polyol alone in combination with aromatic isocyanate, despite its enhanced thermal resistance [11], usually does not provide the desired fire resistance properties for the final material but makes it possible to achieve these with a lower consumption of flame-retardant additives than aliphatic polyols.

The main sources of aromatic rings in polyols are terephthalic acid (or dimethyl terephthalate) and phthalic anhydride. Isophthalic acid is rarely used for cost effectiveness reasons. The synthesized polyols are virtually identical (when terephthalic acid or dimethyl terephthalate is used). They have different properties when using acid isomers (phthalic anhydride or isophthalic

or terephthalic acid) for the synthesis. Due to the differences in their structure, their use in the synthesis produces mainly differences in the type and amount of condensation by-product, i.e., methanol when dimethyl terephthalate is used, and water when phthalic anhydride and terephthalic acid are used. The synthesis using terephthalic acid will yield twice as much condensation water than when phthalic anhydride is used. Therefore, phthalic anhydride is the most cost-attractive aromatic unit out of the above range, even if it is typically approx. 20% more expensive than terephthalic acid [28]. The use of rPET to produce aromatic polyester polyols, apart from cost benefits, is an important area in the chemical recycling of PET waste [29, 30].

The method of substitution of the aromatic ring in the polyol molecule is essential both for its properties and for the resulting properties of the foam. The underlying causes of these differences have not been covered in studies but the role of the substitution method of the aromatic ring in determining the structure/property relationship has been emphasized [31]. It is known that the aromatic polyester polyol obtained with phthalic anhydride requires free space due to the side-chain benzyl residue, while allowing van der Waals intramolecular interactions between the ether moieties [32].

This paper sets out to present the influence of aromatic units derived from phthalic anhydride and terephthalic acid (as sourced from rPET) on the physicochemical properties of the polyol, foam formation properties, and especially on the thermal stability of foams obtained on their basis.

EXPERIMENTAL PART

Materials

The following materials were used for the synthesis of polyester polyol: PET from colourless, washed rPET flakes from post-consumer PET bottles (Lerg-PET, Poland), ethylene glycol (PKN Orlen S.A., Poland), diethylene glycol (Brenntag Polska Sp. z o. o., Poland), polyalkylene glycol (polyglycol PR 600, Clariant, Germany) with an average molecular weight of 600 g/mol, phthalic anhydride (Chem Distribution B.V., the Netherlands) and butylene oxide (Fascat 4100, PMC Organometallic, USA) as a catalyst.

To obtain polyurethane foams synthesised polyester polyols and diphenylmethane diisocyanate (Suprasec[®] 5025, Huntsman, Germany) with the functionality of 2.7 and NCO groups content of 31 wt% were used. In addition, silicone L-6620 (Momentive, Germany) was used as a surfactant, an 85% aqueous formic acid solution (Brenntag Polska) used as a blowing agent. Potassium 2-ethylhexanoate dissolved in diethylene glycol (15% Potassium Hex-Chem, Borchers, Germany) and *N,N,N',N'',N'''*-pentamethyl diethylenetriamine (PMDETA, Niax Catalyst C-5, Momentive, Germany) were used as a catalytic system.

Table 1. Formulas of the synthesized polyols

Polyol	Content rPET wt%	Step 1 – rPET glycolysis		Step 2 – Polyol synthesis		
		rPET mol	Diethylene glycol mol	Polyglycol PR 600 mol	Phthalic anhydride mol	Ethylene glycol mol
P-1	50	6.10	6.10	0.86	0	0
P-2	40	4.88	6.10	0.86	1.22	1.22
P-3	30	3.66	6.10	0.86	2.44	2.44
P-4	20	2.44	6.10	0.86	3.66	3.66
P-5	10	1.22	6.10	0.86	4.88	4.88
P-6	0	0	6.10	0.86	6.10	6.10

Synthesis of polyester polyols

The synthesis was carried out with a constant number of moles of diethylene glycol, ethylene glycol and PR 600 polyglycol, with a variable number of moles of terephthalic and orthophthalic units (Table 1) in a glass reactor with a capacity of 4 litres equipped with a cooler and a condensate trap in nitrogen atmosphere using the Fascat 4100 catalyst. Polyol P-1 contained only terephthalic units. In subsequently synthesized polyols, the number of moles of terephthalic units was reduced, and the orthophthalic units and ethylene glycol were increased by that amount, thus maintaining a constant molar ratio of hydroxyl to carboxyl groups. Polyol P-6 contained only orthophthalic units. Polyester polyols P-1 to P-5 were synthesized in two steps. In the first step, recycled PET was glycolyzed using diethylene glycol; the process was carried out at 230°C until a clear solution was obtained. The reaction mixture after glycolysis was maintained at 230°C for another 1 h. Then, in the second step, polyglycol PR 600 and a certain amount of phthalic anhydride and ethylene glycol were introduced into the resulting glycosylate. The synthesis of polyol P-6 was carried out in one step using only phthalic anhydride.

The molar formulas of the ingredients used for the synthesis are presented in Table 1.

Preparation of polyurethane-polyisocyanurate foams

Polyurethane-polyisocyanurate foams were prepared by manual mixing. The formulas for the preparation of foams featured constant amounts of ingredients. The following additives were introduced to 100 g of synthesized polyester polyol: Silicone L-6620 – 3 g, PMDETA – 0.1 g, Potassium Hex-Chem – 1.5 g, 85% formic acid – 5 g. Suprasec® 5025 was added to the mixture of polyol with additives in an amount to maintain the isocyanate index equal to 1.38 wt%, the amount oscillated around 150 g. Flame retardants were not used and no combustible substances were used for foaming. Formic acid with a concentration of 85% was used as the blowing agent. The foams obtained in this way differed only in the content of terephthalic and orthophthalic units in such proportions as in the synthesized polyols.

Polyester polyols characterization

Viscosity was performed on a CAP2000 PLUS L cone-plate viscometer (Brookfield, Canada) according to EN ISO 3219 at 25°C, using a No. 3 cone spindle and a speed of 60 rpm. The acid number (AV) was determined according to the PN-EN ISO 2114 standard by titration with an aqueous solution of potassium hydroxide against the bromothymol blue indicator. The hydroxyl number (HV) was determined in accordance with the PN-EN ISO 2554 standard. The density was measured in accordance with the PN-EN ISO 2881-1 standard by titration with methanolic potassium hydroxide against the thymol blue indicator. Glycol content was determined using a TRACE GC ULTRA (ThermoFisher Scientific, Massachusetts, USA) gas chromatograph with FID detector and a TRACE TR-WAX 30 m × 0.32 mm ID × 0.5 µm column. The reactivity study was carried out according to its own methodology. Suprasec® 5025 was added to 120 g of the obtained polyol. The amount of Suprasec® 5025 was determined based on the amount of polyol used, the average content of NCO groups, the LOH, LK values and the water content of the polyol. The resulting solution was stirred for 15 seconds with a mechanical stirrer. Then, the time of reaching the temperature of 100°C and the maximum temperature was determined for the sample.

Polyurethane-polyisocyanurate foams characterization

The foaming time properties, i.e.: cream time (time from mixing component A with component B to the start of the volume rise of the mixture, this is accompanied by a colour change), gel time (time after which the viscosity of the mixture is high enough to enable gelled fibrils to be taken out of the foam), tack-free time (the time after which the foam surface is no longer sticky to the touch) was determined during the preparation of each foam. The measurements were made using an electronic stopwatch. Oxygen index was determined in standardized device (Fire Testing Technology Limited, East Grinstead, Great Britain) and conditions according to PN-EN ISO 4589-2. The samples used for the measurement had the shape of cuboid beams with dimensions of

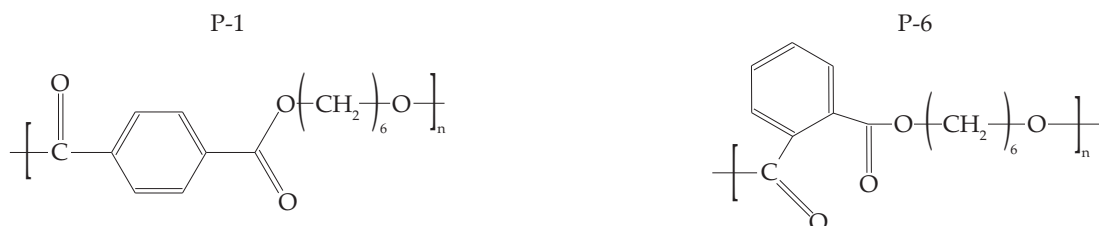


Fig. 1. The general structural formulas of P-1 and P-6 polyester polyols

Table 2. Determined properties of the synthesized polyester polyols

Polyol	rPET content %	Viscosity mPas	Hydroxyl number mg KOH/g	Density g/cm ³	GE content wt%	GDE content wt%	Water content wt%
P-1	50	5075	311.7	1.210	5.9	10.1	0.083
P-2	40	2700	308.5	1.220	6.0	10.3	0.046
P-3	30	2625	309.2	1.223	5.8	9.7	0.030
P-4	20	2425	344.8	1.224	6.7	10.8	0.070
P-5	10	2275	311.6	1.224	6.4	10.4	0.080
P-6	0	2237	311.2	1.223	5.9	10.8	0.030

Table 3. Results of the reactivity test

Polyol	Reactivity test		
	Time to 100°C s	Time to T_{max} s	T_{max} °C
P-1	168	489	148.0
P-2	160	428	157.0
P-3	192	471	156.7
P-4	315	630	152.9
P-5	499	823	152.7
P-6	791	1170	149.6

Table 4. Foaming time properties for the foams

Polyol	Cream time s	Gel time s	Tack-free time s
P-1	10	52	85
P-2	9	53	80
P-3	11	54	86
P-4	12	62	103
P-5	14	69	126
P-6	15	72	126

approx. 140 × 10 × 10 mm. Single-flame source test was carried out according to PN-EN ISO 11925-1 in a specialized chamber (Fire Testing Technology Limited, East Grinstead, Great Britain). TGA analysis (thermal stability and mass loss as a function of temperature) were tested using the STA 449 F5 Jupiter (Netzsch, Selb, Germany) in Al₂O₃ breaker crucibles vol. 5 ml. Test portions weighing approx. 50 mg were taken for testing. The tests were carried out in the temperature range of 25–950°C at a heating rate of 20°C/min. The measurements were carried out in the atmosphere; air 60 ml/min, nitrogen 10 ml/min.

RESULTS AND DISCUSSION

Polyester polyols properties

The obtained polyols had a functionality of 2, a low acid value below 1 mg KOH/g, and a hydroxyl value 308–312 mg KOH/g. A large difference in viscosity is notable (Table 2). Polyols P-1 and P-2, which contain the most terephthalic units, have the highest viscosities and solidify to a sticky form after a few days. This may be caused by their greater tendency to crystallize. The introduction of orthophthalic units results in a more interwo-


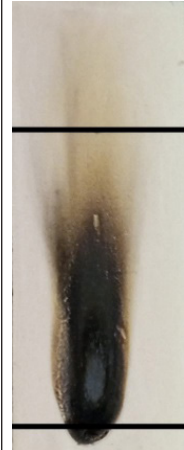


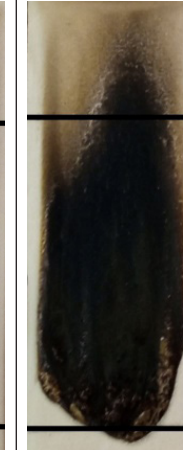
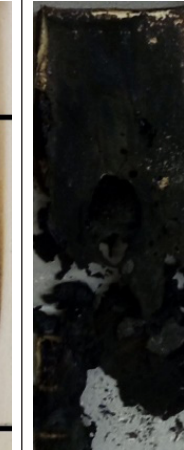
ven molecular structure of the polyol, which does not show a tendency to crystallize. Polyols P-3 to P-6 have lower viscosities and retain clarity in appearance [33].

The resulting polyols are also characterized by a difference in reactivity in reaction with isocyanate (Table 3). Polyols with a higher content of terephthalic structures have very high reactivity. The time to the temperature of 100°C for polyol P-6 is 168 s and is successively longer for polyols with an increasing share of orthophthalic units. For polyol P-6 containing only orthophthalic units, the time is 791 s. The increased reactivity of terephthalic polyols may result from their linear structure (which reduces steric hindrance and thus promotes the reaction

Table 5. Foams oxygen index

Polyol	rPET content wt%	Oxygen index %
P-1	50	21.8
P-2	40	21.5
P-3	30	21.2
P-4	20	21.2
P-5	10	21.3
P-6	0	20.7

Table 6. Results of the single-flame source test

Polyol	P-1	P-2	P-3	P-4	P-5	P-6
150 mm limit reached	NO	NO	YES	YES	YES	YES
Test result						

of isocyanate groups with hydroxyl groups). Processing properties of the resulting foams obtained from polyester polyols are shown in Table 4.

Polyurethane-polyisocyanurate foams properties

Oxygen index

The oxygen index was determined for the foams. The foams had no flame retardants and were characterized by a relatively low isocyanate index of 1.38, which is defined as the molar ratio of isocyanate groups to hydroxyl groups. Table 5 presents the results of the oxygen index tests. The foam made with polyol P-1 containing the largest amount of terephthalic units has the highest index value. The index values decrease with the increase in the content of orthophthalic units in polyols. The lowest index value of 20.7% was obtained for the foam made with polyol P-6 containing only orthophthalic units.

Single-flame source test

The foams were exposed to direct flame in the single-flame source method. When exposed to fire, the foam contracts, and melts at the same time, to form a black char that increases burnout resistance. The test results

are presented in the form of photos (Table 6). We found that the foams P-1 and P-2 containing the largest share of terephthalic units form compact hard char and extinguish immediately after the burner flame is removed, and the height of the flame does not exceed 150 mm. Subsequent foams P-3 and P-4 exceed the limit height of 150 mm while, however, exhibiting self-extinguishing properties once the flame source is removed. Foams P-5 and P-6 get burned completely. The relationship is very clear: the reduction in the share of terephthalic units and their replacement with orthophthalic units results in the formation of charred residues, which form an increasingly weaker barrier against burnout of the foam, up to the full burn of the foam containing only orthophthalic units.

TGA analysis

TGA results are presented in Figure 2 and listed in Table 7. Thermal stability and the degree of charring depend on the structure of the polyol. Based on the TGA analysis, a clear relationship between the share of terephthalic units and the thermal decomposition was observed. The foam based on polyol P-1 containing only terephthalic units has a mass loss of 5% at 248°C, while the foam based on polyol P-6 containing only orthoph-

Table 7. Thermal properties of the foams determined by TGA

Polyol	$T_{5\%}^{\circ\text{C}}$	$T_{25\%}^{\circ\text{C}}$	$T_{50\%}^{\circ\text{C}}$	$T_{75\%}^{\circ\text{C}}$	$T_{\text{max}1}^{\circ\text{C}}$	$T_{\text{max}2}^{\circ\text{C}}$
P-1	248.6	338.1	539.7	631.0	277.0	578.3
P-2	234.4	319.5	533.2	621.9	275.5	573.5
P-3	248.9	320.8	543.0	626.2	278.5	579.2
P-4	243.5	317.8	552.7	648.1	274.8	583.8
P-5	242.4	307.8	541.8	635.3	273.9	579.9
P-6	243.1	300.8	527.2	618.0	273.1	578.6

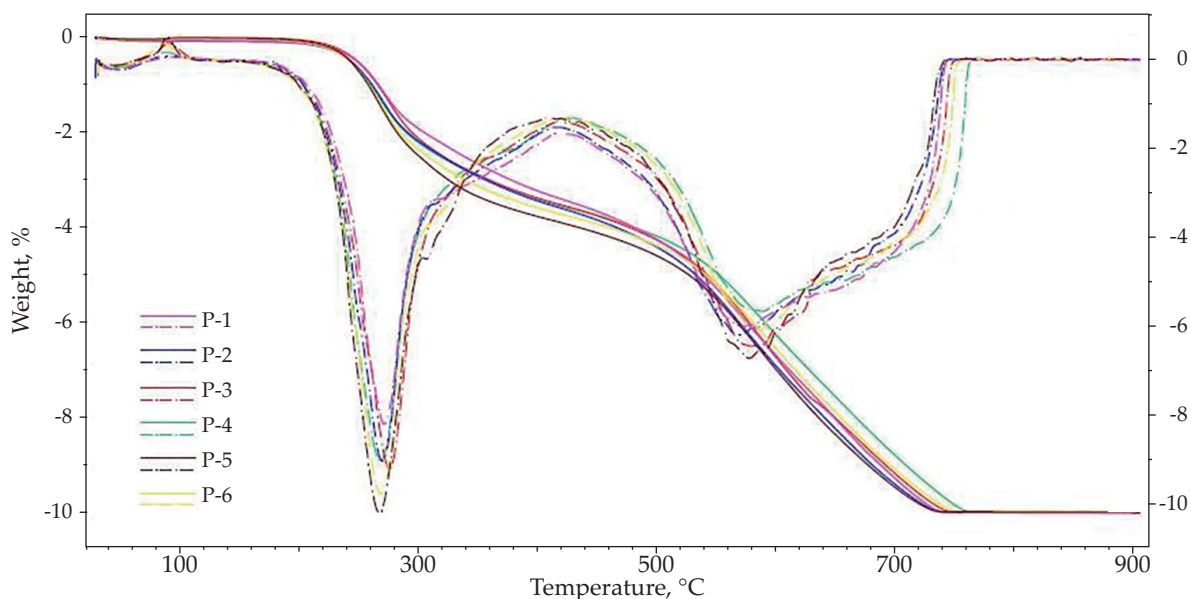


Fig. 2. TG (line) and DTG (line-dot) curves

thalic units displays the same mass loss at 243°C. Mass losses occur at higher temperatures in polyols containing more terephthalic units. In each of the presented stages of mass loss from 5 to 75%, the situation is analogous, *i.e.*, with the increase of terephthalic units, a specific mass loss occurs at increasingly higher temperatures. TGA analysis also shows two phases of weight loss due to double maximum rates of decomposition rates ($T_{\max.1}$ and $T_{\max.2}$).

CONCLUSIONS

In a direct flame test, a reduction in the flammability of foam containing aromatic terephthalic units was demonstrated in comparison to foam containing orthophthalic units. With an increase in the share of terephthalic units, a more compact, non-disintegrating char layer was observed, which caused the flame to go out immediately after the burner is removed. The foam containing only orthophthalic units disintegrated completely after combustion. Terephthalic units have likely the ability to promote char formation on the surface of the foam, which is much more resistant to burnout than the char layer produced by foam containing aromatic orthophthalic units. This lends these foams self-extinguishing, non-dripping and non-disintegrating properties in fire conditions. TGA showed better thermal stability for foams obtained with a higher proportion of terephthalic units, which is evidenced by a 5–30°C higher decomposition temperature. In addition, foams containing a higher proportion of terephthalic units had a higher oxygen index, which proves their higher fire resistance.

The beneficial properties of terephthalic polyols, manifested in increased resistance to fire, make it possible to reduce the amount of flame retardants added in industrial foam-based production processes. For example, in

the production of sandwich panels with the use of typical orthophthalic polyols, a flame retardant TCPP (tris(1-chloro-2-propyl) phosphate) is added in an amount of 10 to 15%. Preliminary laboratory tests confirmed the above assumption; however, they are not covered by the analyses presented in this paper. It is justified to advance the research in this respect as the development of practical applications is well supported by both economic considerations, given the reduction in the amount of flame retardants used in foams, and ecological considerations given the options to recycled PET for the synthesis of polyols.

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