Temperature stability and thermal properties of polyurethane-polyisocyanurate foams obtained using products of citric acid condensation

Joanna Liszkowska[1), *)], Bogusław Czupryński[1)], Joanna Paciorek-Sadowska[1)]

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Abstract: Three products were obtained from the condensation of citric acid with: propane-1,2-diol with the catalyst Tyzor TPT (HDCA1), propane-1,2-diol without a catalyst (HDCA2) and propane-1,3-diol with the catalyst Tyzor TPT (HDCA3). We measured the viscosities (from 3972 mPa · s for HDCA1 to 27 986 mPa · s for HDCA3), densities (about 1200 g/cm^3), hydroxyl values (280–427 mg KOH/g), and acid values (23–52 mg KOH/g) of the HDCAs. The thermal resistance of the HDCAs were assessed under dynamic conditions. The temperature ranges of 5, 10, 20 and 50 % weight loss for HDCA polyols were, respectively: 174–194 °C, 230–234 °C, 263–303 °C, and 314–364 °C. The HDCAs were used in the further synthesis of rigid polyurethane-polyisocyanurate foams (PUR-PIR) and their physical qualities assessed with reference to foams produced from an industrial standard (Rokopol RF 551). The authors examined the thermal properties (thermogravimetry, differential thermogravimetry and differential scanning calorimetry) of the foams, as well as the thermal stability: dimensional, volume and mass. The number of foam degradation stages was determined, as well as the speed of degradation of specific chemical bonds and percentage mass loss during all stages. We determined the temperature of the foam's first weight loss, the extrapolating temperature of the foam's weight loss, the temperature of the start of the foam's rapid decomposition, and the temperature of the foam's highest speed of weight loss, the temperatures of 5 %, 10 %, 20 % and 50 % mass loss were measured (respectively: 208–223 °C, 230–260 °C, 280–300 °C, 345–366 °C). The enthalpy related to each individual stage of foam degradation was examined using DSC (three endotherms and one exothermic peak).

Keywords: rigid polyurethane-polyisocyanurate foams, esterification, thermogravimetry, differential thermogravimetry, differential scanning calorimetry, propane-1,2-diol, propane-1,3-diol.

Stabilność temperaturowa i odporność termiczna pianek poliuretanowo-poliizocyjanurowych otrzymanych z udziałem produktów kondensacji kwasu cytrynowego

Streszczenie: Otrzymano trzy produkty kondensacji kwasu cytrynowego z: propano-1,2-diolem w obecności katalizatora Tyzor TPT (HDCA1), propano-1,2-diolem bez katalizatora (HDCA2) oraz propano-1,3--diolem w obecności katalizatora Tyzor TPT (HDCA3). Zbadano ich lepkość (od 3972 mPa · s dla HDCA1 do 27 986 mPa · s dla HDCA3), gęstość (ok. 1200 g/cm^3), liczbę hydroksylową (280–427 mg KOH/g) i kwasową (23—52 mg KOH/g) oraz odporność termiczną w warunkach dynamicznych. Zmierzono temperaturę 5, 10, 20 i 50 %-owego ubytku masy polioli HDCA (odpowiednio: 174–194 °C, 230–234 °C, 263–303 °C, 314–364 °C). Wytworzone hydroksyalkilowe pochodne użyto do syntezy sztywnych pianek poliuretanowo-poliizocyjanurowych (PUR-PIR). Zbadano właściwości termiczne pianek (metodami analizy termograwimetrycznej, różnicowej analizy termograwimetrycznej i różnicowej kalorymetrii skaningowej) oraz ich stabilność termiczną: wymiarową, objętościową i masową. Określono liczbę etapów degradacji pianek, szybkość degradacji poszczególnych wiązań chemicznych i procentowy ubytek masy na wszystkich etapach, temperaturę 5, 10, 20 i 50 %-owego ubytku masy pianek (odpowiednio: 208–223 °C, 230–260 °C, 280–300 °C, 345–366 °C). Określono entalpię poszczególnych etapów degradacji pianek metodą DSC (trzech pików endotermicznych i jednego egzotermicznego).

Słowa kluczowe: sztywne pianki poliuretanowo-poliizocyjanurowe, estryfikacja, analiza termograwimetryczna, różnicowa analiza termograwimetryczna, różnicowa kalorymetria skaningowa, propano-1,2-diol, propano-1,3-diol.

[1)] Kazimierz Wielki University, Faculty of Mathematics, Physics and Technical Science, Chodkiewicza 30, 85-064 Bydgoszcz, Poland.

[*)] Author for correspondence; e-mail: liszk@ukw.edu.pl

Current research studies on polyurethanes focus on, among other aspects, the search for new raw materials that could enable the improvement of the properties of new products with a minimal financial outlay [1–5]. Polymer thermal stability, durability at higher temperatures, is one of the most important factors in determining the useful application of these materials [6, 7]. Raw materials with an increased thermal stability affect the overall thermal stability in the product [8, 9]. Hence, in order to increase the thermal stability of polyurethanes, powder fillers that are resilient to decomposition at higher temperatures are added [10–12].

Insulation materials for building applications need good and long term thermal stability over a wide temperature range from -30 °C to 90 °C. Rigid polyurethane foam (PUR/PIR) insulation materials can withstand temperatures of up to 250 °C for short periods with no adverse effects [13, 14].

The thermal properties of tribological, biodegradable polyurethanes were examined by Karalus and others [13]. They specified that the thermal degradation of polyurethanes occurs in two or three stages. The $T_{2\,\%}$ temperature corresponds to the 2 % mass loss of the sample, which is a result of the emission of readily volatile products, *e.g.*, steam H_2O. When examining the PUR materials, this temperature increased with the amount of incorporated rigid sections, but decreased with an increasing amount of branches.

Thermogravimetry (TG)/derivative thermogravimetry (DTG) analyses of polyurethanes from vegetable oils were carried out by Lopes and others [14]. They found that the PURs produced from polyols derived from vegetable oil, and without it, resulted in similar properties.

The thermal properties and thermal stability of polyurethanes obtained from glycolysates were investigated by Datta and others [15, 16]. The thermal stability investigation shows that the main decomposition occurs at temperatures of about 400 °C. The main products of thermal decomposition are carbon monoxide, carbon dioxide, compounds containing ether and hydroxyl groups, and probably acetaldehyde. Based on TG curves, it was concluded that polyurethanes obtained from glycolysates were thermally stable up to 270 °C. The influence of carbon fillers on the thermal properties of polyurethane foams was examined by Ciecierska and others [17]. It was found that both CNTs and graphite have a minor impact on the decomposition process during thermal degradation of polyurethane. The use of carbon fillers has a minor impact on the degradation process in air. The degradation process involving the emission of volatile products in air began earlier and at lower temperatures for the composites containing graphite.

The thermal and thermomechanical properties of low-density, rigid, polyurethane foams obtained from different aromatic polyols were investigated by Żabski and others [18].

This article describes the influence of polyols on the thermal resistance of PUR-PIR foams under static and dynamic conditions. It is a continuation of the physicomechanical [19] and flammability [20] examinations of rigid foams produced with hydroxyalkyl derivatives of citric acid (polyols).

The aim of the research is to investigate the possibility of replacing a petrochemical derivative polyol (Rokopol) with polyols originating from sustainable bioproducts (citric acid) in PUR-PIR foams. Those polyols, in the form of hydroxyalkyl derivatives of citric acid (HDCA), were produced in the Department of Chemistry and Polyurethanes' Technology at UKW in Bydgoszcz, Poland. The cost of obtaining new HDCA polyols is lower than the cost of synthesizing petrochemical polyols due to the low price of the raw material used for their synthesis – technical citric acid. Tests were performed to determine the optimum amounts of the polyols in the foam formulations. The influence of HDCAs on the thermal resistance of PUR-PIR foams was determined in comparison to the thermal resistance of the foam that contained an industrial standard (Rokopol RF 551, F0 reference foam). The purpose of this study was to produce raw materials to obtain foams with little altered dimensions, volume and mass when heated to 120 °C. The use of polyols with better thermal stabilities widens the temperature range of their application. PUR-PIR foams should also show the highest possible resistance to higher temperatures during their dynamic heating to 800 °C. The purpose for increasing the thermal stability in PUR-PIR foam products obtained with thermally stable polyols was to increase the range of applications of PUR-PIR products. The usefulness of the polyols for the synthesis of foams with increased thermal stability was determined. The temperatures for 5 %, 10 %, 20 % and 50 % mass loss were measured for foams during their heating, and the mass of the foam residue was determined when heated to 800 °C temperature. The temperature of the beginning of mass change (T_1), the beginning of decomposition (T_2), and the temperature of the beginning of the highest mass loss rate (T_{max}) of PUR-PIR foams were determined.

EXPERIMENTAL PART

Materials

Materials for the synthesis of HDCA1, HDCA2 and HDCA3

A technical monohydrate of citric acid (2-hydroxypropane-1,2,3-tricarboxylic) N 1560 produced by Brenntag Polska Sp. z o.o. Kędzierzyn Koźle was used to synthesize HDCA1, HDCA2 and HDCA3. Two glycols were also used: propane-1,2-diol (1,2-PD), propane-1,3-diol (1,3-PD), (POCh, Gliwice). Tetraisopropyl titanate Tyzor TPT (produced by Du Pont) was used as a catalyst.

Materials for the synthesis of PUR-PIR foams

As a reference polyol, polyoxypropylenediol (polyether polyol – Rokopol RF 551, with hydroxyl number 420 mg KOH/g, molecular weight 660, functionality 4.5), a product of Chemical Plants PCC Rokita S.A. in Brzeg Dolny, was used to prepare rigid PUR-PIR foams. The catalyst in the process of foam preparation was anhydrous potassium acetate (POCh Gliwice) applied in the form of a 33 % solution in diethylene glycol (Catalyst 12) and DABCO 33LV (Hülls, Germany) – 33 % solution of 1,4-diazabicyclo[2.2.2]octane in diethylene glycol. The stabilizer of the foam structure was poly(oxyalkilene siloxane) surfactant Tegostab 8460 (Witco, Sweden). Carbon dioxide formed in the reaction of water with isocyanate groups acted as the blowing agent. Moreover, liquid flame retardant tris-(2-chloropropyl)phosphate – Roflam P (Albright and Wilson, Great Britain) was introduced into the foam composition. Technical polymeric diisocyanate Ongronat 30-20 (BorsodChem, Hungary), whose main component was 4,4'-diphenyl-methane-diisocyanate (MDI), was used. The density of Ongronat 30-20 at 25 °C was 1.23 g/cm^3, viscosity 200 mPa · s, and the content of NCO groups was 31.0 %. Polyether and diisocyanate were characterized according to standards: ASTM D 2849-69 and ASTM D 1638-70.

Synthesis of polyols and foams

Preparation of condensates HDCA1, HDCA2 and HDCA3

The syntheses of hydroxyalkyl derivatives of citric acid (HDCA) were performed by esterification. The method is described in an earlier article [18]. To synthesize HDCA1, 96 g CA (citric acid) and 144 g 1,2-PD were used. The temperature of the reaction was 143–155 °C, time 6.5 h, yield 70.5 %. For the synthesis of HDCA2, we used 96 g CA and 114 g of 1,2-PD (temperature 154 °C, time 9.5 h, yield 72 %). HDCA3 was synthesized from 96 g CA and 114 g 1,3-PD (temperature 142 °C, time 5 h, yield 89.4 %). The quantities of raw materials used in the reactions result from the reaction stoichiometry 1 : 3 (CA : diol) for HDCA2 and HDCA3 and 1 : 3.8 for HDCA1. HDCA1 and HDCA3 syntheses were performed in the presence of 0.36 g of catalyst (Tyzor TPT; 0.06 % for HDCA1 and 0.17 % for HDCA3 in relation to the sum of the mass of CA and diol).

Synthesis of the rigid PUR-PIR foams

The foam was prepared on the laboratory scale by a one-stage method from a two-component system at the equivalent ratio of -NCO to -OH groups equal to 3 : 1. Component A was obtained by the thorough mixing (1800 rpm, 10 s) of Rokopol RF 551 from 1 *R* (*R* – chemical equivalent) (66.8 g) to 0.5 *R* (33.4 g), Catalyst 12 (6.7 g), catalyst DABCO (2.9 g), fire retardant Roflam P (47.6 g), surfactant Tegostab 8460 (5.4 g), and porophor (3.15 g of distilled water). The equivalent of hydroxyl groups R_{OH} was calculated according to equation:

$$R_{OH} = 56\,100/L_{OH} \quad (1)$$

where: L_{OH} – hydroxyl number of polyol.

The amount of water necessary for foaming was lowered proportionally to the amount of water in the condensates. Component B was polyisocyanate Ongronat 30-20 of an amount of 250.7 g. The amount of isocyanate was chosen based on the ratio of isocyanate groups to hydroxyl groups, which for the rigid polyurethane-polyisocyanate foams was 3 : 1.

Hydroxyalkyls (HDCA1, HDCA2 or HDCA3) were added to the amount from 0.1 *R* to 0.5 *R* (Table 1).

Table 1. Amount of polyols (in equivalent *R*) added to compositions of foams

Foam	Polyol			
	Rokopol	HDCA1	HDCA2	HDCA3
F0	1.0	0	0	0
F1	0.9	0.1	0	0
F2	0.8	0.2	0	0
F3	0.7	0.3	0	0
F4	0.6	0.4	0	0
F6	0.9	0	0.1	0
F7	0.8	0	0.2	0
F8	0.7	0	0.3	0
F9	0.6	0	0.4	0
F11	0.9	0	0	0.1
F12	0.8	0	0	0.2
F13	0.7	0	0	0.3
F14	0.6	0	0	0.4
F15	0.5	0	0	0.5

Components A and B were mixed (1800 rpm, 10 s) at their respective volumes of mass ratio and poured into an open rectangular tray of internal dimensions 190 × 190 × 230 (mm). In this way, three series of foams were obtained. The first, containing HDCA1 in its composition (foams F1–F5), the second with HDCA2 (foams F6–F10) and the third produced in the presence of HDCA3 (foams F11–F15). The reference foam F0 was synthesized from the petrochemical polyol Rokopol RF 551.

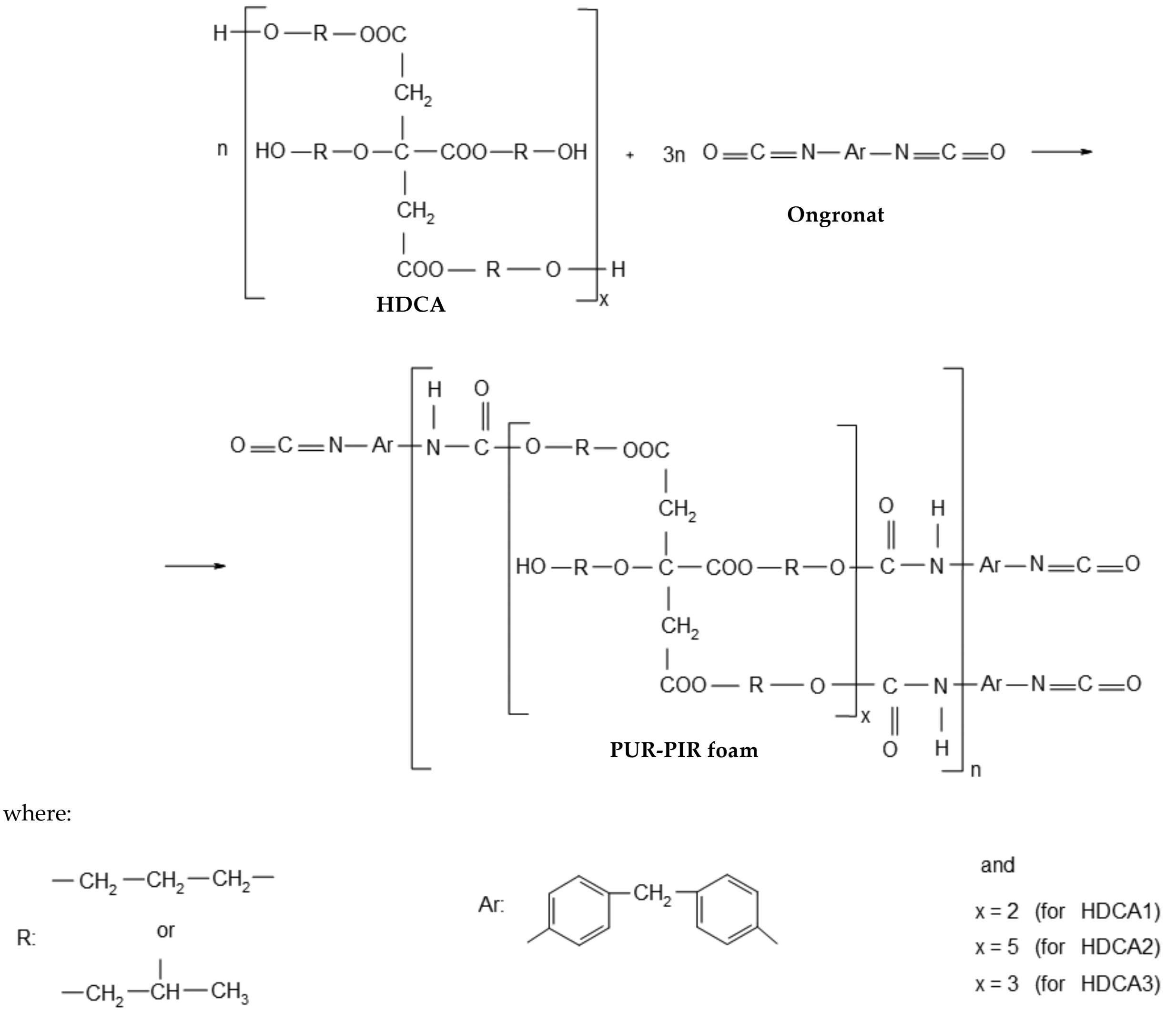
The course of synthesis of a hydroxyl derivative with a polyisocyanate (without contamination of side reactions) is illustrated in Scheme A.

The structure of the obtained foams was examined using FT-IR and published [18, 19, 21]. The examination showed the presence of ester, ether, isocyanurate, urethane chemical bonds, and the groups: -C, -CH$_2$, -C-, -N=C=O.

Methods of testing

Determination of properties of the citrates

After synthesis, the obtained products of condensation (HDCA1, HDCA2 and HDCA3) were cooled and analyzed. The following properties were determined: viscosity (PN-86/C-98082.04, Hoeppler viscosimeter), density (PN-92/C-04504), water content (PN-81/C-04959, by Carl Fisher's method), pH (microcomputer pH-meter CP-551), hydroxyl and acid numbers (PN-93/C-89052.03).



Scheme A

Methods of analysis of PUR-PIR foams

After removing the foams from the molds, they were heated for 4 h at a temperature of 120 °C. They were then seasoned for 48 h at a temperature of 20 ± 4 °C (in order to evaporate the gaseous substances and let the reactions come to an end), cut into pieces and their thermal stability and thermal resistance properties were measured.

Thermal stability of foams

Changes in sample dimensions under increased temperature (120 °C) were determined in parallel and perpendicular to the growth direction in relation to initial dimensions, volume and weight of the sample according to ISO 1923:1981. The calculations were performed according to the formulas (Equations 2–4):

$$\Delta l_z = \frac{l_z - l_{0z}}{l_{0z}} \cdot 100\ \% \tag{2}$$

$$\Delta l_p = \frac{l_p - l_{0p}}{l_{0p}} \cdot 100\ \% \tag{3}$$

$$\Delta V = \frac{V - V_0}{V_0} \cdot 100\ \% \tag{4}$$

where: l_{0z} – sample size before temperature control, parallel to the growth direction (mm);

l_z – sample size after thermostating, parallel to the growth direction (mm);

l_{0p} – sample size before thermostating, perpendicular to the direction of growth (mm);

l_p – sample size after thermostating, perpendicular to the direction of growth (mm);

V_0 – sample volume before thermostating (mm^3);

V – volume of the sample after thermostating (mm^3).

Measurement of changes in weight

Changes in sample weight were determined at increased temperature (120 °C) in relation to the initial sample weight according to PN-ISO 4590:1994. The calculations were performed based on the formula (Equation 5):

Table 2. Characteristics of polyols

Polyol	Hydroxyl number mg KOH/g	Acid number mg KOH/g	Content of water %	Density kg/m^3	Viscosity mPa · s	pH
Rokopol	420	max. 0.1	max. 0.1	1049	3224	–
HDCA1	280	52	2.3	1200	3972	2.2
HDCA2	300	23	1.2	–	–	5.5
HDCA3	427	31	2.65	1218	27 986	4.5

Table 3. Mass loss of polyols at T_1, T_2, T_3, T_{max}

Polyol	Start of weight loss		Start of decomposition		Start of highest rate of mass loss		Maximum of thermal effect	
	T_1 °C	Mass loss %	T_2 °C	Mass loss %	T_3 °C	Mass loss %	T_{max} °C	Mass loss %
Rokopol	160	1	205	5	375	19	411	70
HDCA1	70	2	190	4	220	6	307	49
HDCA2	68	1	180	4	245	10	320	46
HDCA3	115	0.5	160	4	300	16	366	53

$$\Delta m = \frac{m_0 - m}{m_0} \cdot 100\ \% \qquad (5)$$

where: m_0 – mass of the sample before thermostating (g); m – mass of the sample after thermostating (g).

Thermal properties of foams

The samples were dusted with a layer of gold about 6 nm thick. The thermostability was measured using two methods:

– In the first the TG Q500 thermogravimetric analyzer produced by TA Instruments was used. The temperature range was from 0 °C to 1000 °C. The weights of the samples were 80 mg. The heating speed was 10 °C/min. The examination was conducted under nitrogen.

– The second method was performed under an oxidizing atmosphere in air using a derivatograph operating in the Paulik-Paulik Erdey system (Hungary) produced by MOM Budapest. The range of heating was conducted from 0 °C to 1000 °C. The weights of the samples were about 100 mg. The heating speed was 5 °C/min. The examination was conducted in air. The prepared samples with crucibles and differential thermocouple ends were placed in the furnace. After performing the mentioned tasks, the examination started.

Differential scanning calorimetry

The examination of changes occurring in foams under heat was conducted using a differential scanning calorimeter DSC Q200 by TA Instruments with built-in Advanced Tzero technology. Foam examinations were conducted in the range from 0 °C to 400 °C, under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Properties of polyols

The thermal stability has a large significance in determining the usefulness of polyols for PUR-PIR foam syntheses. The thermal stability of the selected new compounds, the products of condensation of citric acid and propane-1,2-diol with a catalyst (HDCA1), propane-1,2-diol without a catalyst (HDCA2) and propane-1,3-diol with a catalyst (HDCA3) in an atmosphere of air and nitrogen was determined. The compounds with parameterized characteristics (Table 2) were used for rigid foam production according to the compositions shown in Table 1. The influence of polyols (HDCA) on the thermal stability and resistance of the obtained materials (F1–F15 PUR-PIR foams) was determined. The obtained condensates were liquids with straw (HDCA1), light yellow (HDCA2) or honey (HDCA3) colors. Despite the high viscosity values for HDCA2 and HDCA3 (they were hard to measure with the available methods at 25 °C), they were used in the foams because they mixed perfectly with the other raw materials. Their pH was also not much different from the petrochemical Rokopol (4.5), hence they will not affect the processing equipment available on the market.

Thermal properties of polyols

TG and DTG of HDCA polyols

TG thermographic analyses of the obtained HDCA polyols were done under nitrogen. Also, the thermo-

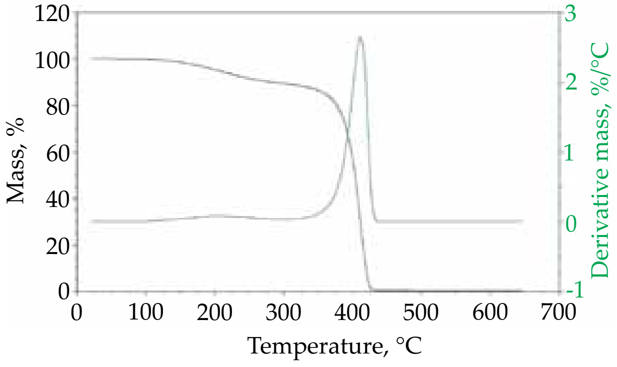


Fig. 1. TG and DTG of Rokopol

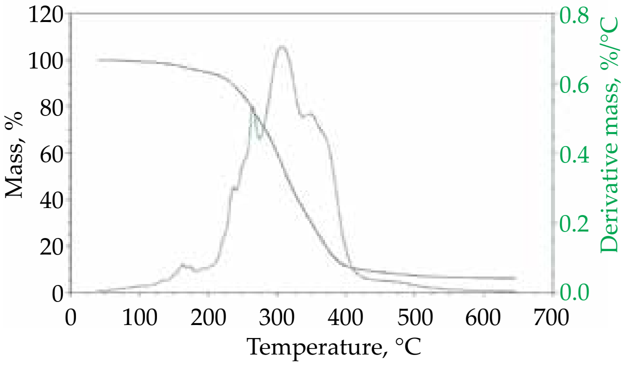


Fig. 2. TG and DTG of HDCA1

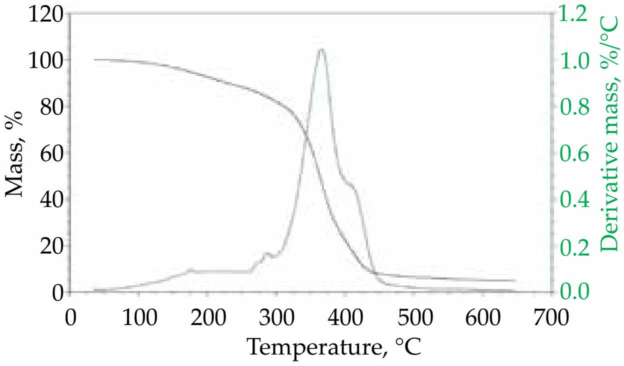


Fig. 3. TG and DTG of HDCA3

graphic analyses of the petrochemical Rokopol were performed for comparison (Table 3). The Rokopol thermograph (Fig. 1) shows two degradation stages. The second stage is very prominent, and the change in the first stage is very minimal. The main stage at T_{max} = 412 °C can be assigned to the decomposition of ether bonds in this polyether polyol.

The degradation of the HDCA1 polyol occurred in two stages and it can be seen that the second stage is more complex. The DTG graph shows additional small peaks overlapping the main peak (Fig. 2).

The TG curves of the HDCA3 polyol degradation (Fig. 3) have a similar course as for HDCA1 and HDCA2 (second stage). The complexity of the second stage is visible. The DTG graph shows four processes around peak number 2. One curve is shifted towards higher temperatures.

The beginning of the mass change (T_1), the beginning of decomposition (T_2), and the temperature of the beginning of the highest mass loss rate (T_{max}) (the maximum of the thermal effect) were determined for HDCA and Rokopol (Table 3) [22]. The percentile mass loss was measured at those temperatures. The temperatures of 5 %, 10 %, 20 % and 50 % mass loss for the foams ($T_{5\,\%}$, $T_{10\,\%}$, $T_{20\,\%}$, $T_{50\,\%}$) and the speed (v) of the decomposition process of the polyols in subsequent stages, as well as their residue at 800 °C (Table 4) were recorded. The TG curve shows the T_{onset} and T_{endset} temperatures (a so called result of peak curve extrapolation), which is marked at the intersection of the tangents of the peak with the extrapolated baseline. The results are presented in Table 5. It should be noted that mostly the T_{endset} of the first stage is also the T_{onset} of the second stage.

The HDCA citrates lost up to 2 % of their mass by the T_1 temperature (Table 3). The beginning of mass loss for citrates comprises a wide range of temperatures, from 70 °C (HDCA1) to 115 °C (HDCA3), and for the petrochemical Rokopol, the T_1 was 160 °C. The results can be attributed to the elimination of water particles from the products during their heating. The beginning of the decomposition happened at temperatures from 160 °C (HDCA3) to 190 °C (HDCA1), and the T_2 for Rokopol is a little higher (205 °C).

The petrochemical Rokopol decomposes completely at 800 °C but the other polyols do not. The largest amount of decomposition residue was left after the HDCA1 – 6 %, and the HDCA3 left 5 % residue. The v_2 is from 0.7 %/°C (HDCA1) to 1.0 %/°C (HDCA3), and for the Rokopol it is 2.7 %/°C. The difference in decomposition speed of HDCA1 and HDCA3 polyols comes from the content of different alkyl fragments present in the hydroxyalkyl derivatives of the citric acid [21].

Table 4. Thermal stability examination results (in nitrogen atmosphere)

Polyol	$T_{5\,\%}$ °C	$T_{10\,\%}$ °C	$T_{20\,\%}$ °C	$T_{50\,\%}$ °C	Residue at 800 °C %	v_1 %/°C	v_2 %/°C
Rokopol	205	284	378	404	0	0.1	2.7
HDCA1	194	234	263	314	6	0.1	0.7
HDCA2	183	232	271	338	5	0.1	0.8
HDCA3	174	230	303	364	5	0.1	1.0

Table 5. Extrapolated temperature of the peak beginning (T_{onset}) and end (T_{endset}) of subsequent decomposition stages

Polyol	Stage 1		Stage 2	
	T_{onset} °C	T_{endset} °C	T_{onset} °C	T_{endset} °C
Rokopol	136	275	275	404
HDCA1	145	210	210	395
HDCA2	121	230	223	401
HDCA3	98	270	270	430

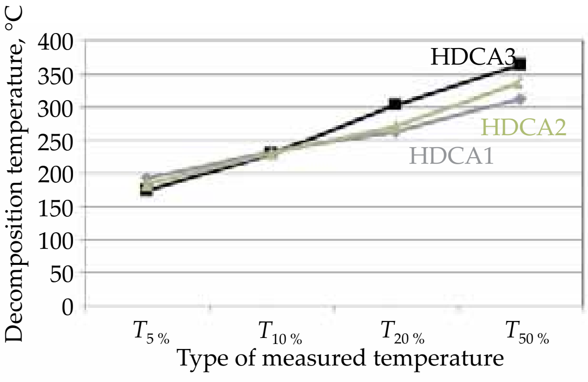


Fig. 4. The dependence of polyol thermostabilities on decomposition temperature

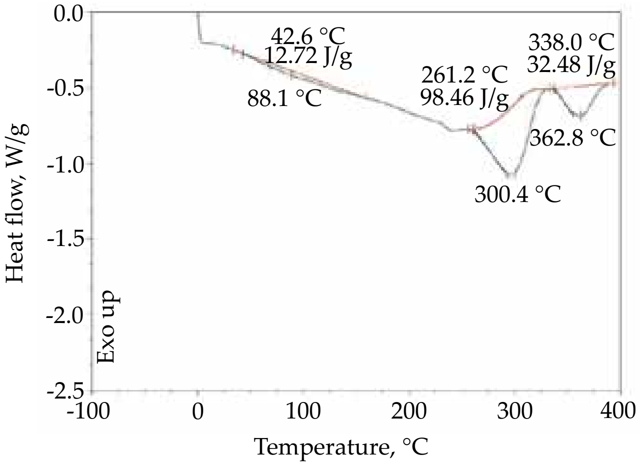


Fig. 5. DSC of HDCA1

The largest weight loss for HDCA3 was observed at T_{max} = 366 °C (70 %) and, compared to the weight loss of Rokopol RF, it is 17 % lower (at T_{max} Rokopol equal to 411 °C). The thermal stability is described as the temperature at which the compounds lose 5 % or 10 % of their mass ($T_{5\%}$, $T_{10\%}$) and 20 % of their mass ($T_{20\%}$). The temperature of 50 % mass loss was also noted (Table 4). It was also observed that the 5 % mass loss under a nitrogen atmosphere of selected compounds occurs in the temperature range 174 °C (HDCA3) to 205 °C (Rokopol), and the 10 % mass loss occurred in the temperature range 230 °C (HDCA3) to 284 °C (Rokopol). The examined temperature, in which a 20 % mass loss of the citrate was noted, was in the range from 263 °C (HDCA1) to 378 °C (Rokopol). However, the lowest $T_{50\%}$ was 314 °C (for HDCA1) and the highest was 404 °C (for Rokopol). The T_{max} was lowest for the HDCA1 (307 °C) and highest for Rokopol (411 °C). The higher $T_{20\%}$ and $T_{50\%}$ for the Rokopol are the result of the presence of ether bonds in this compound, which decompose at 350 °C. HDCA polyols, on the other hand, contain ester bonds in their chains, whose dissociation temperature is 260 °C. Based on the thermal stability results (Table 4), it can be concluded that the thermal stability increases along with the temperature for the HDCA3 in comparison to its decrease in HDCA1. The increase can be attributed to the structure of HDCA3 and, to be more precise, the presence of hydroxyalkyl bonds. HDCA3 contains the $\text{-CH}_2\text{-}\overset{|}{\text{C}}\text{H-CH}_3\text{-}$ fragment, while others contain the $\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ group. This dependency is clearly visible on the graph (Fig. 4). The thermal stability for the described compounds is lower than the thermal stabilities for industrial polyols used in the production of rigid foams. Namely, the highest mass loss for the industrial PUR polyol – Rokopol, in the temperature of the maximum thermal effect (411 °C), equals 70 %, and for the produced HDCA polyols it is as follows: 49 % at T_{max} = 307 °C (HDCA1), 53 % at T_{max} = 366 °C (HDCA3).

DSC of HDCA compounds

The changes in the obtained HDCA condensates in the temperature range from 0 °C to 400 °C were examined using the DSC method (Fig. 5). Based on the DSC thermograms, it was observed that the HDCAs start to melt over a very wide range of temperatures (Table 6). The DSC curve of the HDCA3 polyol has a slightly different course than HDCA2 or HDCA1. These polyols have three endothermic processes but they differed in their enthalpies (*H*). The enthalpy of the specific processes and the temperatures were noted in Table 6.

The beginning of HDCA1 melting occurs at 42.6 °C. The lowest temperature of the beginning of melting was observed for HDCA3 and it was 21.6 °C. The enthalpy of the first peak (H_1) observed in the melting temperature peaks was from 6.22 J/g to 12.72 J/g. A second endothermic peak was also noted on the DSC curve. Temperatures within peak 2 were very different for individual polyols from 103.8 °C (HDCA3) to 300 °C (HDCA1). The H_2 value for this peak was 8.53 J/g (for HDCA3) and 98.46 J/g (for HDCA1). The last (third) peak was significantly different for HDCA3 compared to the other polyols, which is reflected in its different enthalpy value (Table 6).

Table 6. Thermal changes in Rokopol and HDCA compounds

Polyol	Sample weight mg	Start of melting °C	Temperature and enthalpy (*H*) of thermal transformation					
			Peak 1 °C	H_1 J/g	Peak 2 °C	H_2 J/g	Peak 3 °C	H_3 J/g
Rokopol	3.2	17.1	41.7	6.22	266.1	43.27	376.3	17.91
HDCA1	4.4	42.6	88.1	12.72	300.4	98.46	362.8	32.48
HDCA2	4.0	33.2	55.1	8.34	252.1	88.45	370.1	30.11
HDCA3	3.7	21.6	46.1	7.02	103.8	8.53	346.0	223.58

Table 7. Examining series of F0–F15 foams after 48 h of heating at 120 °C

Foam	Changes in dimensions parallel to the growth direction Δl_z %	Changes in dimensions perpendicular to the growth direction Δl_p %	Change of volume ΔV %	Change of weight Δm %
F0	0	0	0	0
F1	0	-0.0019	1.9	0.35
F2	0	-0.009	0	0.9
F3	-0.98	-0.019	1.0	0.6
F4	-1.0	-0.0099	1.9	0.87
F6	-1.9	-0.0059	1.9	0.17
F7	0	-0.0019	1.0	0
F8	0	0	1.9	0
F9	0	0.011	1.2	0
F11	-0.5	-0.24	-0.1	1.4
F12	-0.27	-0.1	2.7	1.8
F13	-0.31	-1.4	-2.8	1.7
F14	-1.18	-0.98	-2.9	1.4
F15	0.23	-0.55	-0.25	1.3

Thermal properties of PUR-PIR foams

The method of thermogravimetric analysis helped assess the thermal stability of the examined PUR-PIR foams. Analysis of the temperature stability, on the other hand, was based on the linear dimension changes (parallel and perpendicular to the growth direction), and mass and volume changes at 120 °C (Table 7).

Temperature stability of foams

The dimensional stability of rigid foams is particularly important when they are used in the packaging and building industries. The creation of empty spaces, *e.g.*, in packages, can destabilize the transported cargo. The temperature stability depends on the used components (polyisocyanate and polyols). However, the polyol components used in the premixes have the highest influence here [22]. The thermal stability of the foams was determined from linear dimension changes (parallel to the growth direction – Δl_z and perpendicular to the growth direction Δl_p), volume changes (ΔV) and mass changes

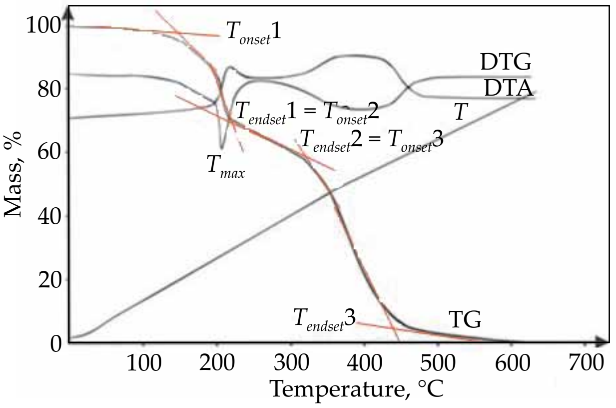


Fig. 6. Sample thermogram of rigid F0 foam

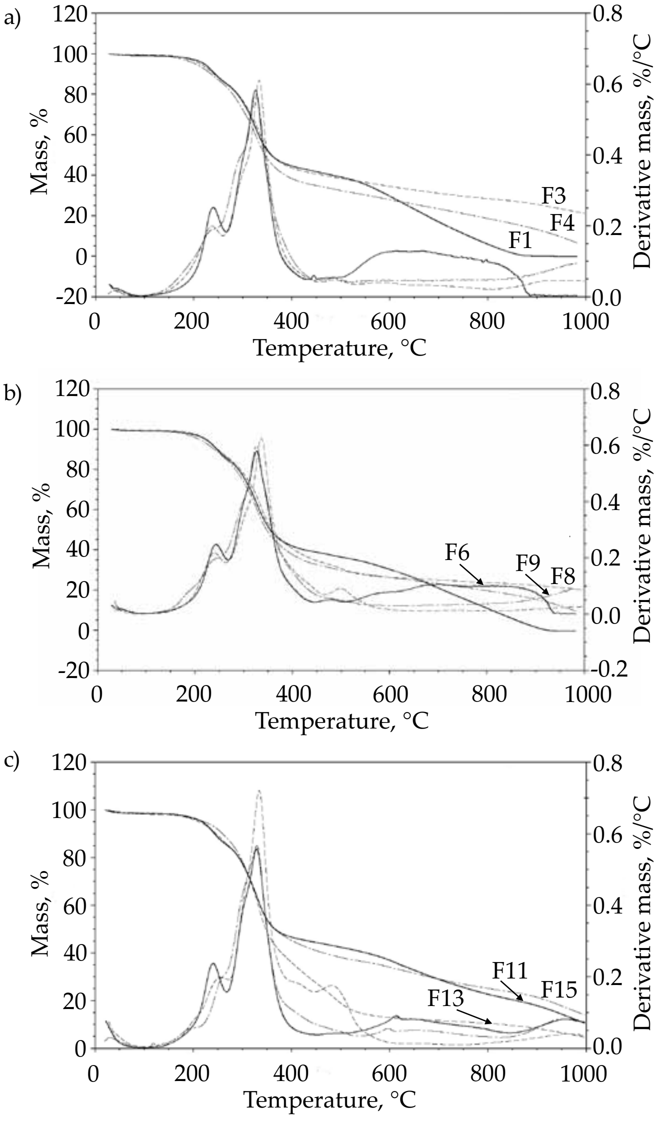


Fig. 7. TG and DTG of foams: a) series with HDCA1, b) series with HDCA2, c) series with HDCA3

T a b l e 8. Start of the change of mass (T_1), beginning of decomposition (T_2) and beginning of the highest rate of mass loss of PUR-PIR foams (in air atmosphere) at different stages (T_{max}); v_1, v_2, v_3 – degradation rate of steps 1, 2 and 3; F1–F4 – foam with HDCA1, F6–F9 – foam with HDCA2, F11–F15 – with HDCA3

Foam	Start of the change of mass		Highest rate of mass loss		v_1 %/°C	v_2 %/°C	v_3 %/°C
	T_1 °C	Weight loss %	T_{max} °C	Weight loss %			
F0	170	1	335.0	50	0.2	0.50	0.05
F1	185	1	326.3	38	0.2	0.60	0.05
F2	182	2	330.2	40	0.2	0.60	0.05
F3	180	2	335.1	35	0.2	0.60	0.05
F4	178	3	330.2	22	0.2	0.58	0.05
F6	200	1	326.9	45	0.25	0.59	0.05
F7	190	2	332.1	43	0.20	0.60	0.10
F8	180	2	337.1	42	0.20	0.60	0.10
F9	179	2	326.2	38	0.20	0.60	0.05
F11	175	1	329	35	0.25	0.55	0.10
F12	175	1	331	32	0.20	0.65	0.15
F13	175	1	334	8	0.20	0.75	0.18
F14	175	1	330	34	0.20	0.65	0.10
F15	175	1	329	36	0.20	0.55	0.05

(Δm) – Table 7. The obtained values suggest the foams have high stabilities, which are in the range of stability of materials used in the thermoinsulating industry and others. The Δl_z and Δl_p do not exceed 1.5 %. Changes in volume did not exceed 3 % and the Δm were lower than 2 %. The high dimensional stability of PUR-PIR foams can be attributed to the presence of isocyanurate bonds in the examined foam products.

Heat resistance

To determine the characteristics of the foams' heat resistance, their thermogravimetric analysis under oxygen in dynamic conditions was conducted. A sample thermogram of rigid foam is illustrated in Fig. 6.

Based on the TG curve (weight change) and DTG curve (derivative weight change) the following characteristic quantities were measured: the temperature of the foams' first weight loss (T_1), the extrapolating temperature of the foams' first weight loss (T_2), the temperature of the beginning of the foams' rapid decomposition (T_3, calculated in compliance with ISO 7111 standard as a point of tangents' intersection), and the temperature of the foams' greatest speed of weight loss (T_{max}, corresponding to the extreme on the DTG curve). The extrapolated temperature of the beginning (T_{onset}) and the end (T_{endset}) of subsequent decomposition stages was determined. The T_{onset} of stage 1 ($T_{onset}1$) overlaps with the T_2.

The TG foam curve generally had a three stage course (Fig. 7). However, a slight decrease in the foam's mass is observed already at around 45 °C. At this temperature, diffusion of CO_2 in the foam (which filled the foam cells during its synthesis) occurs. Figure 7 shows the thermograms of a series of foams containing HDCA1, HDCA2 or HDCA3.

For foams containing the HDCA polyols, the maximum speed of the degradation process (T_{max1}) in stage 1, occurs in the temperature range of 233 °C (F9)–256 °C (F13). The temperature of the end of this effect ($T_{endset}1$) is around 270 °C. At the same time, it is the temperature of the beginning of the foam sample degradation in the second stage of decomposition ($T_{onset}2$). The maximum speed of this process in the second stage occurs at a temperature of almost 340 °C. The mass loss in this temperature range is from around 8 % (F13) to around 55 % (F0). The second stage ends around 420 °C and it is simultaneously the beginning of the final, third stage, where 7.5–16.3 % mass loss occurs. This last thermal effect is related to the decomposition of isocyanurate bonds and is complete by a temperature of around 600 °C ($T_{endset}3$).

Differential thermogravimetric curves (DTG) were generated, which describe the speed of mass loss as a function of temperature (Fig. 7). The measured speed of foam degradation process in stage 1 (v_1) is 0.2–0.25 %/°C, in stage 2 (v_2) is from *ca.* 0.50 %/°C to *ca.* 0.75 %/°C, and in stage 3 (v_3) from 0.05 %/°C to 0.18 %/°C – Table 8. The difference is probably related to the number of branches in the foam.

The more branches present in the foam, the lower the access of oxygen to its interior. This is related to the so-called free space between macromolecules [22, 23]. This branch difference in the foam is caused by the addition of various citrates into the polyol premix.

The beginning of the degradation is close to $T_{5\%}$. The $T_{5\%}$ is considered to be the temperature at which degradation

T a b l e 9. Results of foam thermal properties (under nitrogen atmosphere); marked in the text

Foam	$T_{5\,\%}$ °C	$T_{10\,\%}$ °C	$T_{20\,\%}$ °C	$T_{50\,\%}$ °C	The residue at 800 °C %	T_{max1} °C	T_{max2} °C	T_{max3} °C	$T_{onset}1$ °C	$T_{endset}1 = T_{onset}2$ °C	$T_{endset}2 = T_{onset}3$ °C	$T_{endset}3$ °C
F0	226	255	304	387	30	252	336	480	150	260	400	550
F1	221	243	289	358	0	238	326	495	110	260	440	500
F2	217	242	290	359	7	238	330	498	120	257	445	500
F3	215	241	295	359	30	237	333	486	130	255	450	500
F4	214	235	280	345	22	237	327	484	110	248	450	525
F6	221	245	289	354	0	241	327	477	175	263	450	520
F7	222	246	300	358	26	239	336	499	150	265	458	540
F8	224	230	300	350	30	248	345	502	130	269	465	570
F9	208	239	283	347	20	233	326	515	124	260	456	560
F11	212	243	293	366	17	239	329	620	170	265	378	750
F12	212	245	296	360	15	240	331	512	160	270	400	600
F13	212	246	300	348	12	256	334	481	120	275	450	550
F14	214	255	297	359	15	244	330	500	140	265	510	610
F15	223	260	296	366	38	245	329	595	150	260	550	650

T a b l e 10. Study of the thermal transformations of foams using the DSC method in P1 and P2 peaks (foams with 0.3 *R* of polyol)

Foam	Endothermic peaks							
	P1				P2			
	$T_{onset}1$ °C	T_{max1} °C	$T_{endset}1$ °C	H_1 J/g	$T_{onset}2$ °C	T_{max2} °C	$T_{endset}2$ °C	H_2 J/g
F3	35.5	80.9	137.5	29.38	211.2	261.9	279.8	19.28
F8	32.8	80.5	120.1	25.44	212.7	260.9	279.2	25.74
F13	33.4	81.0	133.0	28.98	214.0	275.3	287.8	19.86

T a b l e 11. Study of the thermal transformations of foams using the DSC method in P4 and P3 peaks (foams with 0.3 *R* of polyol)

Foam	Endothermic peak				Exothermic peak			
	P4				P3			
	$T_{onset}4$ °C	T_{max4} °C	$T_{endset}4$ °C	H_4 J/g	$T_{onset}3$ °C	T_{max3} °C	$T_{endset}3$ °C	H_3 J/g
F3	313.1	325.8	349.5	21.67	279.8	294.2	312.0	13.91
F8	314.3	326.9	349.9	18.65	279.2	294.5	312.5	18.65
F13	299.3	318.1	349.0	38.19	275.3	275.3	299.0	13.69

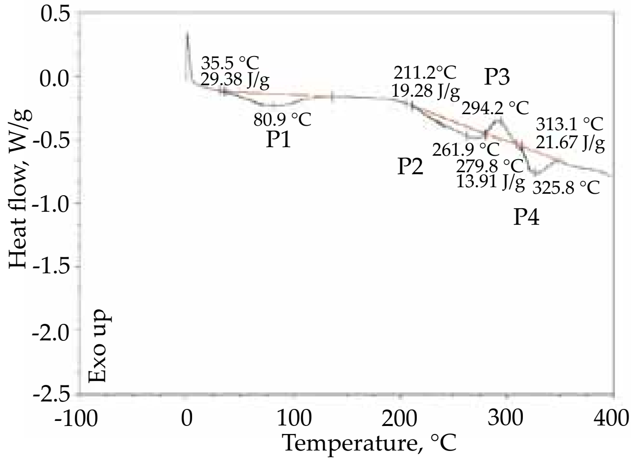


Fig. 8. DSC curves of P3 foam heated under a nitrogen atmosphere

starts. It has values from 208 °C (F9, foam containing 0.4 *R* of HDCA2) to 226 °C (F0, reference foam) for the examined foams. The cause in the differences between the $T_{5\,\%}$ temperature is probably related to the number of branches in the foams. Different hydroxyalkyl derivatives (HDCA) with different structures and in different amounts (from 0.1 *R* to 0.5 *R*) were used for the foam synthesis.

The TG graphs have a three-stage course. The first stage starts at $T_{onset}1$ (about 110–175 °C) and ends at $T_{endset}1$ (about 248–275 °C) – Table 9. The following bonds most likely decompose: the urethane bonds (with a dissociation temp. of 200 °C), carbodiimide (with a dissociation temp. of 240 °C) and ester bonds (with a dissociation temp. of 260 °C). The second stage of foam degradation, with temperatures between $T_{onset}2$ (248–275 °C) and $T_{endset}2$ (378–550 °C), and the third stage from $T_{onset}3$ (378–550 °C) to $T_{endset}3$ (500–750 °C), are related to each other by the decomposition of isocyanurate bonds (with a dissociation temp. of 300 °C) and ether bonds (with a dissociation temp. of 350 °C). $T_{onset}1$ is the lowest for foams with HDCA1, and the highest for foams with HDCA3.

DSC of rigid PUR-PIR foams

The DSC thermograms recorded during the heating of the samples are presented in Fig. 8. This data was the basis for determining the extrapolated values of the beginning and end temperatures of the change, the temperature of subsequent processes and enthalpies (*H*) of those changes. The DSC examination performed under a nitrogen atmosphere shows that four main changes with different energetic characters occur in the foams. Three endothermic peaks (P1, P2, P4) and one exothermic peak (P3) were observed. At the temperature of *ca.* 30 °C, the beginning of the first endothermic $T_{onset}1$ peak can be observed, this correlates with the substance moving from the first form to the second (Table 10). The transition from the second form to the third begins at the $T_{onset}3$ temperature (*ca.* 280 °C), and from the third form into the fourth at a $T_{onset}4$ (*ca.* 300 °C) – Table 11. The first peak below 100 °C (P1 peak) is related to the evaporation of water, and the next two are related to the decomposition of the urethane bond (near 260 °C, P2 peak) and the cyanurate bond (around 320 °C, P3 peak). The change at the P3 peak is probably the result of reactions occurring between the products of foam decomposition. These are: degradation of urethane and urea bonds, degradation of groups of ether polyoxypropylene fragments of the polyol (Rokopol), and at higher temperatures: decomposition of carboimides and isocyanurates. The energetic effects of these changes in anaerobic conditions have an endothermic nature. However, in the first stage of polyurethane depolymerization, at *ca.* 150 °C, oligomeric isocyanates and diols are recreated, and they can react with the produced micromolecular compounds (acting as possible oxidants). This can explain the observed slight, exothermic effect in the 275–313 °C temperature range.

CONCLUSIONS

Hydroxyalkyls: HDCA1, HDCA2, HDCA3 were synthesized from citric acid and diols (propane-1,2-diol and propane-1,3-diol) by esterification. HDCA1 and HDCA3 syntheses were performed in the presence of 0.36 g catalyst (Tyzor TPT). When the thermal stability (in nitrogen atmosphere) of the industrial polyol (Rokopol RF 551) was compared with the described hydroxyalkyl derivatives of citric acid (HDCA), a higher temperature for the start of mass change and decomposition, as well as the temperature of maximum thermal effect, was observed for the HDCA citrates. The obtained HDCAs decomposed at a slower rate than petrochemical Rokopol. The course of TG curves is similar for all polyols and has a two-stage character. However, complexity in the second stage in the HDCAs was observed. The difference in degradation rates in HDCA polyols is a result of different types of chains of alkyl fragments. This, on the other hand, is a result of their synthesis with the use of different diols (propane-1,3-diol and propane-1,2-diol). The TG examinations showed that the foams containing HDCA and Rokopol are characterized by three-stage thermal degradations and similar thermogravimetric curve profiles. The temperature of the beginning of degradation $T_{5\,\%}$ exceeds 200 °C. The end sample mass of 800 °C is varied and is in the wide range from 0 % (F1 – reference foam and F6 – foam contained 0.1 *R* of HDCA1) to 38 % (F15 – foam contained 0.5 *R* of HDCA3).

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Contact: Aleksander Prociak, + 48 12 628 30 16, aprociak@pk.edu.pl
Maria Kurańska, + 48 12 628 27 47, maria.kuranska@gmail.com

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