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Glycolysis of rigid polyurethane-polyisocyanurate foams

Summary — A rigid polyurethane-polyisocyanurate foam (PUR-PIR) was synthesized. Then it was ground in a plastic shredder and a ball mill. The resulting milling product was then glycolysed in diethylene glycol with addition of ethanolamine and zinc stearate. The foam was added at consecutive stages in batches, so that the total amount of the foam at consecutive stages was 20, 40 and 60 g. The resulting product of each stage was a brown liquid (WI, WII and WIII). Properties of these products were then investigated in order to determine their usability to synthesize new foams. It was found that the best reusable was the WIII glycolysate and adding it in various quantities 3 new foams (GW0.1, GW0.2 and GW0.3) were obtained. Properties of these foams were investigated and as a result usability of the glycolysates to produce PUR-PIR foams was stated.

Keywords: glycolysis, polyurethane-polyisocyanurate foam, diethylene glycol, ethanolamine, viscosity, hydroxyl number.

GLIKOLIZA SZTYWNYCH PIANEK POLIURETANOWO-POLIIZOCYJANUROWYCH

Streszczenie — Zsyntezowano sztywną piankę poliuretanowo-poliizocyjanurową (PUR-PIR). Następnie zmielono ją w rozdrabniaczu do tworzyw sztucznych i młynie kulowym. Powstały przemiał poddano glikolizie w glikolu dietylenowym z dodatkiem etanoloaminy i stearynianu cynku. Piankę w kolejnych etapach glikolizy dodawano porcjami, tak że w tych etapach jej całkowita ilość wynosiła odpowiednio 20 g, 40 g i 60 g. Otrzymano w każdym etapie ciekły produkt barwy brązowej (WI, WII, WIII). Zbadano właściwości powstałych produktów w celu określenia ich przydatności do syntezy nowych pianek. Oceniono, że do ponownego użycia najlepiej nadaje się glikolizat WIII i stosując jego dodatek w różnych ilościach otrzymano trzy nowe pianki (GW0.1, GW0.2 i GW0.3). Zbadano właściwości tak otrzymanych pianek i na tej podstawie stwierdzono przydatność glikolizatów do wytwarzania pianek PUR-PIR.

Słowa kluczowe: glikoliza, pianka poliuretanowo-poliizocyjanurowa, glikol dietylenowy, etanoloamina, lepkość, liczba hydroksylowa.

Continuous growth of polyurethane application is observed in the market. They are applied in various fields of life, among others, in refrigerating, footwear and building industries [1—5], for manufacturing of brushes and insulation [6] or in medicine [7]. That is why more and more both post-production and post-use waste products remain.

Management of polyurethane (PUR) waste products is mainly performed by chemical recycling (glycolysis, hydrolysis, glycolysis combined with amines) [8—13]. Low-molecular weight glycols with no more than 6 carbon atoms (ethylene, diethylene, propylene, butylene, dipropylene) and addition of amines with no more than 8 carbon atoms (monoethylamine, dimethylamine, diethyltriamine) are usually applied [14, 15]. Presence of amine lowers decomposition temperature and accelerates the reaction. A less popular method is digestion in caprolactam or ammonia.

Catalysts in glycolysis are divided into three types: metal salts and hydroxides, metaloorganic compounds and amines [16].

The product obtained as a result of glycolysis can be most often directly applied to synthesis *e.g.* new PUR foams [11, 17].

During cutting of products from a source foam block, waste products remain. The aim of the studies was glycolysis of waste produced from “original” rigid polyurethane-polyisocyanurate (PUR-PIR) foam of the specified structure. Moreover, the properties of “original” foam and the effect of glycolysate on properties of the “new” syntesized foams have been determined. The structures and properties of obtained foams were compared. The foam and the waste product are characterized by the same composition and properties.

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EXPERIMENTAL

Materials

The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol, L_{OH} = 495 mg KOH/g, produced by NZPO "Rokita", Brzeg Dolny, Poland) were used as received.

The polyisocyanate with trade name Ongromat 20-30 (whose main component is diphenylmetane 4,4'-diisocyanate, technical grade, density at temp. 25 °C of 1.23 g/cm^3, viscosity of 200 mPa · s, produced by BorsodChem, Hungary) were also used. As it was determined according to the ASTM D 2849-69 and ASTM D 1638-70 standards this polyisocyanate contained 31.0 % of isocyanate groups.

An anhydrous potassium acetate in the form of 33 % solution in diethylene glycol (Catalyst-12, POCh Gliwice, Poland) and triethylenediamine DABCO 33LV (Hülls, Germany) in the form of 33 % solution in dipropylene glycol were applied as catalysts in foam composition.

The polysiloxanepolyoxyalyleneoxydimethylene surface-active agent (Silicone L-6900, Witco, Sweden) was used as stabilizer of the foam structure.

The liquid antipirene tri(2-chloro-1-methyl-ethyl) phosphate (Antiblaze TMCP, Albright and Wilson, United Kingdom) was also introduced into the foams.

The porophor — carbon dioxide was formed in reaction of isocyanate with water.

Synthesis of the rigid polyurethane-polyisocyanurate foam

The foam (W) was prepared in a laboratory scale with one-stage method from the two-component system at the equivalent relation of NCO to OH groups equal to 3:1. The component A was obtained by the precise mixing (1800 rpm, 10 s) of the suitable amounts of substances: 55.65 g of Rokopol, 7.2 g of Catalyst-12 and 3.1 g of DABCO as a catalysts, 51.6 g of Antiblaze as antipirene, 5.2 g of Silicone L-6900 as a surface-active agent and 3.8 g of distilled water as a porophor. Component B was 284 g of polyisocyanate Ongromat CR 30-20. Both components were mixed (1800 rpm, 10 s) at respective volume ratio and poured onto an open rectangular tray of dimensions 195 × 195 × 240 mm. Parameters of process were measured during the synthesis. After expanding, the foam was removed from the tray and thermostated for 4 h at the temperature of 120 °C. Then it was seasoned for 48 h at the temperature of 20 ± 4 °C and cut to samples of respective dimensions. The basic properties were determined according to the valid standards.

After cutting, the waste foams were ground in a plastic shredder (UKW-RU/A-170) and then milled in Janetzky's ball mill. At the next step, glycolysis of the waste was performed.

Glycolysis of PUR-PIR foam W

Glycolysis of the milled foam was performed in a three-neck flask of 250 cm^3 in diethylene glycol (80 g) and ethanolamine (20 g) in presence of zinc stearate (1.5 g). The flask was equipped with reflux condenser, a thermometer and a mechanical stirrer in order to prevent the foam sticking. The mixture was heated in heating jacket to the boiling point (160 °C). Then foam recyclate was added in batches. Glycolysis was performed in three stages. At the first stage 20 g of foam was used, temperature of decomposition was 160 °C and the time of decomposition was 10 min. After this stage WI sample was drawn. At the second stage 20 g of foam was added, temperature was increased to 210 °C and after next 20 min WII sample was drawn. At the third stage the temperature 210 °C was maintained for 90 min. WIII sample was the final product of the decomposition.

The temperature and time applied at particular stages were selected experimentally to get most of the foam completely decomposed.

The samples of glycolysate were cooled and analysed in order to find a sample characterized by properties similar to these observed for polyol used in industrial synthesis of foams. Finally WIII sample was chosen to synthesis of foams.

Synthesis of the rigid PUR-PIR foams

The product of glycolysis obtained from W foam and named WIII was used to synthesis of new GW foams, with the same method as W. The only difference in GW synthesis procedure in comparison to W synthesis was replacing a part of used Rokopol with respective amount of WIII glycolysate, according to values listed in Table 1.

Table 1. The type and amount of polyol used in synthesis of GW foams

Type of polyol	Unit	Symbol of sample			
		W	GW0.1	GW0.2	GW0.3
Rokopol RF-55	g	55.65	54.0	44.5	38.9
	chemical equivalent	1	0.9	0.8	0.7
WIII	g	—	9.6	19.2	28.7
	chemical equivalent	—	0.1	0.2	0.3

Methods of testing

Determination of properties of the foam glycolysis products

The following parameters of glycolysis product were determined: hydroxyl number (PN-93/C-89052.03), acid number (as the mass of KOH in mg required to neutralize 1 g of glycolisate products), viscosity (PN-86/C-98082.04, Hoeppler viscosimeter), density (PN-92/C-04504), solubility (1 g of glycolysate was mixed with 10 cm^3 of different solvents and solubility was appraised), contents of glycol (gas chromatograph Agilent Technology 6890N), water contents (PN-81/C-04959, by Carl Fisher's method) and pH (microcomputer pH-meter CP-551).

Determination of the rigid foam properties

The prepared "original" and "new" foams were removed from the tray and thermostated for 4 h at the temperature of 120 °C. Then they were seasoned for 48 h at the temperature of 20 ± 4 °C and cut into samples of respective dimensions.

The structure of foams was investigated using Eclipse 400 POL microscope (Canon, Japan) with transmitting light and 4 times magnification.

Compressive strength was determined using strength machine Tira Test 2200 according to ISO 844:1993: DIN 53420 standard.

Brittleness was tested according to ASTM C-421-61 standard.

Softening point was measured using Vicat apparatus according to DIN 53424 standard.

Density was measured according to ISO 845-1988.

The change of mass and volume after 48 h of thermostating at temperature 120 °C was determined.

Thermal resistance was tested using derivatograph operating in Paulik-Paulik Erdey system (MOM Budapest, Hungary). Testing was performed within the range of temperature from 20 to 800 °C at heating rate 5 °C/min. The weight of the sample was about 90 g. Studies were carried out in the air atmosphere. The reference matter was Al_2O_3.

During the heating the following parameters were determined: T_1 — temperature of loss in mass by 5 %, T_2 — temperature of loss in mass by 10 %, T_{max} — temperature of the highest rate of loss in mass.

Thermal conductivity (λ) was determined using "FOX 200" apparatus (Lasercomp). The sample size was: 200 × 200 × 25 mm. The method comprised determination of the amount of heat conveyed by a sample of material in the unit of time during steady heat flow, when the temperature difference was stabilized on the opposite sides of the sample studied. The measurements were made in series, at 0.5 s intervals.

Amount of closed cells was determined according to PN-ISO 4590:1994 and water absorbability according to DIN 53433 standard.

Flammability was investigated using horizontal test according to PN-78/C-05012 standard and simplified chimney test (vertical — Butler's) according to ASTM D3014-73 standard.

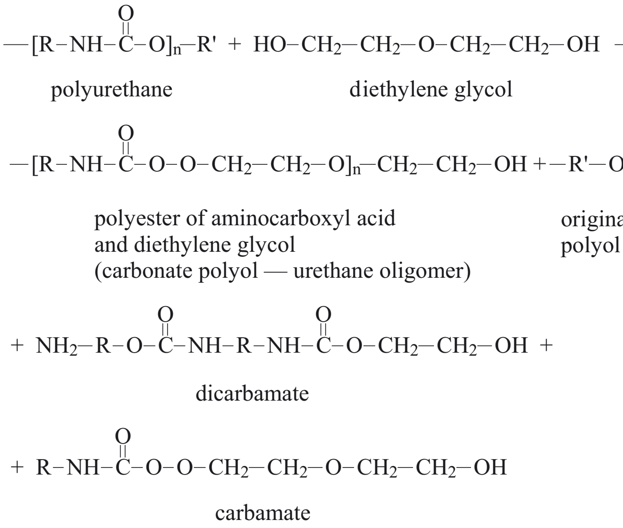
The IR analysis was performed with Vector (Brücker) spectrophotometer. The KBr technique in the range from 400 cm^{-1} to 4000 cm^{-1} was applied.

RESULTS AND DISCUSSION

Glycolysis of PUR-PIR foam

Reaction of polyurethane with diethylene glycol

Diethylene glycol partially reacts with polyurethane what results in formation of the initial polyol and polyester. Among the reaction products, dicarbamate and monocarbamate can be found besides polycarbamate:



$$\underbrace{-[R-NH-\overset{O}{\overset{||}{C}}-O]_n-R'}_{\text{polyurethane}} + \underbrace{HO-CH_2-CH_2-O-CH_2-CH_2-OH}_{\text{diethylene glycol}} \longrightarrow$$

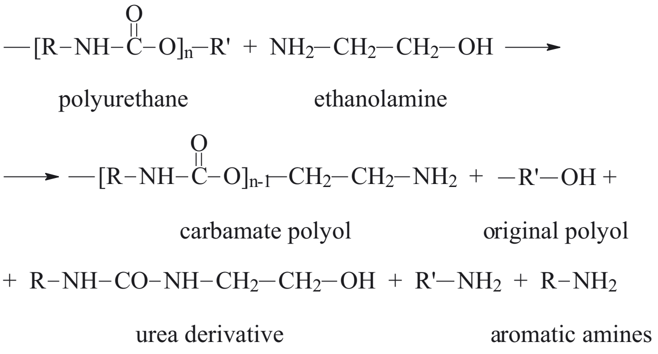
$$\underbrace{-[R-NH-\overset{O}{\overset{||}{C}}-O-O-CH_2-CH_2-O]_n-CH_2-CH_2-OH}_{\text{polyester of aminocarboxyl acid and diethylene glycol (carbonate polyol — urethane oligomer)}} + \underbrace{-R'-OH}_{\text{original polyol}} +$$

$$+ \underbrace{NH_2-R-O-\overset{O}{\overset{||}{C}}-NH-R-NH-\overset{O}{\overset{||}{C}}-O-CH_2-CH_2-OH}_{\text{dicarbamate}} +$$

$$+ \underbrace{R-NH-\overset{O}{\overset{||}{C}}-O-O-CH_2-CH_2-O-CH_2-CH_2-OH}_{\text{carbamate}} \qquad (1)$$

Reaction of polyurethane with ethanolamine

In reaction of polyurethane with triethanoloamine, carbamate polyol, original polyol, urea derivative and aromatic amines are formed:



$$\underbrace{-[R-NH-\overset{O}{\overset{||}{C}}-O]_n-R'}_{\text{polyurethane}} + \underbrace{NH_2-CH_2-CH_2-OH}_{\text{ethanolamine}} \longrightarrow$$

$$\longrightarrow \underbrace{-[R-NH-\overset{O}{\overset{||}{C}}-O]_{n-1}-CH_2-CH_2-NH_2}_{\text{carbamate polyol}} + \underbrace{-R'-OH}_{\text{original polyol}} +$$

$$+ \underbrace{R-NH-CO-NH-CH_2-CH_2-OH}_{\text{urea derivative}} + \underbrace{R'-NH_2 + R-NH_2}_{\text{aromatic amines}} \qquad (2)$$

Properties of glycolysis products

Glycolysis was performed at the temperature range and time suitable to achieve complete foam decomposition (160—210 °C). Addition of waste foam forced increase in temperature and longer time of mixture heating since undecomposed foam milling was observed as amount of foam was increased.

As it is can be seen from the results listed in Table 2 that viscosity of glycolisate increased from 530.3 mPa · s (contents of milled foam — 20 g) to 711.4 mPa · s (content of foam — 60 g) as the amount of foam powder in

T a b l e 2. Properties of glycolysate obtained in three stages of foam glycolysis

Symbol of glycolysate	Viscosity (temp. 25 °C) mPa · s	Density (temp. 25 °C) kg/m^3	Hydroxyl number mg KOH/g	Acid number mg KOH/g	pH	Content of diethylene glycol, wt. %	Content of water wt. %
WI	530.3	1000.0	374.4	49.4	8.0	50.77	0.8
WII	617.1	1053.0	377.3	44.8	7.2	50.66	0.7
WIII	711.4	1125.0	292.9	34.0	5.2	45.10	0.5

the product increased. However, hydroxyl and acid numbers decreased as the contents of milled foam was increased. The glycolysate obtained is soluble in common solvents and polyols applied to the synthesis of rigid foams. Contents of unreacted glycol in the product of foam decomposition was about 50 wt. %. Glycol was not distilled off since the glycolysis product in this form was usable for synthesis of "new" PUR-PIR foam as a "new" polyol. Glycol was a chain extender. Higher amount of waste foam in the product of glycolysis resulted in viscosity increase and consequently it was difficult to obtain homogeneous mixture with original polyol and polyisocyanate. Therefore lower amount of waste PUR-PIR foam in relation to amount of glycol and amine was used.

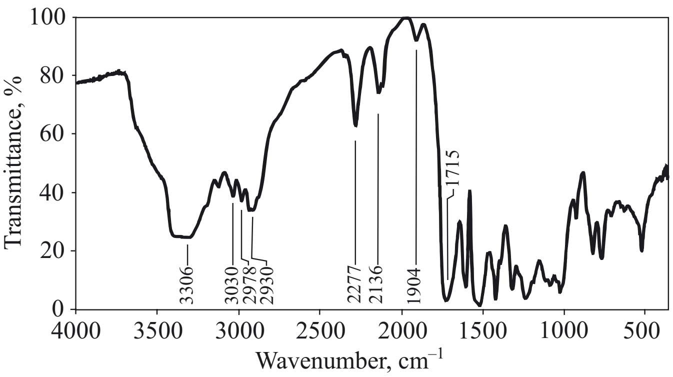


Fig. 1. IR spectrum of glycolysate WIII

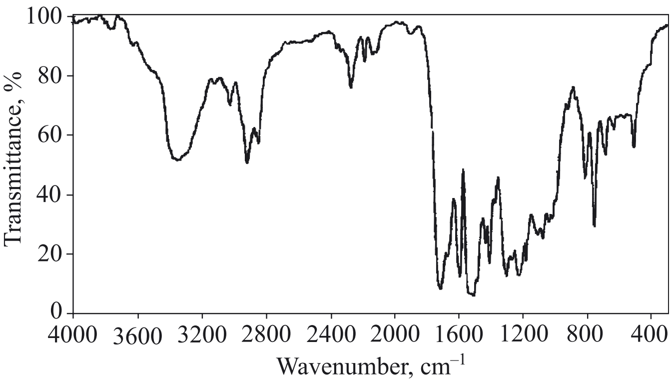


Fig. 2. IR spectrum of PUR-PIR foam W

The pH value decreased from 8.0 (WI) to 5.2 (WIII). pH values probably depend on the degree of triethanolamine conversion. The degree of conversion increases as the amount of waste foam is increased in the mixture.

Analysis of the IR spectrum of the product of foam decomposition (glycolysate WIII) presented in Figure 1 showed, among others, a wide band of hydroxyl groups (range from 3500 to 3250 cm^{-1}).

Properties of "original" and "new" rigid foam

It was found that amount of glycolysate had an effect on the functional properties of foams. As it can be seen from the results presented in Table 3 the time parameters of foam processing were greater and the density increased from 36.9 kg/m^3 (foam W) to 66.0 kg/m^3 (GW0.3 foam). The volume and mass were unchanged after 48 h of thermostating at temp. 120 °C — Table 2. Compressive strength decreased as the amount of glycolysate was increased in foam composition from 477.5 kPa (GW0.1 foam) to 305.0 kPa (GW0.3 foam), however, it was higher for all foams with glycolysate (GW0.1— GW0.3 foams) than for standard foam without glycolysate (W foam). Residue after combustion (retention) of foams increased from 76.6 % (W, standard foam) to 94.5 % (foam with 0.3 of chemical equivalent of glycolysate — GW0.3).

T a b l e 3. Properties of rigid PUR-PIR foams

Symbol of foam	Start time, s	Time of expanding, s	Time of gelation, s	Apparent density kg/m^3	Compressive strength, kPa	Residue after combustion, %	Water absorbability, %	Thermal conductivity mW/mK	Softening point, °C
W	17	18	37	36.9	221.7	76.6	1.80	35.54	230
GW0.1	12	30	30	37.3	477.5	92.6	1.27	34.31	205
GW0.2	16	42	86	50.2	402.5	93.4	1.11	34.11	210
GW0.3	19	58	125	66.0	305.0	94.5	1.00	34.04	214

Analysis of "original" foam W using IR spectroscopy confirmed presence of isocyanurate (1400—1410 cm^{-1}) and urethane (1720—1730 cm^{-1}) bonds (Figure 2). These bonds are characteristic to the rigid foams.

Figure 3 shows brittleness of foams in function of glycolysate content. The brittleness decreased from 42.0 % (W) to 14.4 % (GW0.3) with increase of glycolysate content.

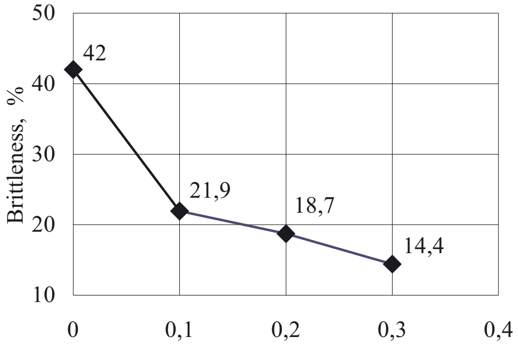


Fig. 3. Dependence between brittleness and contents of glycolysate in foam

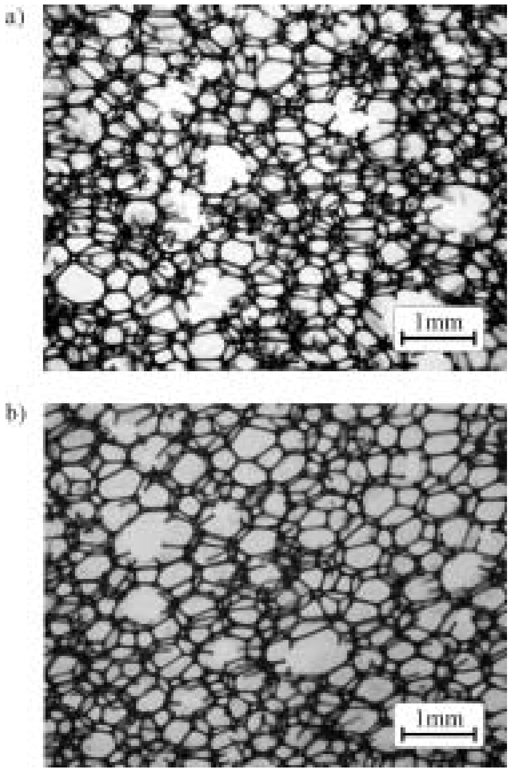


Fig. 4. Structure of: a) standard foam — W, b) foam with 0.1 of chemical equivalent of glycolysate — GW0.1; 4x magnification, transmitting light, microscope Eclipse 400 POL, Canon

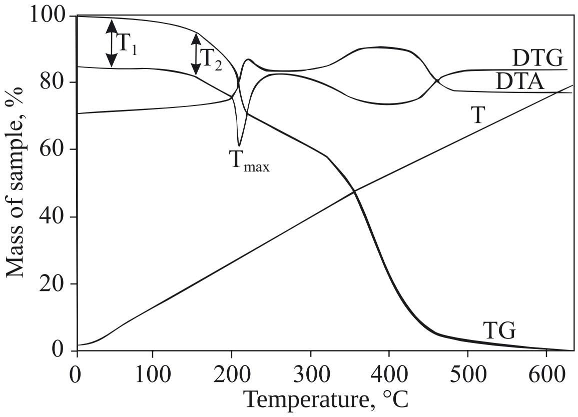


Fig. 5. Derivatogram of foam W

Addition of glycolysate to foam composition improved the structure of foam. It can be seen on microscope photographs presented in Figure 4 that lower amount of opened cells is observed in the "new" foam GW0.1 than in the "original" one W. The amount of glycolysate in the foam has no effect on change in cell sizes. No agglutinations were observed in the foam structure.

The foams were subjected to thermogravimetric analysis. Exemplary derivatogram of W foam is shown in Figure 5. The results of thermal resistance investigation are listed in Table 4. Temperature of loss in mass by 5 % decreased from 85 °C (W) to 63 °C (GW0.3). Temperature of loss in mass by 10 % decreased from 250 °C (W) to 219 °C (GW0.3). Temperature of the highest rate of loss in mass also decreased from 320 °C to 298 °C.

Drop of temperature of foam loss in mass by 5 and 10 % was probably caused by diffusion of carbon dioxide, which performed a role of porophor. It was formed as a result of reaction between excess isocyanate groups (-NCO) and water. At temperature within the range from 85 °C to 125 °C, diffusion of triethanolamine from foams can also occur. It is applied in the form of 33 % solution in diethylene glycol as a catalyst of reaction between polyisocyanates and polyols. Decomposition of foams under influence of temperature is accompanied by pyrolysis consisting of destruction of the foam chemical structure and thermooxidizing destruction by oxygen from the air.

Table 4. The results of thermal resistance investigations of foams; T_1 — temperature of loss in mass by 5 %, T_2 — temperature of loss in mass by 10 %, T_{max} — temperature of the highest rate of loss in mass

Symbol of foam	T_1, °C	T_2, °C	T_{max}, °C
W	85	250	320
GW0.1	68	222	300
GW0.2	66	220	299
GW0.3	63	219	298

Temperature of the highest rate of loss in mass is probably connected with decomposition of urea as a result of reaction of polyisocyanate with water and urethane groups.

CONCLUSIONS

As a result of glycolysis of the "original" waste PUR-PIR with diethylene glycol and ethanolamine, the glycolysate terminated by hydroxyl groups was obtained. Viscosity of the glycolysate allowed its further application for synthesis of "new" rigid PUR-PIR foams. The glycolysate obtained was characterized by hydroxyl number of 292.9 mg KOH/g. It means that it is suitable for composing the polyurethane system applied to produce rigid foam.

The "new" foams with glycolysate were characterized by two times higher compressive strength and by four times lower brittleness in comparison with "original" foam. Residue after combustion of foam increased by almost 20 %. Glycolysis of the rigid foam is a proper form of foam waste management. Compressive strength of foam containing product of glycolysis (GW0.1) is 2 times higher than that of standard foam *i.e.* "original" (W). Decomposition of waste foam (after optimizing of reaction conditions and amounts of raw materials) allows obtaining glycolysate which can be applied to synthesis of foams in amount of 0—0.3 of chemical equivalent in relation to the amount of industrial polyol. Glycolysis of the rigid PUR-PIR foam in diethylene glycol and ethanolamine is an effective form of the foam waste management.

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