

Thermal Properties of Polyurethane-Polyisocyanurate (PUR-PIR) Foams Modified with Tris(5-Hydroxypentyl) Citrate

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Abstract

New polyol (citrate) for the production of PUR-PIR foams was obtained. The hydroxyl number of the obtained compound is 496 mg KOH/g. The amount of water in the new compound was 0.98%. Due to this amount, the foam recipe does not need to be modified. The obtained foam series contain from 0.1 R to 0.5 R of the new compound. The $T_{5\%}$ values were higher by about 50% for the foams examined under nitrogen. The foams showed similar $T_{10\%}$ values under both atmospheres. The $T_{20\%}$ were higher by around 15°C for foams heated in nitrogen. The difference in the $T_{50\%}$ was circa 150°C and foams heated in oxygen registered better value. The foams showed slight decrease in the $T_{5\%}$, $T_{10\%}$, $T_{20\%}$ and $T_{50\%}$ values in both atmospheres, as well as a decrease in the softening temperatures, along with the increasing amount of the tris(5-hydroxypentyl) citrate compound in them. New compound is new product, doesn't described in literature. It has good thermal properties as industrial polyols but it is cheaper. Foams with this product have good thermal properties and they may be used in the building industry for thermal insulation.

Keywords: Polyurethane foam; Citric acid; Pentane glycol; Thermal properties; TG

Introduction

Constant technological development in the polymer field and widening the range of their use impose great requirements regarding their properties. One of the demands for macromolecular compounds is thermal stability during processing and their application. In the recent years it has become more important to obtain polymers with increased thermal stability.

The term "thermal stability" is often used to describe thermal durability or resistance, as well as heat resistance. Polymers with higher thermal stability are characterized by: higher temperatures of melting, softening and thermal decomposition, smaller mass loss during heating in higher temperature, higher heat deflection temperature under load, and less significant changes of their properties (physical, mechanical and chemical) during short-term and long-term exposure to higher temperature. Those parameters are usually considered as criteria for the assessment of specific polymer's thermal stability. The improvement of thermal stability can be achieved by various measures: by choosing the right structure, by increasing the crystallinity level, by incorporating strongly polar or stereoregular groups, by limiting the rotation range in the chain using high-volume groups, by cross-linking, by using cyclic monomers [1,2]. In the temperature above 400°C, almost all polymers decompose in the presence of oxygen. The literature sources also describe that foam's thermal stability decreases along with the lowering of foam's density. In lower temperatures, the speed of foam decomposition is comparable in vacuum, oxygen and nitrogen environments, however in higher temperatures the foam decomposes the quickest in vacuum, and the slowest in oxygen environment [3].

The method of synthesizing polyurethane foams with increased resistance was described by Ożóg and Lubczak [4-6]. The authors proved that by adding polyetherol produced with cyamelure ring to foams, they increased their thermal resistance.

Polymers' thermal stability is connected to their chemical structure, the bond energy between individual atoms comprising the material (energy of dissociation into radicals). Multiple bonds (e.g., C=N, C=C) or bonds containing e.g., boron, nitrogen, silicon: C-F, B-O, B-N, Si-O, have high energy value. The thermostability of polymers, in which those bonds are present, is higher than in polymers with only C-C

polymers. The type of environment plays a significant role here as well, e.g., the substituents' character, the type of neighboring atoms, and so-called "macroscopic" factors, such as the structural unit and the structure of the entire macromolecule, especially the cyclic structure and the bridges between aromatic and heterocyclic links.

To determine the comparison scale of different polymers, the term "polymer's half-live temperature" was introduced. The sample heated for 45 minutes loses 50% of its initial mass (Th thermostability) [1,2].

When it comes to foams, thermal and heat resistance are significant parameters, especially when the foams are used in construction (e.g., as insulation) or automotive industries [7]. Thermal resistance is related to foam's physical changes taking place under increased temperature and applied force. They are often characterized by providing softening temperature and the method of determining it [8]. In polyurethane foams, the softening temperature is lower by couple dozens of degrees from the foams' decomposition temperature. Thermal resistance is related to the worsening of properties connected to mass loss. Those properties change due to changes in temperature during foam utilization in specific conditions. The material decomposes and molecules with smaller molecule weight are produced [9].

Thermal resistance of polyurethane foams is mainly related to the thermal dissociation temperature of the weakest bonds in them. Depending on the raw materials used and the equivalence ratio of -NCO to -OH groups, the urethane bonds (with dissociation temp. of 200°C) can be present along with ester bonds (with dissociation temp. of 260°C), ether bonds (with dissociation temperature of 350°C), allofanian bonds (with dissociation temp. of 106°C) and other bonds [9-14].

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As a result of a reaction with polyisocyanurate, when using water to produce CO₂ (porophor), urea and biuret bonds are created with the dissociation temperature of 250°C and from 130°C to 145°C respectively [15]. When there is too much polyisocyanurate in relation to polyol, isocyanurate bond with the dissociation temperature of circa 300°C and carbodiimide bond with the dissociation temperature of circa 240°C are introduced into the chain of the macromolecular compound.

Thermal properties of the polyurethanes are dependent on their mechanical properties [16]. Foams with closed cells show higher thermal stability than those partially comprising of open cells. The mass loss of polyurethane foams depends on the porophor used for their production [17].

Besides the abovementioned, the types of polyol used for the synthesis, as well as the conditions (nitrogen, oxygen atmosphere) have an influence on foams' thermal properties [12]. The study conducted under nitrogen showed that foams are less stable in higher temperatures (250-400°C) than the same foams examined under oxygen. The amount of polyol in rigid polyurethane foams also has an influence on their thermal properties [18]. The increase of, for example, bio-polyol, produced based on sugar cane, causes a shift of foam's first weight loss temperature towards higher temperatures.

Often the temperature at which 5% (T_{5%}) or 10% (T_{10%}) mass loss is reached (in relation to the initial mass) is taken as a measure of thermal stability. Thermal stability examinations are conducted under neutral atmosphere (nitrogen, oxygen), oxidizing atmosphere (oxygen, air) or under other gases, e.g., carbon dioxide [19].

Moreover, the term "thermal analysis", in accordance with ICTAC (*International Confederation for Thermal Analysis and Calorimetry*) recommendations, describes the analysis of the dependencies between substance's specific property and its temperature, towards which the sample is heated or cooled in controlled environment [20]. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are the most popular techniques of thermal analysis used in polymer analysis. The examination of polymer structures using thermal analysis techniques is rather widely applied [21]. However, some special attention needs to be directed towards such phenomena as: determining the crystallinity level of a polymer, the glass state phenomenon, determining the range of melting temperatures, and measuring the enthalpy of phase changes. Especially interesting seems to be the use of DTA and DSC techniques in the examination of polymers' thermal and oxidation stability. The TGA technique determines the relation of the mass of the sample to the steadily increasing temperature, and to the time of the sample heating in constant temperature [19].

Particularly interesting is the combination of thermogravimetry with thermal analysis because during single analytical procedure, simultaneously two parameters are being measured, i.e., changes in the mass and thermal effects. In the case of distilling or subtilizing products (e.g., enriching supplements), the decomposition temperature has the value of the temperature, at which the first changes in thermogravimetric curve (TG or DTG) can be observed [22]. Differential scanning calorimetry (DSC) enables the measurement of the difference in heat streams flowing among the model foam, examined sample and the sensor. The measurement is performed in isothermic conditions or with programed temperature increase. The DSC curve (as well as DTA) registers thermal effects using characteristic points, e.g.,

- ❖ Temperature of thermal effect start T₀/ end T_k
- ❖ Temperature of extreme point T_{max}
- ❖ Effect amplitude at the extreme point ΔT_{max}
- ❖ Square surface of thermal effect S [23-26]

Thermal decomposition (degradation, destruction) is an important issue considering polyurethanes. Macromolecular compounds react, among others, with oxygen when subjected to heat and UV radiation, which can result in changes in chemical composition, degradation or destruction. Products capable of further reactions are created, which initiate depolymerization reactions, e.g., in reaction with oxygen, a hydrogen peroxide group, that can break into radicals capable of further reactions, is created in the polymer chain.

A process of polymer decomposition called pyrolysis can take place under the influence of high temperature in the atmosphere of neutral gas or in vacuum. As a result of this process, volatile gases and polymer fragments are produced. The temperature and the speed of polymer pyrolysis depends on its thermal stability and chemical reactions of the decomposition (i.e., depolymerization, destruction and degradation) happening in current conditions. For the material to be decomposed, an adequate energy needs to be supplied which will be sufficient to break the bonds between individual atoms, from which those compounds are built. The amount of polymer activation energy decides whether this reaction can take place.

Thermal decomposition of the materials is an endothermic and an irreversible process initially conducted under externally supplied heat and later on, under heat produced during the burning process. Due to the fact that the material surface warms up quicker than the lower layers, a gradient of temperatures is created and the pyrolysis speed is the largest on the material surface. When the material has a large specific surface area, the surface heating decides about the pyrolysis speed. In relation to that, foamed materials, spongy, in the form of foil, etc. that have large specific surface area are the largest fire hazard in the presence of air. During thermal decomposition, depending on the material type, the following products may be produced:

- a) flammable gases or vapors that burn in the presence of air (methane, ethane, ethylene, formaldehyde, acetone, carbon oxide),
- b) nonflammable gases or gases that does not burn in the presence of air-carbon dioxide, hydrogen chloride, hydrogen bromide, water steam,
- c) liquids, usually partially decomposed polymer and organic compounds with large molecular weight
- d) solid products-usually charred remains, charcoal or ash,
- e) shattered solid particles or polymer fragments in the form of smoke [13,27,28].

The synthesis of new cheap polyol for rigid PUR-PIR foams was the aim of the research. The polyol was synthesized using the cheapest carboxyl acid available on the market. The synthesis of the new compound using the acid was possible because it contained the -OH functional groups. The availability of this acid enabled the synthesis of a cheap polyol. The properties of the obtained polyol were not much different from the industrial polyols, which makes it suitable for foam synthesis. The foam obtained using the polyol have properties similar to the foams obtained using industrial polyol (Rokopol RF551).

Experimental and Methods

Characteristics of raw materials

The Rokopol RF551 polyether (polyoxypropylenehexol with 400÷440 mgKOH/g hydroxyl number, molecular weight of 660) produced by Zakłady Chemiczne PCC Rokita S.A. in Brzeg Dolny (Table 1), and a technical diisocyanate Ongromat CR 30-20 produced in Hüls (Hungary), whose main component is diphenylmethane 4,4'-diisocyanate, were used to prepare rigid PUR-PIR foams. The density of Ongromat at 25°C was 1.23 g/cm³, viscosity was 200 mPa.s and the content of NCO groups was 31.0%. The polyether and diisocyanate were characterized according to ASTM D 2849-69 and ASTM D 1638-70 standards. The catalyst used to produce the foams was anhydrous potassium acetate (POCh Gliwice) applied in a form of 33% solution in diethylene glycol - DEG (catalyst 12), and "DABCO 33LV" (triethylenediamine, Hüls, Germany) applied in a form of 33% solution in DEG. The foam structure stabilizer was polyoxosilanepolyoxyalkene surfactant, Silicone L-6900" (Witco, Sweden). Carbon dioxide formed during a reaction of water with isocyanate groups acted as blowing agent. A liquid flame retardant Roflam P (TCPP, tri(2-chloro-1-methylethyl) phosphate), Albright and Wilson, Great Britain, was added to the foams. Foam synthesis was conducted by adding new compound E16.

For obtaining new E16 and the monohydrate N 1560 2-hydroxypropane-1,2,3-tricarboxylic acid produced by Brenntag Poland LLC company in Kędzierzyn Koźle (storage in Toruń) was used. The amount of water in the acid was 7.5-8.8%. The acid was dried in ventilated drier until the water volume reached 3.35%. The water amount was measured in a moisture analyzer according to the PN-A-79005-04/1997 Polish Standard. The 1,5-pentanediol (1,5-PD) - E16 was used in the synthesis (producer - POCh, Gliwice).

E16 compound was added to the foams in the amount of 0.1 to 0.5 R (equivalent) to the Rokopol RF551 quantity, which was reduced from 0.9 to 0.5 R.

The synthesis process of tris(5-hydroxypentyl)-2-hydroxypropane-1,2,3-tricarboxylate (E16) for PUR-PIR foams

New compound was synthesized by esterification with solvent method. In reaction 1, 1,5-pentanediol (1,5-PD) was used as alcoholic compound, producing E16 compound (equation 1). In this reaction the 2-hydroxypropane-1,2,3-tricarboxylic acid was the acidic compound.

In synthesis 1, 0.04% of the catalyst was used which was the Lewis acid by the name of tetraisopropyl titanate (market name-Tyzor TPT) produced by Du Pont. It is a transparent, yellowish liquid, very sensitive to moisture, with a freezing temperature of 19°C. It crystallizes in low temperatures (however after rising the temperature again, it is re-useable). It contains 28.1% TiO₂. Its molecular mass equals 284 g/mol, density in 20°C is 0.95 g/cm³, viscosity 3.5 mPa.s, boiling temperature 232°C. It mixes with most organic solvents.

Synthesis was conducted in three-neck glass flask (500 ml vol each) equipped with reflux condenser, thermometer, stirrer and Deana-Stark's head. The reaction took place under xylene. The generated water was collected in the head. Flask contained 1,5-PD in the amount of 156 g, which was mixed with 2-hydroxypropane-1,2,3-tricarboxylic acid (96 g). 0.096 g of catalyst was added at the end of synthesis 1. Flask was heated for about 20 minutes in an electric bath (until the acid dissolved, i.e., about 85°C). It was heated until the substances inside them boiled. From this moment the reaction time was measured. Synthesis 1 took

8.5 hours altogether. The temperature of the reaction was 161°C. As a result of the synthesis 1 (Scheme 1) was citrate (polyol).

Obtaining PUR-PIR foams

The foams were prepared on a laboratory scale using one-stage method from 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 - 1800 rpm, mixing time 10 s) of the appropriate amount of Rokopol RF-551, new compound E16, catalysts, flame retardant, surface-active agent and porophor (water). The amount of water was reduced by the content of water in E16. Component B was Ongromat 30-20 (Table 1). Both components were mixed (10 s mixing time) in an appropriate mass ratio and were poured into a metal open rectangular mould with dimensions of 195 × 195 × 240 mm (internal dimensions). Serie P16 (with E16) of foams was obtained by this method.

For raw materials containing reactive hydroxyl groups, a so-called R equivalent was calculated according to the equation:

$$R = \frac{56100}{L_{OH}}$$

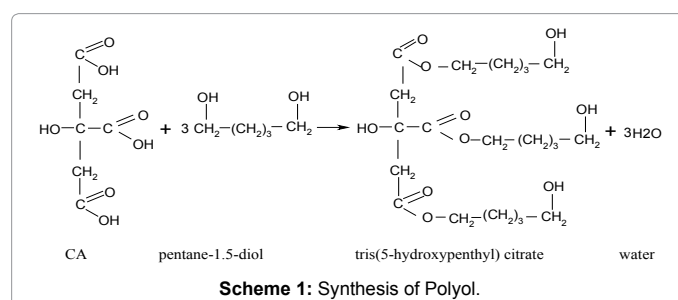
in which L_{OH} – stands for the hydroxyl number.

Measurements

Citrate: Hydroxyl number of citrate was performed according to WT/06/07/PURINOVA formula, Purinova Bydgoszcz. The viscosity at the temperature of 25°C (EN ISO 12058-1) using a Hoeppler viscometer. The density of polyols in the pycnometer was measured at 25°C (298 K) according to PN-92/C-04504. Depends on the number of hydroxyl number of E16 used in the foam and the polyisocyanate

Compound	Unit	W	P16.1	P16.2	P16.3	P16.4	P16.5
Rokopol RF-55	R	1	0.9	0.8	0.7	0.6	0.5
	g	66.8	60.1	53.4	46.8	40.1	33.4
E16	R	0	0.1	0.2	0.3	0.4	0.5
	g	0	6.4	12.9	19.3	25.7	32.2
Silicon Tegostab 8460	g	4.7	4.7	4.7	4.7	4.7	4.7
	%mas.	1.5	1.5	1.5	1.5	1.5	1.5
DABCO	g	2.9	2.9	2.9	2.9	2.9	2.9
	%mas.	0.9	0.9	0.9	0.9	0.9	0.9
Catalyst 12	g	6.7	6.7	6.7	6.7	6.7	6.7
	%mas.	2.1	2.1	2.1	2.1	2.1	2.1
Roflam P	g	47.6	47.6	47.6	47.6	47.6	47.6
	%mas.	15	15	15	15	15	15
Water	R	0.7	0.7	0.7	0.7	0.7	0.7
	g	3.15	3.14	3.14	3.13	3.12	3.11
Ongromat 30-20	R	3.7	3.7	3.7	3.7	3.7	3.7
	g	250.7	250.7	250.7	250.7	250.7	250.7

Table 1: Formulation for P16 foam series.



necessary to produce foam. Density and viscosity are very important during the processing process. 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 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.

Foams: Times of foam processing were measured during foaming i.e., start time, time of expansion and time of gelation (always counted from the moment of mixing of all components). Start time -to achieve a state of cream, which is the start of volume expansion foam). Time of expansion-increase the time until you have the maximum foam volume. Time of gelation-total gel time until the free surface of the foam stops to attach a clean glass rod.

During the synthesis and right after its end, the temperature of processes occurring inside the foam was measured for 1.5 h. The temperature changes were measured using thermocouple, whose sensor was placed inside the foam. The measurements were taken every minute.

Foams were thermostated for 4 h at the temperature of 120°C. They were then seasoned for 48 h at temperature of 20 ± 4°C and cut into pieces.

Their thermal properties as well as changes in linear, volume and mass dimensions were determined under increased temperature (120°C) in relation to initial sample length, volume and weight according to ISO 1923:1981 and PN-ISO 4590:1994.

Thermal resistance (thermostability) was measured with a derivatograph operating in Paulik-Paulik Erdey system produced by MOM-Budapest. Softening point was measured with Vicat apparatus in compliance with DIN 53424 standard, changes in linear dimensions, volume and weight after 48 hours of thermostating in ventilated drier at 120°C. Heating to 1000°C under oxygen or nitrogen with heating rate of 5°C/min.

Softening temperature was made by Vicat according to PN-EN ISO 306:2005. Determining the temperature in which a normalized needle immerses into the surface of the tested sample 1 mm deep, under appropriate weight with the temperature rising at steady speed.

The examination of melting point was conducted using camera Boetius.

The examination of changes in foams was conducted using DSC Q200 differential scanning calorimeter by TA Instruments. The apparatus range of work is from -90°C to +725°C (foams examinations were conducted in a range from 0°C to 400°C). The apparatus has built in Advanced Tzero technology. The DSC examination was performed under nitrogen and oxygen atmospheres. The weighted portion was 4 mg.

Thermal resistance (thermostability) was measured in two ways:

a. In air atmosphere with a derivatograph operating in Paulik-Paulik Erdey system produced by MOM-Budapest. Heating speed was 5°C/min, weighted portion was 100 mg. Heating to 1000°C

b. Under nitrogen atmosphere using thermogravimetric analyzer: TG Q500 by TA Instruments. Heating to 1000°C. The sample's weighted portions were 80 g. Heating speed was 10°C/min

FTIR examinations were performed using FTIR Spectrophotometer: Nicolet iS10 by Thermo Scientific, with spectrum range from 7800 to 350 cm⁻¹ and with maximum resolution capability <0.4 cm⁻¹ with DTGS detector.

FTIR analysis was marked in compliance with the standards in force. Laser beam (in an infrared spectrum of 4000 to 500 cm⁻¹) was passed through a sample in form of film, liquid substance (polyol) or a pill (foam sample in KBr). The presence of function groups in the compound was being determined.

Elemental analysis of E16 was performed using EA 1108 Carlo-Erba analyzer (Vario). Content of carbon and hydrogen were measured.

Number-average molecular weight (M_n), weight-average molecular weight (M_w), z-average molecular weight (M_z) and molecular weight distribution were determined using Viscotec T60A gel chromatograph equipped with three detectors' system: RI (refractive index detector), LS (light scattering detector) and DV (viscometer detector). Separation has been performed using two independent columns: PSS SDV (of 7.8 mm × 300 mm size with TSK bed-100 and 1000 Å pore diameter gel, using the following recording parameters: temperature 25 ± 0.1°C, volume flow of eluent 1 ml/min, the injection loop volume of 20 ml, concentration of polymer solution 4-5 mg/ml, analysis time 30 min. THF was used as eluent (distilled from over sodium prior to use). Calibration was based on common polystyrene references.

The remaining physico - mechanical properties (endurance, brittleness, absorptiveness, heat conductivity and others) will be the subject on other papers.

Results and Discussion

Citrate E16

In the laboratory the Department of Chemistry and Technology of Polyurethane resulted the product of synthesis of 2-hydroxypropane-1.2.3-tricarboxylic acid (citric acid) with pentane-1.5-diol with the use of 0.04% catalyst (Tyzor TPT) named tris(5-hydroxypentyl) citrate (E16). It is characterized by 496 mgKOH/g hydroxyl number. It is a straw-yellow liquid characterized by 496 mgKOH/g hydroxyl number. The hydroxyl number is the basic parameter of the oligomerol that is needed to calculate the polyurethane compound recipe. Based on that, the R equivalent is determined, which corresponds to the amount of compound containing hydroxyl groups (oligomerol) in relation to the amount of remaining foam components. The R equivalent is calculated according to the following equation (5):

$$R = \frac{56100}{HN} \quad (5); \text{ R-equivalent, HN - hydrogen number}$$

It is very important to arrange the foam recipe and to determine the amount of water in the used polyurethane polyol. Water is added to the foam as a blowing agent. Excess water can cause cracking of the foam cells or even its fall. The value of hydroxyl number is within the range of HN of industrial polyols. As a result of that, the foaming process of PUR foams with the addition of the new E16 compound should progress similarly to the synthesis of foams with polyols available on the market.

The results of the examination of the new E16 compound show that density (equaling 1.053 g/cm³) does not limit the possibilities of using it in apparatuses for the synthesis of rigid PUR-PIR foams. The E16 viscosity (equaling 10364.1 mPa·s) is close to the viscosity that should be characteristic of raw materials used in standard appliances for PUR processing available on the market, i.e., 15000 mPa·s.

Also, the pH value of E16 (5.1) is close to the range defined by the pH of standard polyols [from 6.5 (Rokopol RF-55) to 8.7 (Rokopol 4845)]; that is why there is no need to expect great differences in the process of obtaining rigid PUR foams containing various amounts of E16, which was added instead of the commercial polyols.

The E16 compound contained 0.98% of water. The amount of water in the polyol is a significant parameter, especially in foams foamed with water. When the recipe is being determined, the amount of water in the oligomerol needs to be accounted for to choose the right water amount for foaming. The polyol added to polyurethane foams should not contain more than 1% of water.

As a result of the reaction using Dean Stark head, 27.7 cm³ of water was distilled which was in correspondence with the stoichiometric calculation of water amount (27.0 cm³).

The melting temperature was determined using Boetius apparatus. The method's principle was to observe the moment, when there would be the complete disappearance of crystallinity phase as a result of constantly increasing temperature. The T_i melting temperature of the acid component used in the synthesis of the new E16 compound (citric acid) was 158°C, and the T_r was 164°C. However, for the newly obtained E16 compound $T_i=190^\circ\text{C}$, $T_r=270^\circ\text{C}$.

The percentage value of carbon in the E16 compound was 54.31%, which is close to the calculated value (53.09%). The amount of hydrogen is 9.25% and it also did not deviate from the calculated value, which equals 7.96%. The examined molecular mass of the E16 compound is 310 g/mol and differs by 10% from the value calculated molecular weight.

Thermal properties of E16

Heat resistance plays a significant role in determining whether a specific polyol is useful for foam synthesis. Using a polyol with better thermal stability increases the temperature range of foam application. The E16 thermal stability was tested under neutral atmosphere (in nitrogen). The results were compared with the thermal stability of the industrial Rokopol RF551 (Tables 2 and 3). Based on TG curve (weight change) and DTG (Figure 1) curve (derivative weight change) the following characteristic quantities were measured (Table 3): the temperature of the foam's first weight loss (T_1 , °C), the temperature of beginning of the decomposition (T_2 , °C), and the temperature of the foam's highest speed of weight loss, so-called maximum of thermal effect (T_{max} , °C, corresponding to the extreme on the DTG curve).

During the first stage of E16 decomposition (up to 135°C temp.) it can be observed that the compound lost circa 1.5% of its weight. This can be attributed to the water vaporizing after it was released due to the breaking of hydroxyl bonds. The quickest mass loss, which was circa 20%, can be observed at 292°C temperature, i.e., before reaching the square surface equal to the heat effect ($T_{max}=366.1^\circ\text{C}$).

Polyol	Temperature of the foam's first weight loss		Temperature of beginning of the decomposition		Maximum of thermal effect	
	T_1 , °C	Mass loss, %	T_2 , °C	Mass loss, %	T_{max} , °C	Mass loss, %
Rokopol RF551	160	1	205	5	411	70
E16	135	1.5	169	4	366	55

Table 2: Temperature of the beginning of mass change, decomposition start and the beginning of quickest mass loss in the E16 compound (in nitrogen atmosphere).

Polyol	$T_{5\%}$, °C	$T_{10\%}$, °C	$T_{20\%}$, °C	$T_{50\%}$ (T_h), °C	Pozostałość w temp. 800°C, %
Rokopol RF 551	205	284	378	404	0
E16	170	212	292	358	1,5

Table 3: Thermal stability of E16 compound (in nitrogen atmosphere).

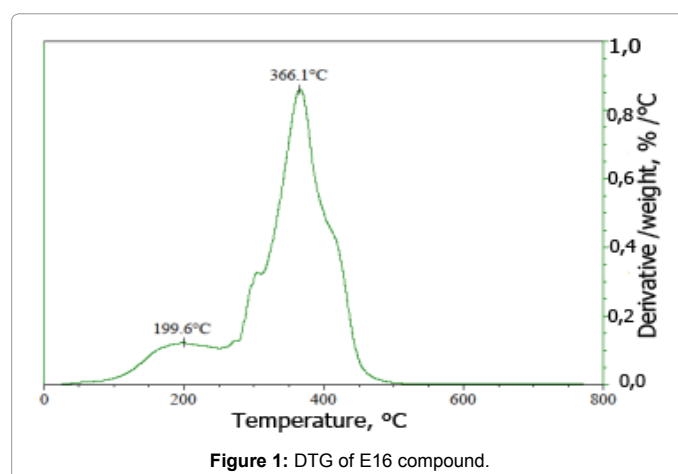


Figure 1: DTG of E16 compound.

The thermostability was defined as the temperature, at which the compound loses 5% or 10% of its mass. A so-called temperature of compounds half-live (T_h) was also determined, at which the 50% mass loss occurred. The 5% mass loss under nitrogen atmosphere for the E16 (Table 4) occurs at 170°C temp., and the 10% at 212°C temp. The 20% mass loss for the E16 compound was also determined (292°C). Moreover, the T_h was 358°C, and the T_{max} was equal 366°C. At 800°C temperature, only 1.5% of the E16 is left (as ash).

The heat resistance of the described E16 compound is lower by over a dozen percent from the industrial polyols used in rigid foam production. Namely, the quickest mass loss (of 70%) under nitrogen atmosphere in case of industrial used polyol-Rokopol RF-551-is reached at maximum thermal effect $T_{max}=411^\circ\text{C}$. In the case of the E16, the highest mass loss (at $T_{max}=366^\circ\text{C}$) is 55%.

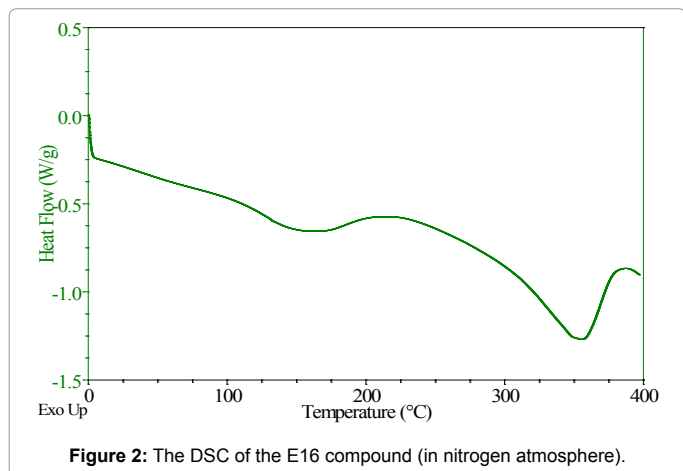
When comparing the thermal stability (under nitrogen atmosphere) of the industrial polyol (Rokopol RF-551) with the applied E16 compound, a lower temperature of the beginning of mass change by 15.6% can be seen for the E16, lower temperature of the decomposition start by 17.5% and lower temperature of the maximum of thermal effect by 10.9%.

An examination of the E16 compound, obtained in the laboratory of the Department of Chemistry and Polyurethanes' Technology, was performed using DSC method under nitrogen atmosphere. Based on the DSC curve (Figure 2), two endothermic changes were observed. The beginning of E16 melting at 108°C. The proper melting temperature is 147°C and the enthalpy (H) at this point is 50.5 J/g. Second endothermic peak was also observed on the DSC curve. The beginning of melting happens at 304°C temperature, and the proper melting occurs at 354°C, enthalpy H=165 J/g. The first peak is connected to the degradation of -OH bonds and with the loss of water, which absorbed only 50.5 J/g of the heat. The second peak is related to the degradation of ester bonds, for which 165 J/g of the heat was needed.

Processing and thermostating parameters of PUR-PIR foams (P16)

The obtained E16 compound was used as a component in polyol premix for rigid PUR-PIR foams instead of the industrial Rokopol RF551. A series of 16.0-16.5 foams containing 0-0.5 R of the E16 was produced this way.

The addition of E16 had an effect on the processing parameters of the foams that increased lineally along with the increase of the E16 compound (Table 4). The increase in those parameters is caused by



Foam	Start time, s	Growth time, s	Gelation time, s
P16.0	10	30	27
P16.1	17	44	46
P16.2	19	48	44
P16.3	20	53	65
P16.4	21	60	82
P16.5	25	61	92

Table 4: Processing parameters of P16 foams.

the greater viscosity of polyol premix, whose value rises along with the amount of E16 in it. Therefore, the premix viscosity not only has an effect on the mixing of the components, but also on the elongation of processing times. The foaming speed influences the cellular shape. If the foaming reaction proceeds slowly, the cells become isotropic in shape which positively influences the application properties of the foamed materials, as they show identical values regardless of the examination direction.

The temperature changes during 90 minutes were determined in the foam (16.3 foam) after its production and taking it out of the mould (Figure 3). The time was measured from the moment of foam's rising start. In the first 29 minutes, the temperature outside of the foam increases and reaches the maximum value (132°C) in the 29th minute of the examination. This value stays unchanged for couple of minutes and then the temperature falls to 119°C, and in the 41st minute the cooling of the foams begins. A rapid decrease can be observed in the time from 41st and 53rd minute. Later on, a more gentle decrease is seen for the next 71 minutes until the 67°C temperature is reached (after 91 minutes of examination). The changes in temperature during foam's seasoning in the first 1.5 hours, after it is produced, are caused by the changes occurring in the foam due to the occurring reactions. The increase of the reaction mixture temperature is caused by the exothermic reactions of isocyanate groups with water.

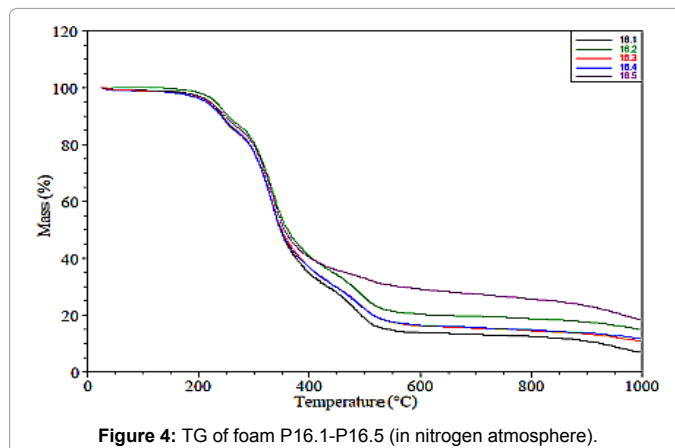
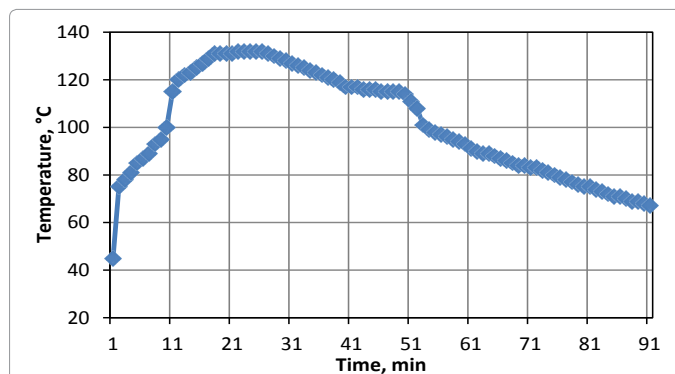
The amount of E16 compound in the foam does not have any effect on the mass change after 48 h of foam's thermostating in the 120°C temperature (Table 5). The values range from 1.1% (P16.1 foam containing 0,1R of the E16 compound) to 1.2% (foams P16.2 and P16.5) and to 1.4% (foams P16.3 and P16.4). A lack of visible linear dependency can be seen when it comes to changes in dimensions or volume of the foams after 48 h of thermostating, in relation to the amount of tris(5-hydroxypentyl) citrate (E16) in them. Those changes are very small and do not exceed 2.5% are probably are caused by the reaction in the presence of foams which occur during tempering foams.

Thermal and heat parameters of PUR-PIR foams (P16)

The TG foam analysis was conducted in neutral atmosphere in nitrogen (Figure 4) and in oxidizing atmosphere (mixture of nitrogen and oxygen). Based on TG curve (weight change) and DTG curve (derivative weight change) the following characteristic quantities were measured (Table 6): the temperature of the foam's first weight loss (T_1 , °C), the temperature of beginning of the decomposition (T_2 , °C), and the temperature of the foam's highest speed of weight loss, *tzw.* so-called maximum of thermal effect (T_{max} , °C, corresponding to the extreme on the DTG curve).

Table 6 shows the dependence of T_1 , T_2 , T_{max} temperatures on the amount of E16 in foam series 16 in nitrogen atmosphere. With the increasing amount of OR (equivalent) to 0.5 R of the E16, the temperature of the first foam's weight loss T_1 (the beginning of weight change) slightly decreases from 77°C (16.0 foam containing 1 R of industrial Rokopol RF-551) to 75°C (16.5 foam containing 0.5 R of E16). The addition of more and more E16 also causes the decrease in beginning of the decomposition T_2 , from 293°C (16.0 foam) to 219°C (16.5 foam). E16 additive does not affect the temperature of the beginning of the fastest decomposition (T_{max}) of the foam and as soon as the loss of weight in T_{max} . The decrease in temperature of the beginning of the decomposition from 293°C (16.1) to 217°C is caused by a slightly poorer thermal stability of the added E16, in comparison to the thermal stability of Rokopol RF-551.

The foams' thermostability is described as $T_{5\%}$ and $T_{10\%}$, and as $T_{20\%}$ (Table 7). A so-called "polymer's half-live temperature" was also determined-a temperature, in which the sample lost 50% of its initial weight (thermostability T_h). The temperature $T_{5\%}$, $T_{10\%}$, $T_{15\%}$,



Foam	Sample's dimensions changes according to the growth direction $\Delta l_z, \%$	Sample's dimensions changes opposite to the growth direction $\Delta l_z, \%$	Volume change, $\Delta V, \%$	Mass change $\Delta m, \%$
P16.0	0.0	0.0	0.0	0.0
P16.1	-1.10	-1.10	-0.90	1.1
P16.2	-0.17	0.05	1.10	1.2
P16.3	0.02	2.10	1.08	1.4
P16.4	0.01	1.60	2.40	1.4
P16.5	-0.06	-0.38	-1.20	1.2

Table 5: The stability of lineal dimensions, volume and mass of the foams after 48 hours of thermostating in 120°C temp.

Foam	First weight loss		Beginning of the decomposition		Maximum of thermal effect	
	Temp. $T_1, ^\circ\text{C}$	Weight loss, %	Temp. $T_2, ^\circ\text{C}$	Weight loss, %	Temp. $T_{max}, ^\circ\text{C}$	Weight loss, %
In nitrogen atmosphere						
16.0	80	0.5	205	4	336	30
16.1	77	0.5	293	5	334	55
16.2	76	0.5	225	3	336	53
16.3	75	0.5	214	5	334	56
16.4	75	0.5	210	4	334	59
16.5	75	0.5	217	4	336	52
In air atmosphere						
16.0	50	0.5	200	4	304	35
16.1	70	0.5	160	3	299	28
16.2	70	0.5	160	3	299	28
16.3	70	0.5	160	3	298	27
16.4	70	0.5	160	3	298	27
16.5	70	0.5	160	3	297	26

Table 6: The temperature of the foam's first weight loss (T_1), the temperature of beginning of the decomposition (T_2) and the temperature of beginning of the fastest decomposition of the (T_{max}) (in nitrogen and in air).

Foam	$T_{5\%}, ^\circ\text{C}$	$T_{10\%}, ^\circ\text{C}$	$T_{20\%}, ^\circ\text{C}$	$T_{50\%} (T_n), ^\circ\text{C}$	The residue at 1000°C temp, %
In nitrogen atmosphere					
16.0	226	255	304	387	19
16.1	221	243	293	348	7
16.2	231	253	302	360	15
16.3	214	241	292	350	15
16.4	213	241	292	348	12
16.5	212	240	291	345	10
In air atmosphere					
16.0	200	270	303	480	0
16.1	174	248	286	500	0
16.2	174	249	286	500	0
16.3	174	249	286	499	0
16.4	174	250	287	499	0
16.5	174	250	287	499	0

Table 7: Thermal stability of PUR-PIR foams (in nitrogen and in air atmosphere).

$T_{20\%}$ decrease with increasing amounts of the new compound tris (5-hydroxypentyl)-2-hydroxypropane-1,2,3-tricarboxylate in the case of testing on TG under nitrogen. Can't be observed linear relationship between the quantities in foam of described above compound and $T_{50\%}$. The addition of the compound doesn't affect the $T_{5\%}$, $T_{10\%}$, $T_{15\%}$, $T_{20\%}$ for TG test under nitrogen, and they are suitably 174°C, 250°C, 287°C and 500°C. In comparison with the reference foam 16.0 observed decreasing T_5 of about 26%, $T_{10\%}$ and $T_{50\%}$ of about 20°C and $T_{15\%}$ of about 15°C.

Softening point decreases from 230°C (16.0 foam without E16) to 169°C (16.5 foam with 0.5 R of E16) (Figure 5). The lowering of softening temperature is caused by the addition of 0-0.5 R of the E16 compound to the P16 foam series.

Temperatures of transformation studied by DSC method taking place within the 16.3 foam in an oxygen atmosphere and under a nitrogen atmosphere show the Figure 6. Foam examination using DSC method under oxygen atmosphere only registers foam decomposition starting at around 170°C temperature.

In the DSC chart (16.3 foam sample, Figure 6) of the examination conducted under nitrogen for 16.0-16.5 foams, three endothermic peaks are visible at T_a , T_b and T_c temperatures (sample 16.3 foam, Figure 6). Depending on the amount of E16 in the foams, the peak shift in time is not large and reaches maximum of 2 minutes (for the 16.5 foam in relation to the 16.0 foam). The enthalpy in respective temperatures (T_a , T_b , T_c) is about: 34 J/g, 9 J/g, 32 J/g.

The first T_a peak (at around 75°C temp.) is related to the diffusion of carbon dioxide from the foams, which acts as the porophor. It is created as a result of the reaction of excess isocyanate groups with water. At this temperature, a diffusion of triethylenediamine (DABCO) from the foams can occur. DABCO, as a 33% solution in dipropylene glycol, is used as the catalyst for PUR synthesis reaction.

The T_b peak is related to the decomposition of the urea (at 250°C) (produced as a result of polyisocyanate reaction with water) as well as to the decomposition of urethane group (at 200°C). In 260°C temperature also ester bonds decompose. The T_b for the 16 foam series is about 275°C. The last endothermic peak in T_c temperature is connected to the thermal dissociation of isocyanurate bonds (whose decomposition starts at 300°C temperature). The T_c for foams from 16 series, is 330°C.

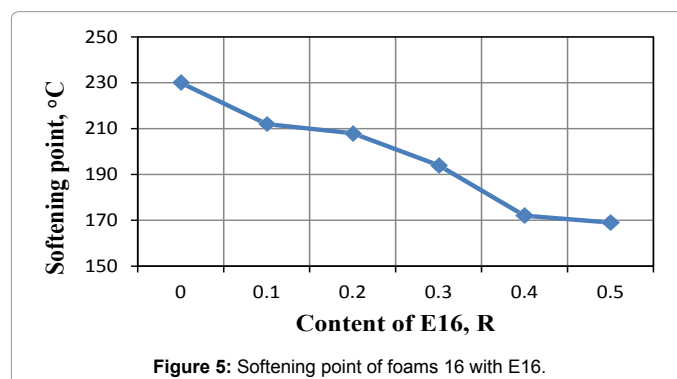


Figure 5: Softening point of foams 16 with E16.

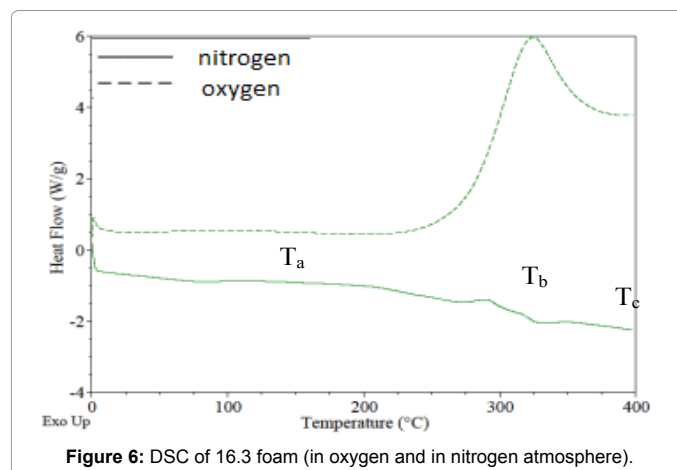


Figure 6: DSC of 16.3 foam (in oxygen and in nitrogen atmosphere).

Conclusion

New tris(5-hydroxypentyl) citrate as raw material for the production of PUR-PIR foams was obtained., the hydroxyl number of the polyols used in its synthesis must be determined. The hydroxyl number of the obtained compound is 496 mgKOH/g. The amount of water in the new compound was 0.98%. Due to this amount, the foam recipe does not need to be modified. The obtained foam series contain from 0.1 R do 0.5 R of the new compound. The foams, whose thermostability was examined, are characterized by higher T_1 , T_2 , T_{max} temperatures under nitrogen atmosphere, and by lower temperatures under oxygen. Moreover, under oxygen atmosphere the foams decomposed completely, and under nitrogen, 12-19% of the residue remained. The $T_{5\%}$ values were higher by about 50% for the foams examined under nitrogen. The foams showed similar $T_{10\%}$ values under both atmospheres. The $T_{20\%}$ were higher by around 15°C for foams heated in nitrogen. The difference in the $T_{50\%}$ was circa 150°C and foams heated in oxygen registered better value. The foams showed slight decrease in the $T_{5\%}$, $T_{10\%}$, $T_{20\%}$ and $T_{50\%}$ values in both atmospheres, as well as a decrease in the softening temperatures, along with the increasing amount of the tris(5-hydroxypentyl) citrate compound in them. The resulting tris(5-hydroxypentyl) citrate may be used in the synthesis of PUR-PIR rigid foam. The obtained foams can be successfully used as insulating boards (as a laminate), and as protective packaging during transport of the equipment, devices and glass.

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