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Tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate for rigid PUR-PIR foams

Abstract: A new compound was synthesized from 2-hydroxy-1,2,3-propanetricarboxylic acid (citric acid) and diethylene glycol (DEG). Compound, tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT) rated properties in terms of suitability for the rigid polyurethane-polyisocyanurate (PUR-PIR). Rated properties of THT eg., acid number, density, pH, solubility. The resulting product was characterized by hydroxyl number 405.2 mg KOH/g and viscosity 4879.7 mPa·s. Compound used to foams in amounts of from 0.1 equivalents to 0.5 equivalents instead of Rokopol RF551. The results of rigid foams showed that the amount of THT in the foam significantly affects the compressive strength of foams. Its amount does not affect the apparent density of foam, retention and thermal conductivity. The foams are characterized by small values of fragility.

Keywords: 2-hydroxy-1,2,3-propanetricarboxylic acid; diethylene glycol; polyurethane-polyisocyanurate foams.

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1 Introduction

A large assortment of polyols is available on the market to the polyurethane industry. Reaction products of adipic acid with glycols or terephthalic acid waste fractions are used most commonly [1]. High quality polyols are synthesized on the basis of glycerol which is a cheap waste product [2].

Since the synthesis of polyurethanes is still expensive, attempts are made to develop cheaper methods of raw materials synthesis for PU production. A cheap method of production, e.g., polyol for polyurethanes, is their chemical recycling [3–9], in which waste polyurethanes are once more applied for synthesis of PU. Glycolysates for synthesis of polyurethanes were applied among others by Datta and Rohn [10, 11]. Substrates for synthesis of PU can also be obtained from other materials, for example, a mixture of PU with PET [12]. Simultaneously, the problem of waste disposal, which is without doubt one of the key problems of our civilization, can be resolved. Synthesis of polyols by esterification, etherification or glycolysis is time-consuming and thus energy-consuming (takes place in the temperature range 150°C–220°C). Therefore, attempts are made to find the effective catalysts in order to reduce time of these reactions [13].

In the production process of polyols for PU, it is also important to maintain properties of PU which have not deteriorated and which meet requirements of consumers. A very important parameter is, e.g., heat conductivity or a problem of polyurethane flammability. Therefore, modifications of polyols are intended to reduce flammability [4–19].

Raw materials for polyurethanes can also be obtained from organic waste such as citric acid [20], which should play a major role in synthesis of elastomers [21, 22]. However, its application has not been widely published and confirmed. Therefore, products of synthesis of this acid with glycols were used for preparation of rigid PUR-PIR foams, which is the subject of this paper.

The aim of the studies is to synthesize the new compound from 2-hydroxy-1,2,3-propanetricarboxyl acid and to investigate the effects on properties of rigid polyurethane-polyisocyanurate (PUR-PIR) foams. Application of the obtained compound tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT) is expected to improve, among others, brittleness and other parameters of foams.

2 Materials and methods

2.1 Materials

Polyester with the trade name Rokopol RF-551, poly(oxypropylene)diol (with hydroxyl number 420 mg KOH/g, molecular weight=660) product of Chemical Plants

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PCC Rokita S.A. in Brzeg Dolny and technical diisocyanate (Ongromat 30-20), made in BorsodChem, Hungary, the main component of which is 4,4′-diphenylmethane diisocyanate were used to prepare rigid PUR-PIR foams. The density of Ongromat 30-20 at temperature of 25°C was 1.23 g/cm^3, viscosity was 200 mPa·s and content of NCO groups was 31.0%. Polyether and diisocyanate were characterized according to standards: ASTM D 2849-69 and ASTM D 1638-70. The catalyst in the process of foam preparation was anhydrous potassium acetate (POCh Gliwice) applied in the form of 33% solution in diethylene glycol (DEG) (catalyst 12) and DABCO 33LV (triethylenediamine, Hülls, Germany) used as 33% solution in DEG. The stabilizer of the foam structure was poly(oxyalkylene siloxane) surface-active agent Silicone L-6900 (Witco, Sweden). Carbon dioxide formed in the reaction of water with isocyanate groups acted as a blowing agent. Moreover, a liquid flame retardant, i.e., tri(2-chloro-1-methylethyl) phosphate with trade name Antiblaze TMCP (Albright and Wilson, UK) was introduced into the foam composition. For the synthesis of the new compound and for preparation of catalyst 12 used DEG, POCh Gliwice.

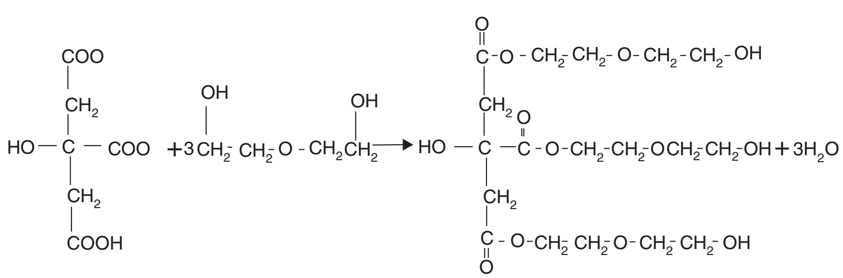
2.2 Techniques

2.2.1 Preparation of new compound (THT)

THT was synthesized by esterification reaction by the solvent method. The alcohol component was DEG and the acid component was 2-hydroxy-1,2,3-propanetricarboxyl acid.

Esterification was conducted in three-neck glass flask (volume of 500 ml) equipped with a reflux condenser, stirrer and Dean-Stark's head. The reaction was performed in xylene medium. The released water was collected in the head. The mixture consisting of 2-hydroxy-1,2,3-propanetricarboxyl acid (96 g) and glycol DEG (159 g) was poured into the flask. The flask was heated in an electric bath until acid dissolution. Citric acid was dissolved at a temperature of about 85°C during 20 min. The time of reaction was counted from the moment when the mixture in the flask began to boil (about 125°C). Temperature of reaction increased within the range from 128°C to 156°C. Parameters of esterification are presented in Table 1.

THT was synthesized from 1 mole (96 g) of 2-hydroxy-1,2,3-propanetricarboxyl acid (citric) and 3 moles (135 g) of DEG [Eq. (I)]:



(I)

Citric acid THT water

Every 30 min, the quantity of liberated water was measured. Every 30 min reactions were controlled by determination of acid number and pH of the product obtained. The product delaminated into two layers: the upper was xylene and the lower was polyol. Xylene was distilled off to Dean-Stark's head. Residual xylene was evaporated in a vacuum drier. Properties of the obtained compound were determined.

In order to examine the usefulness of the newly obtained compound for synthesis of PUR-PIR foams, their properties were determined according to the obligatory standards.

Table 1: Parameters of esterification of diethylene glycol (DEG) with citric acid.

Name of polyol	Citric acid (g)	Glycol		Temp. of reaction (°C)	Reaction time (h)	The amount of distilled water (cm^3)	
		Name	Amount (g)			Theoretical	Practical
THT	96	DEG	159	128–152	7	27	48.0

THT, tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate.

Very important in the case of using the polyurethane polyol is the knowledge of their content of water. Water is added as a blowing agent in the foam. Excess water can cause cracking of the foam cells or even a fall. The water content was tested by Karl Fisher (PN-81/C-04959), in which the solvent used was a mixture of methanol and carbon tetrachloride in a 1:3 ratio. The titration reagent was Combo. Marking is to dissolve the appropriate test portion of the product in Titraqual (titrant for titration) and potentiometric titration of the solution to the equivalence point. The scope of jurisdiction of polyol was also included to determine its technological features, such as hydroxyl number (WT/06/07/PURINOVA), acid number (WT/06/07/PURINOVA) and the viscosity at a temperature of 25°C (EN ISO 12058-1).

The hydroxyl number was determined according to the standard of PURINOVA, Bydgoszcz. Into the conical flask was weighed 250 ml about 1 g of the product to an accuracy of 0.0002 g, loaded with a magnetic stirrer. Using pipette, 25 ml of the catalyst solution was added and it was stirred with a magnetic stirrer for at least 5 min to dissolve the sample. All was mixed by hand to rinse the walls of the flask and add 10 ml of a mixture of acylation. The contents were stirred with a magnetic stirrer for 15 min and 10 ml of distilled water was added. The flask contents were shuffled by hand and then for 5 min with a magnetic stirrer. After this time, 50 ml of acetone was added and the sides of the flask rinsed. Five drops of indicator solution were added and titrated with a solution of potassium hydroxide to the first change of color to blue. The hydroxyl number expressed in mg KOH/g are calculated according to the equation:

$$L_{OH}=\frac{(V_1\text{-}V_2)\cdot 56.11}{m}+L_k$$

where: V_1 is volume of the solution of potassium hydroxide C_{KOH}=1000 mol/l used for titration of the blank; V_2 is volume of the solution of potassium hydroxide C_{KOH}=1000 mol/l used for titration of the sample; 56.11 is the number of mg of potassium hydroxide equivalent to 1 ml of a solution of potassium hydroxide having a concentration of C_{KOH}=1000 ml/l; m is weighted in quantity of the product in grams (g); and L_k is the acid number of the sample. The result of the arithmetic mean was adopted for two studies and differed from each other by no more than 3 mg KOH/g.

Similarly, the acid number was determined. In an Erlenmeyer flask, 100 cm³ 1.0 g of sample was weighed to the nearest 0.001 g and 20 cm³ solvent was added from a burette. The flask contents were stirred with a magnetic stirrer to dissolve the sample. Phenolphthalein (3–5 drops) was then added and titrated with 0.5 mol alcoholic solution of KOH to the first pink color of the solution. In parallel, a blank test was performed. The acid number was calculated according to the equation:

$$L_k=\frac{(V_1\text{-}V_2)\cdot M\cdot 56.1}{m},\quad \text{mgKOH / g}$$

where: V_1 is the volume of alcoholic KOH solution used for titration of the sample (cm³); V_2 is the volume of alcoholic KOH solution used for titration of the blank test (cm³); m is the mass of the sample (g); and M is KOH solution molarity.

The viscosity was determined using a Hoeppler viscometer. The dynamic viscosity was calculated according to equation: η=t·(p1-p2)·K·F in which η is dynamic viscosity, (m·Pa·s); t is time of descent from top to bottom annular mark (s); p1 is density of ball, g/cm³; p2 is density of fluid, g/cm³; K is ball constant, mPa·cm³/g; F is multipilcator working angle. Used ball number 5 with the following data: diameter=14.002 mm, weight=11.071 g, density=7.7019, has balls: the upper limit was 6.790 and the lower limit was 6.789.

The density of polyols in the pycnometer was measured at 25°C (298 K) according to PN-92/C-04504. This depends on the hydroxyl number of the polyol used in the foam and the polyisocyanate necessary to produce a foam. Density and viscosity are very important during the processing process. The pH of polyols was also measured using the microcomputer CP-551 pH-meter. Organoleptically rated color of THT was milk, bright yellow.

To assess the chemical structure of the polyols, a spectrophotometer Vector of Brücker was used. Foam analysis by IR spectroscopy using the KBr technique was performed in the range of 400 cm^{-1}–4000 cm^{-1}.

Presence of citric acid in the obtained product was determined by dissolving 0.5 g of its sample in 5 ml of water and then, the solution was neutralized with 1 mole NaOH and 10 ml of $CaCl_2$ was added. The mixture was heated to boiling point. As a result of the reaction, a white precipitate was formed, which testified the presence of citric acid.

Qualitative analysis of THT was performed by gas chromatography with flame ionization detection (GC-FID). Analyses were performed by the use of chromatograph (USA TRACE 2200) equipped with a capillary column with a length of 30 m and diameter of 0.32 mm×0.25 µm, 007-5-30W DB5 and detector: GC-FID (gas chromatography flame ionization detector).

2.2.2 Preparation of PUR-PIR foams

The foams were prepared in laboratory scale by a one-stage method from a two-component system at equivalent ratio of NCO to OH groups equal to 3:1. Component A was obtained by thorough mixing (stirrer rotation speed of 1800 rpm, mixing time 10 s) of the appropriate amount of Rokopol RF551, the new polyol, catalysts (catalyst 12; 6.4 g, 2.1% ww and Dabco 2.76 g, 0.9% ww.), flame retardant (Antiblaze TMCP; 46.09 g, 15% ww), surfactant (Silicone L6900; 4.6 g, 1.5% ww) and blowing agent (water). The amount of water was reduced by content of water in the new compound THT; component B was Ongromat 30-20 (added in amount 250.67 g, 3,7R).

Both components were mixed (1800 rpm, 10 s mixing time) in appropriate mass ratio and poured into a metal open rectangular mold with dimensions of 195 mm× 195 mm×240 mm. A series, P2.1–P2.5, of foam were obtained with participation of THT. The newly prepared compound was used to foam composition in amount from 0.1 to 0.5 of chemical equivalent with respect to the amount of Rokopol-RF 551, whose content was reduced from 0.9 to 0.5 of chemical equivalent (Table 2). During the synthesis of PUR-PIR foams, the process of foaming reaction was monitored and measured using a stopwatch at appropriate technological times: start time, rise time, gel time. The start time was the time measured by a stopwatch from mixing all the components until the so-called "state of cream". This is shown by starting to increase the volume of the foam. The rise time was the time measured by a stopwatch from mixing all components of the foam until the maximum volume of the foam. The gel time was the time measured by a stopwatch from mixing all foam components, until the free surface of the foam stops sticking to a clean glass rod.

The foams obtained, after removing them from the mold, were thermostated for 4 h at a temperature of 120°C. Then, they were seasoned for 48 h at a temperature of 20±4°C, cut into pieces and basic properties were determined according to valid standards.

It was noted that there is a close relationship between the properties of polyurethanes and their physical and chemical properties. Research directions of rigid polyurethane foams due to their properties: physical (density, water absorption, flammability), mechanical (compressive strength, brittleness) and electrical equipment (thermal conductivity).

The apparent density of the foams tested was determined using a sample in the form of a cube of side 50 mm according to ISO 845-1988, and the weight ratio of the foam to its geometric volume. Before cutting samples for determination of apparent density, foams were aged for 24 h at room temperature. The samples were then cut to the nearest 0.1 mm and weighed to the nearest 0.1 g.

Determination of water absorbing capacity was performed according to the standard: DIN 53433. The determination method consists of measuring the strength of buoyancy of a sample measuring 150 mm×150 mm×25 mm. They were immersed in distilled water for 24 h. This method applies to any rigid, porous materials, which doesn't react with water. Water absorption is the ratio of the volume of absorbed water to the original volume of the sample expressed as a percentage.

The structure of foams was determined using an optical microscope, Axiotech Carl Zeiss, Hal 100, which simultaneously transmitted and reflected light (magnification 5×). Thermal resistance was measured by a derivatograph operating in the Paulik-Paulik Erdey system, MOM – Budapest). Thermal resistance of the foams was determined under dynamic conditions in air with a heating rate of 5°C/min, at a temperature from 20°C to 800°C.

The content of closed cells was determined according to the standard ISO 4590:1994 method II, using the foam test sample dimensions of 100 mm×30 mm×30 mm. This method involves the determination of the relative pressure drop, previously calibrated for volume models, and the difference in readings on the pressure gauge, one arm of which is open to the atmosphere. This measurement method is designed for the determination of the percentage of closed cells in rigid porous plastics.

Flammability was performed using a thermal imaging camera Vigo V-20E2-25 equipped with a thermoelectrically cooled HgCdTe detector.

The second method was a simplified chimney flammability test (test vertical – Butler) according to ASTM D3014-73. The apparatus used for the flammability test of the vertical test consists of a vertical column with dimensions 300 mm×57 mm×54 mm of which three walls are made of sheet metal, and the fourth is a movable window. The assay was performed on six samples with dimensions

Table 2: Properties of tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT).

Name of polyol	Viscosity at 25°C (mPa·s)	Density at 25°C (kg/m^3)	Hydroxyl number (mg KOH/g)	Acid number (mg KOH/g)	pH	Content of water (%)	Content of glycol (% mas.)
THT	4879.7	994.3	405.2	25.3	6.0	0.3	36 DEG

DEG, diethylene glycol.

of 150 mm×19 mm×19 mm. Before combustion, the sample was weighed to an accuracy of 0.0001 mm, and then placed inside the chimney. Established glass and the sample was applied to the flame of the burner fueled by propane-butane at the time of 10 s. Then, the torch was moved away and a stopwatch measured the time of free samples of smoking and retention (residue after burning) in the vertical test. The retention was calculated according to the equation:

$$R_e = \frac{m}{m_0} \cdot 100\%$$

where R_e is retention; m_0 is mass of the sample before burning (g); and m is mass of the sample after ignition (g).

The chemical structure of the foams was determined by IR spectroscopy (Vector spectrophotometer, Brücker).

Compressive strength was performed with the Tira Test 2200 tensile testing machine, standard ISO 844:1993: DIN 53420. In the foams, skins and sides of the sample were cut in the shape of cubes with an edge length of a side of 50±1 mm. Then the samples were subjected to 10% compressive strain in the direction of foam rise.

Brittleness was determined in accordance with ASTM C-421-61. On the basis of quoted standards, friability is calculated as the percentage loss of foam blocks 12, (cubes having sides of 25 mm) when tested in a standardized unit, in relation to the initial weight. The instrument used to test the fragility of polyurethane foam is a cubic box made of oak, with dimensions 190 mm× 197 mm×197 mm, rotating around an axis at a speed of 60 rpm. Filling the box are 24 blocks with dimensions of 20 mm×20 mm×20 mm oak.

Weight loss in % foam, a measure of its fragility, is determined by the equation:

$$K = \frac{m_1 - m_2}{m_1} \cdot 100\%$$

where m_1 is the mass of the samples before the test (g); and m_2 is the mass of the samples after the test (g).

A softening point was determined using a sample in the form of a cube of sides 20 mm, in the direction of foam rise, according to DIN 53424. The foam samples were subjected to a compressive load of 24.52 kPa at a temperature of 50°C/h. For the softening point, the temperature at which the compression of the foam sample of 2 mm.

The thermal conductivity of foams was determined by examining the coefficient of thermal conductivity. The study sample was subjected to foam dimensions: 200 mm×200 mm×25 mm. To carry out these studies, the camera FOX 200 from Lasercomp was used. It allows the determination of the values in the range of 20–100 mW/(mK). The method of measurement is to determine the amount of heat flowing through the material per unit of time during a given heat flow at a constant temperature difference on opposite sides of the test sample material.

3 Results and discussion

3.1 Research results for new compound

Esterification of DEG with 2-hydroxy-1,2,3-propanetricarboxyl acid resulted in formation of tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT). The product was a light straw colored liquid. Synthesis lasted 7 h. The reaction was stopped after water ceased to collect in Dean-Stark's head. The reaction ran at a temperature of 128°C–156°C (Table 1). During synthesis, a continuous rise of temperature was observed as the reaction proceeded. Viscosity of the product was 4879.7 mPa·s (Table 3). Density was 994.3 kg/m^3. Viscosity of the new compound is three times lower than the highest permissible viscosity (16,000 mPa·s) which should not exceed raw materials used in standard commercially available systems for PUR processing. Density values of the compounds do not limit the possibility of their application in systems for production of polyurethane foams.

The pH values of products was 7.0 (Figure 1). The volume of water formed in reactions was 48.0 cm^3. As the reaction proceeded, the acid number of the product

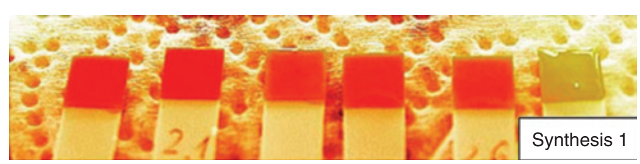


Figure 1: Change of pH during the synthesis of 1.

Table 3: Composition of P2 series foams.

	Unit	W	P2.1	P2.2	P2.3	P2.4	P2.5
Rokopol RF-551	R	1	0.9	0.8	0.7	0.6	0.5
	g	66.78	60.10	53.42	46.74	40.07	33.39
THT	R	0	0.1	0.2	0.3	0.4	0.5
	g	0	6.93	13.85	20.77	27.69	34.62
Distilled water	R	0.7	0.7	0.7	0.7	0.7	0.7
	g	3.15	3.13	3.12	3.11	3.10	3.08

THT, tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate.

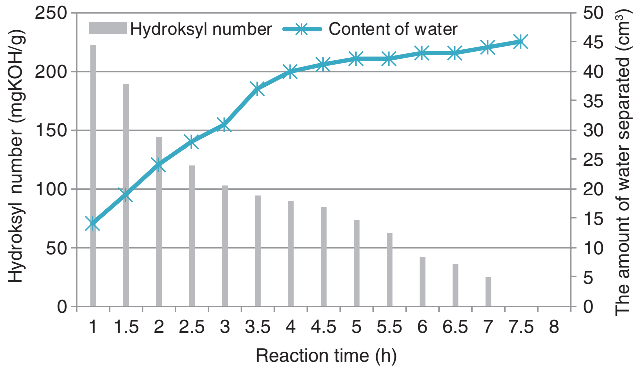


Figure 2: Effect of the quantity of separated water and acid number on the reaction time.

decreased. Finally, at the end of synthesis, it was 25.3 mg KOH/g (Figure 2).

It was found that citric acid was present in the product obtained. Analyses by the Fourier transform infrared (FTIR) method and gas chromatography were performed in order to confirm the above findings. Bands with frequencies typical for groups constituting the new compound were observed in an FTIR spectrum of the newly obtained compound (Figure 3). An absorption band at a wavelength of 1415 cm^{-1} (1) derived from C-O-H (demonstrating presence of carboxylic acid) was observed. Oscillation at a wavelength of 1750 cm^{-1}–1735 cm^{-1} (2) is a C=O band (characteristic of aliphatic esters). The range from 3300 cm^{-1} to 2500 cm^{-1} (3) is a vibrational band stretching O-H groups. Within the range from 1060 cm^{-1} to 1150 cm^{-1} (7), the C-O band of ethers is observed. The vibrations at 3000 cm^{-1} to 2840 cm^{-1} (6) are stretching vibrations of methylene groups.

Twice higher amount of water was collected in Dean-Stark's head then it results from the reaction (Table 1). It proves that a hydroxyl group located at the second carbon atom in trihydroxypropane acid (forming an ether bond presented in FTIR graph) is also involved in the reaction. It results in excessive 9 g of water. The rest, which in the case of reaction 1 is 6 g, can be derived from the partial decomposition of citric acid (total decomposition takes place at 175°C). Chromatographic analysis indicated the presence of citric acid in the product, but its amount was very small (<1%) and it will have no impact on the course of synthesis of PUR-PIR foams.

3.2 Assessment of properties of rigid PUR-PIR foams

The obtained compound was used for synthesis of rigid PUR-PIR foam in amounts from 0.1 to 0.5 of chemical equivalent. A series of orange foams were obtained: P2.1–P2.5. Skins of foams were yellow. IR analysis of P2 foams showed the presence of isocyanurate (1736 cm^{-1}) and urethane (2969 cm^{-1}–2915 cm^{-1}) bonds in the foams. Moreover, the hydroxyl group, OH, was observed within the range from 3136 cm^{-1} to 3360 cm^{-1}.

THT affects properties of foams but there is no effect on changes in linear dimensions and volume of foams after 48 h of thermostating.

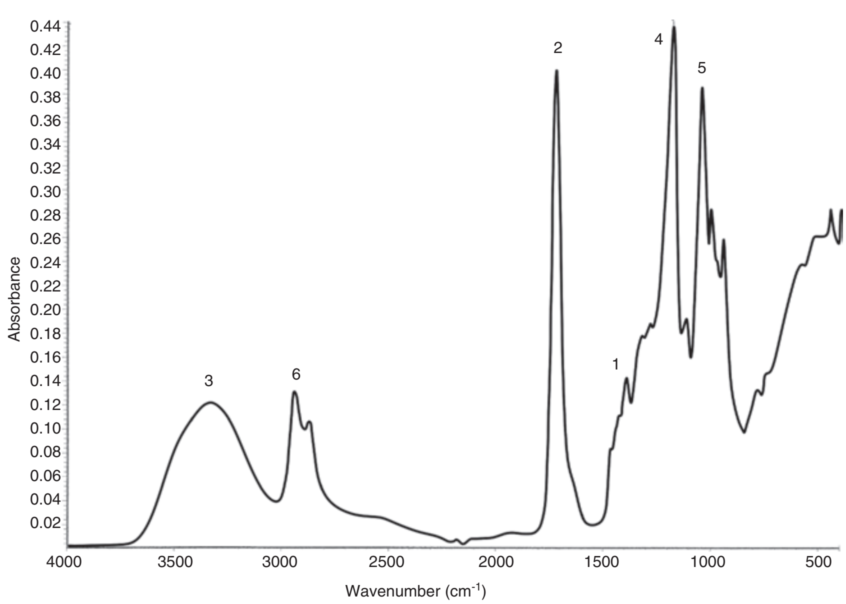


Figure 3: Analysis of Fourier transform infrared (FTIR) spectroscopy of tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT): (1) C-O-H, (2) C=O from ester, (3) O-H, (4) and (5) C-O from esters, (6) CH_2-, (7) C-O from ether.

Table 4: The time series of P2 foam processing.

Foam	Start time (s)	Growth time (s)	Gelation time (s)
W	10	31	28
2.1	11	31	31
2.2	13	32	32
2.3	16	39	38
2.4	20	62	63
2.5	23	82	88

The processing parameters of foams elongate with a higher amount of the new compound in foam composition (Table 4). The start time elongates from 10 s (foam W without THT) to 23 s (P2.5 foam containing 0.5 of chemical equivalent of THT). The time of expansion elongates from 31 s (W) to 82 s (P2.5), however, the time of gelation elongates from 28 s (W) to 88 s (P2.5). The reason for extending the processing parameters is the increasing viscosity of the polyol premix. The viscosity increases as a result of increasing the added amount of THT, which has a higher viscosity then Rokopol.

Addition of THT also had no effect on thermal conductivity. Its value was within the limits from 33 mW/(mK) to 35.5 mW/(mK).

The amount of added product did not affect the density of the foam, but it had a significant impact on the strength of parameters (Figure 4). Compressive strength decreased for series of foams from 212 kPa (P2.1) to 66 kPa (P2.5). Compressive strength of foam W (without THT) is a medial value between foams containing 0.3 and 0.4 of chemical equivalent of polyols and it is 185 kPa.

Evaluation of the flammability of foams indicates that addition of the new polyols to foams obtained on the basis of 2-hydroxy-1,2,3-propanetricarboxylic acid does not affect burning of foams. Retention, i.e., residue after combustion, was within the range from 93% to 96% and it was independent of the type and amount of THT in foam. All foams are self-extinguishing.

The oxygen index was 24.9% for all types of foams. A thermogram of the combustion process on the P2.3 example of foam is shown in Figure 5. The figure illustrates the temperature distribution during burning of the sample. A rapid course of the combustion process is observed. The maximum combustion temperature (649°C) was achieved in a time of 31 s (for instance foam P2.3). Generally, addition of THT based on citric acid does not affect the burning time of the foams. These values are similar to those in the examples.

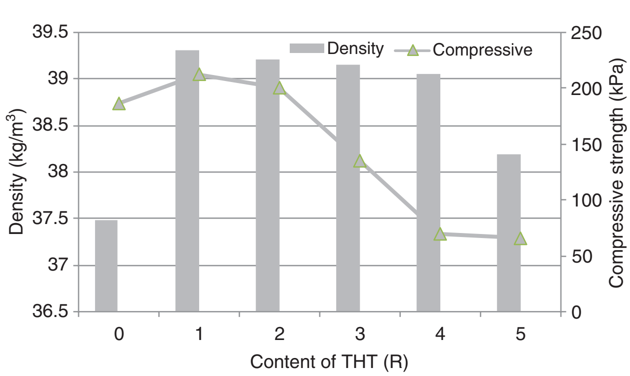


Figure 4: Effect of density and compressive strength of foam on the content of tris(hydroxydietylene)-2-hydroxypropane-1,2,3-tricarboxylate (THT) in foams.

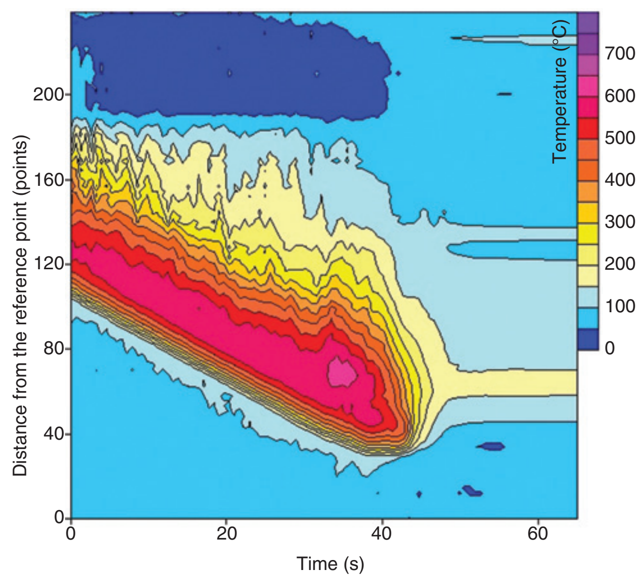


Figure 5: Thermogram of 2.3 foam combustion.

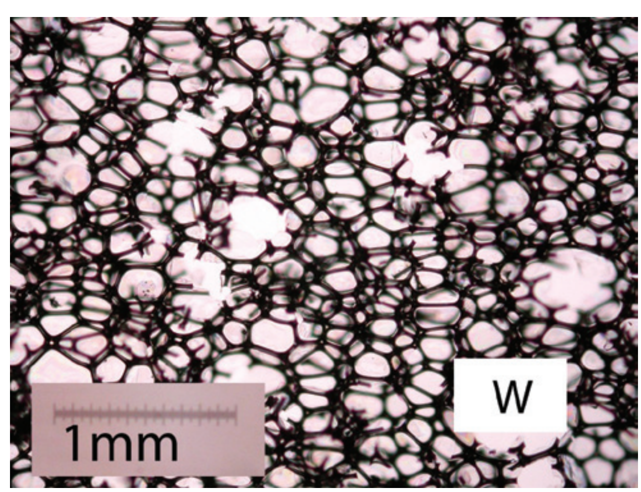


Figure 6: The foam W structure.

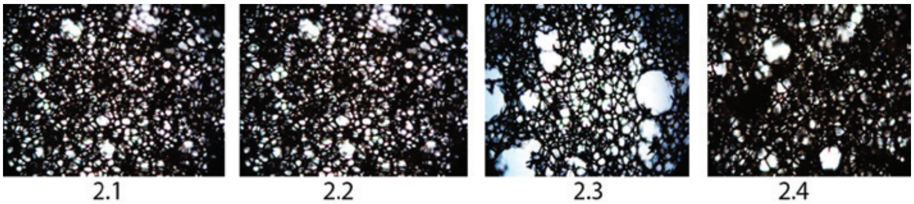


Figure 7: Structure P2-series foams (against the direction of growth).

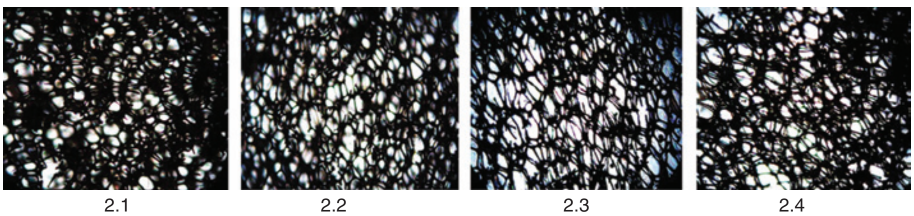


Figure 8: Structure P2-series foams (in the direction of growth).

The lack of clear impact of the amount of THT in foams on flammable properties of these foams also results from the structure of the foams (Figures 6–8). Addition of esters practically does not change this structure. It can be seen that the P2 foams have the same size and small-cell structure. Even microscope images taken according to direction of their expansion showed that the cells were not elongated. This is reflected in the density of foams, which is almost unchanged. The round pores of the foams in the image taken in direction of expansion should demonstrate high resistance of the foams. However, it is not so (strength, described above, decreases with increasing amount of THT in foam).

Closed cells for foams with different content THT is almost constant. The closed cell content decreases slightly (Table 5) to 91.5% (foam W) and to 90.6% (foam 2.5).

The brittleness of the foams also decreases from 28.4% (W) to 13.7% (P2.5). The addition of THT causes a significant decrease compared to the fragility of the reference foam W.

Table 5: Properties of P2 foams series.

Name of foam	Water absorption (% vol.)	Brittlenes (%)	The content of closed cells (% vol.)	Softening point (°C)
W	1.800	28.4	91.5	201
2.1	0.663	25.5	91.8	199
2.2	0.651	23.7	91.4	189
2.3	0.645	20.1	91.1	172
2.4	0.788	13.9	90.8	166
2.5	0.965	13.7	90.6	161

The absorptivity increases (to a small extent) from 0.663% (P2.1) to 0.965% (P2.5) (Table 5). The absorptivity of water for foams of the P2 series reduces more than three-fold in comparison to foam W (1.800%).

No distinct changes in size and shape of cells proved the correct selection of surfactant.

During combustion of 2 g of foams, the amount of emitted gases ranged from 150 cm^3 to 160 cm^3. After combustion, charred residue was obtained in an amount ranging from 1.4 g to 1.5 g. Moreover, small amounts of liquid product were formed, which failed to be investigated. Chromatographic analysis showed, among others, the presence of carbon dioxide (retention time 1.27 min) and carbon oxide (retention time 1.48 min).

Addition of the THT product affected the softening point of the foams (Table 5). It produced a slight decrease to 161°C (foam 2.5) relative to the reference foam (201°C).

The cause of the deterioration of the mechanical properties can be due to unsatisfactory mixing of raw materials. As shown in Figure 7, foam structure also deteriorated (tested against the direction of growth of foam). Open cells were observed with the addition of THT to foams. The image shows the cells of various sizes. It may also be one of the causes of deterioration, for example, compressive strength.

4 Conclusion

As a result of esterification of DEG with citric acid, the new compound THT was obtained. The new compound is less expensive than conventional polyols, as it was obtained with very cheap citric acid. After determining its properties, it was found that it can be used as polyol component for synthesis of rigid PUR-PIR foams. The viscosity of THT was 4879.7 mPa·s and the density was 994.3 kg/m^3. Due to the suitable viscosity and density, THT can be used for the synthesis of polyurethane foams. THT was characterized by hydroxyl number 405.2 mg KOH/g. The content of water was 0.3%. Such a small amount of water can be omitted when preparing a rigid foam formulation containing the synthesized THT. Compounds containing <1% water are particularly useful for foams blown with water and other blowing agents. THT preparation time is relatively short, despite the catalyst is not being used. This allows for significant savings in the synthesis of THT to polyurethanes.

Addition of THT to foams has no effect on density of the foam (about 40 kg/m^3), flammability (retention within the limits 93–96%), oxygen index (24.9%) and thermal conductivity [33–35 mW/(mK)]. The foams are especially useful in construction, home appliances and other devices because of good properties. Characterization showed, for instance, reduced brittleness from 28.4% (W) to 13.7% (P2.5). Absorptivity decreases from 1.8% (foam W) to about 0.6% for other foams. Compressive strength increases from 212 kPa (P.2.1) to 66 kPa (P2.5).

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