Glycolysis of the Rigid PUR-PIR Foam Modified with Starch

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ABSTRACT: Introduction of natural fibbers and natural materials into plastics makes their biodegradation easier. Time of degradation of plastic wastes (also foams) in dump becomes shorter. In order to facilitate biodegradation of foams, starch in amount from 5% to 25% wt with respect to the mass of other components was introduced into polyurethane–polyisocyanurate (PUR-PIR) foams. Starch is susceptible to the action of bacteria in soil and thus, to decomposition. Polyurethane foams can be subjected to easy chemical degradation in glycols. From among all PUR-PIR foams prepared, one foam with optimum properties (S10 containing 10% wt of starch) was selected for further experiments. Then, the waste "origi- nal" foam S10 was subjected to glycolysis in diethylene glycol and ethanolamine (as catalyst). Glycolysate was applied for synthesis of "new" foams. Three foams GS10 containing 0.1, 0.2, and 0.3 of chemical equivalent (ch.eq.) of glycolysate with respect to amount of the original pol- yol Rokopol RF 55 were prepared. Effect of the amount of glycolysis product in foam composition on properties on the "new" foams was studied. Foam W was used as a ref- erence without starch (W). © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biodegradation; polyurethane foam; glycolysis; rigid polyurethane foam

INTRODUCTION

Polyurethanes (PUs) are biodegradable in soil, water, and in wet climate under the action of microorganisms, particularly mildew fungi. Microbiological decomposition of PU takes places by break-down of the individual bonds as follows:

- break-down of the final isocyanate groups
- break-down of urea and amide groups
- detachment and cleavage of urea groups
- rings fission.[1]

In order to hasten decomposition of polyurethane plastic, the polymeric materials of the natural origin such as starch, cellulose, or hitozane, which are decomposed under various conditions (soil, sea water), are introduced into their composition.[2–4] The polymers are modified (for example: plasticization with glycerol) and then added to plastics composition causing their fast decomposition without deterioration of the mechanical properties and simultaneously, they result in improvement of their parameters of processing.[5,6] The advantages of natural fibres are, among others,

low density, ability to acoustic wave damping, and easy recycling.[7] Starch materials used to produce the biodegradable materials should be water resistant. One of the methods to reach this target is modification of starch with compounds containing groups which react with hydroxyl groups of this polysaccharide. Starch forms esters, ethers, and urethane derivatives (in reac- tion with isocyanates).[8]

The synthetic high-molecular compounds (e.g., polyesters, polylactides, and polyamides) are also available on the market; however, costs of their pro- duction are very high.[9]

Biodegradable polymeric nanocomposites are also mentioned in literature.[10,11] They are characterized by low combustibility and high stability.

Moreover, the natural fibres such as straw, phloem, leaf, and grass are applied. The composites fasten with vegetable fibres fall into the following categories:

- biodegradable (ecofriendly/green)—both poly- mer base and filler are subjected to biochemical decomposition by living organisms (bacteria, fungi, and other live microorganisms) and they are divided to biosynthetic, semibiosynthetic, chemosynthrtic,
- biodisintegrable (partly ecofriendly)—polymers with synthetic base and filler from natural fibres, hybrid composites filled with a mixture of cellulose and mineral fibres.[12–14]

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Addition of natural fibres is one of the methods of environment protection. Its advantage is also a low price.

Storage of PUs is troublesome since they occupy a large area due to low density. Moreover, they are biodegradable with difficulty, so time of their storage is very long.[15] Most often, urethane polymers are subjected to chemical degradation with glycols.[16] Ester bonds are the most susceptible to this type of decomposition, less reactive are urethane bonds and the least reactive are ether bonds.[17,18] Processes of hydrolysis and fenolysis are also important here. Digestion in amines, caprolactam, and ammonia is of the secondary importance.[19–21] Compounds terminated both with hydroxyl and amino groups are the products. Moreover, pyrolysis as the method of PU decomposition is described in literature.[1] Depending on conditions of the process, polyisocyanates, isocyanates, polyols, or alcohols are obtained. Among gaseous products, carbon dioxide is dominant. As a result of waste PU pyrolysis at temperature within the range from 400 to 500°C, the products suitable for hydration are formed. The recovered hydrocarbons can be used to produce semi-finished products and then, PU (petrochemical processing).

The aim of our studies was to prepare foams which would be easily biodegradable in soil and therefore their waste materials would not fill waste dumps. For this purpose, 10% w/w of starch was introduced into the foam composition (foam with optimized utility properties). Starch was to accelerate cleavage of the rigid foam bonds.

The waste foams can be managed by recycling, e.g., chemical one (glycolysis, hydrolysis, and other) instead of throwing away.

The next aim of study was glycolysis of the waste rigid polyurethane–polyisocyanurate (PUR-PIR) foam modified with starch. The waste foams were subjected to chemical degradation in diethylene glycol. This method allowed us to obtain polyol suitable for synthesis of the new rigid foams. Effect of the obtained glycolysate (new polyol) on utility properties of the new PUR-PIR foams was determined.

As it is known from Ref. [22], bacteria living in soil promote processes of plastic degradation. One of the types of such bacteria are denitrifying bacteria, which assimilate nitrogen from atmosphere to biosphere and convert it to chemical compounds.

Part of nitrogen gets into the living organisms in the form of nitrate ions NO_3^- generated as a result of various geological and atmospheric processes. Nitrogen bacteria have an enzyme nitrogenase. This enzyme catalyzes reaction of gaseous nitrogen with hydrogen and as a result of this reaction, ammonium and amino acid glutamine are formed. Ammonium which directly gets to soil can also be later converted by nitrifying bacteria to nitrates (III) and nitrates (V).

Nitrates (V and III) are biodegraded in soil and also in water medium [eq. (1)]:

$$4NO_3^- + 5CH_2O + 4H^+ \xrightarrow{\text{denitrifying bacteria}} 2N_2 \uparrow$$
$$+5CO_2 \uparrow +7H_2O \quad (1)$$
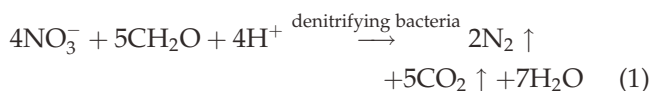
Process of nitrate V bioreduction to nitrogen (N_2) proceeds in stages according to the scheme (scheme 2):

$$2HNO_3 \rightarrow 2HNO_2 \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \quad (2)$$

The reactions proceeding in soil and the compounds formed in nitrogen cycle can cause decomposition of foams in soil.

EXPERIMENTAL

Characteristics of raw materials

The polyether with trade name Rokopol RF-55 (product of oxypropylation of sorbitol $L_{OH} = 495.0$ mg KOH/g, produced by NZPO "Rokita," Brzeg Dolny, Poland) and Ongromat CR 20-30 (technical polyisocyanate whose main component is diphenylmetane 4,4′-diisocyanate, made in Hungary) were used to prepare the rigid PUR-PIR foams. The density of Ongromat CR 30–20 at 25°C was 1.23 g/cm³, its viscosity was 200 mPa s and the content of NCO groups 31.0%. Polyether and polyisocyanate were characterized according to the following standards: ASTM D 2849-69 and ASTM D 1638-70.

An anhydrous potassium acetate (POCh, Gliwice) applied in the form of 33% solution in diethylene glycol (catalyst-12) and "DABCO 33LV" (triethylenediamine, Hülls, Germany) applied in the form of 33% solution in dipropylene glycol were applied as catalysts in the process. The polysiloxanepolyoxyalkylene surface-active agent ("Silicone L-6900", Witco, Sweden) was used as a stabilizer of foam structure.

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

Moreover, a liquid antipirene, i.e., tri(2-chloro-1-methyl-ethyl) phosphate ("Antiblaze TMCP," Albright and Wilson, United Kingdom) was introduced into foams.

Starch Master Bi produced by Novamont (Italy) was applied as a filler. Composition of starch includes: ash—max. 0.35%, the content of mineral substances insoluble in 10% hydrochloric acid—max. 0.06%, sulfur dioxide—max. 50 mg/kg, pollution macroscopic—max. 50 szt/dm², number of aerobic bacteria in 1 g—max. 50,000, the total number of yeasts and molds in 1 g—max. 100, the number of bacilli Bacillus cereus in 1 g, not more than −10, colontitre—0.01.

TABLE I
**Composition of the "Primary" (S10) Rigid Polyurethane–
Polyisocyanurate Foam After Modification with 10% of
Starch and W Foam (reference)**

| Name of material | Amount of material | | | |
	W (g)	S10 (g)	Percentage by weight (%)	Equivalent (R)
Rokopol RF55	60	60	–	1
Silicone L-6900	5.16	5.16	1.5	–
Dabco 33-LV	3.1	3.1	0.9	–
Antiblaze	51.6	51.6	–	–
Catalyst 12	7.2	7.2	2.1	–
Distilled water	3.78	3.78	–	0.7
Ongromat 30-20	286	286	–	3.7
Starch	–	34.4	10	–

Foam W has the same composition as the foam S10 but it did not contain the starch.

Preparation of the "original" PUR-PIR foam with addition of starch and W foam (reference)

The foam was prepared in a laboratory scale by 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 Rokopol RF-55, starch, catalysts, antipirene, and surface-active agent.

Component B was Ongromat CR 30-20 (Table I). Both components were mixed (1800 rpm, 10s) at respective mass ratio and poured onto an open rectangular tray of dimensions 195 mm × 195 mm × 240 mm. The parameters of processing such as start time, time of expansion, and gelation were measured during foaming.[23,24]

Biodegradation of standard S10 foam

The prepared "original" foam S10 was placed in two types of soil materials. A test sample was cut on the circular saw to the bars of 150mm × 20 mm × 20 mm. An effect of time on the degree of foam degradation in soil was studied. The soil material was used in the form of meadow soil and gravel (Table II). Studies were carried out in analogous climatic conditions. Soil materials were monitored during the tests (Table II). Temperature and pH of soil and gravel were determined in 7-day intervals. pH was measured by microcomputer pH-meter CP-551. Humidity of soils was not measured.

Weighted sample (analytical balance, accuracy to do 0.0001 g) was placed in soil on the depth of 35 cm. Studies were conducted for 250 days. Every 50 days the foam was removed from soil, dried, and weighted.

Preparation of S10 foam waste for recycling (grinding)

The "standard" foam S10 containing 10% of starch was first grinded in disc mill UKW-RU/A-170 (Institute of Technology, Casmir the Great University in Bydgoszcz). The diameter of grinding disc was 170 mm. Then, it was grinded in Janetzky's ball mill and powder of the grain size of <1 mm was obtained.

Glycolysis of "standard" foam S10

The "standard" foam containing 10% w/w of starch (S10) was subjected to glycolysis. Glycolysis was performed in glass three-neck flask of 50 mL equipped with reflux condenser, thermometer, and stirrer in order to prevent the foam sintering. The mixture containing diethylene glycol (40 g), ethanoloamine (20 g), and zinc stearate (1.5 g) was introduced into the flask and was heated in heating jacket to boiling point. Then, the dosage by portions of the milled foam S10 obtained according to recipe (Table I) was started. Glycolysis was conducted in four stages. Amount of foam added in IVth stage was equal to 68 g. Parameters of glycolysis are presented in Table III.

Introduction of each new dose of foam required progressive temperature rise from 160°C to 210°C. Time of reaction (total decomposition of foam) was 1.5 h. This method allowed us finally to obtain in IVth stage homogeneous brown product of glycolysis (S10E).

Studies on properties of S10 foam decomposition products (intermediate glycolysates and final product)

Properties of glycolysis products of the "original" foam (S10) were determined from a point of view their usability to prepare "new" PUR-PIR foams.

Viscosity was determined by the use of Hoeppler viscometer. Density of products of decomposition was determined as a ratio of solution mass to the volume. Hydroxyl number and acid number were determined according to factory standard PURINOVA, Bydgoszcz, Poland. The pH value of decomposition products was measured in ready glycolysate by the use of microcomputer pH-meter CP-551.[23]

Amount of unreacted glycol during decomposition of foams was carried out by gas chromatography

TABLE II
Properties of Soil Material Used in Studies on Degradation

| Properties | Kind of soil | |
	Grassland	Gravel
Permeability	Average	Large
Granularity	Average	Large
pH	7.35 (temp. 19.8°C)	7.51 (temp. 19.8°C)

TABLE III
**Parameters of Decomposition of Polyurethane–Polyisocyanurate Foams with Starch
(S10) (I, II, II, IV—Stages of Glycolysis)**

Symbol of foam	Temp. of decomposition (°C)	Time of decomposition, (min)	Amount of foam decomposed (g)	Yield of reaction (%)
S10 I	160	10	10	–
S10 II	180	20	20	–
S10 III	200	30	48	–
S10 IV	210	90	68	63.3

(Agilent Technology 6890N). Products of glycolysis were dissolved in ethanol. Measurement parameters were as follows: nitrogen flow was 35 mL/min, the air flow 350 mL/min, make up gas flow 25 mL/min (nitrogen). Flame Ionization Detector (FID) was used with flame on. Base temperature of FID was 250°C. The oven temperature was from 60°C to 225°C. Inlet temperature was 180°C.

Analysis of foams by IR spectroscopy was performed by Vector specrophotometer (Brücker) with the use of KBr technique within the range from 400 cm^{-1} to 4000 cm^{-1}.

Water content in products of alcoholysis was determined by Karl Fisher's method using pyridine-less reagent (Titraqual) according to PN-81/C-04959 standard. Determination consists in dissolution of the adequate weighted amount of glycolysis product in Titraqual (titrant for titration) and potentiometric titration of the solution to the equilibrium point.

Solubility of the glycolysis product was determined in basic solvents and polyols applied to synthesize the rigid foams.

Synthesis of rigid PUR-PIR foams with glycolysis product obtained from waste S10 foam

Foams containing product of glycolysis were prepared in such a manner that it was added in amount from 0.1 to 0.3 of chemical equivalent (ch.eq.) in relation to the original polyol RF 55, whose amount in foam was reduced from 0.9 to 0.7 of chemical equivalent (Table IV). The other components in foam composition are presented in Table I.

Studies on properties of rigid PUR-PIR foams ("original" S10 and "new" GS10)

The foams prepared, i.e. "original" (S10) and "new" (GS10) containing from 0 to 0.3 of chemical equivalent

of decomposition product of "original" foam (S10) were removed from mould and thermostated for 4 h at temperature of 120°C. Then, they were seasoned for 48 h at temperature of (20 ± 4)°C, cut into pieces and their basic properties were determined according to the obligatory standards (Table V). The details of the experimental methods are described in the article.[21]
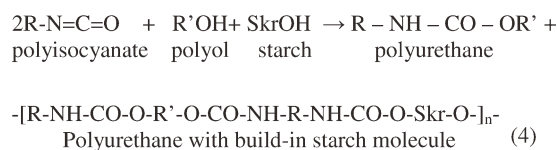
RESULTS AND DISCUSSION

Preparation of S10 foam

Addition of starch to PUR-PIR foam can have an effect on foaming process. At higher temperature, the changes occur in starch on molecular and hypermolecular level. Degradation of polysaccharide chains proceeds.

Starch reacts with polyisocyanate at room temperature. Starch urethane derivatives (carbamate) are obtained [eq. (3)]:

$$SkrOH + 2R - N{=}C{=}O$$
$$\rightarrow -[R{-}HN{-}CO{-}O]_n{-}Skr{-}OH \quad (3)$$
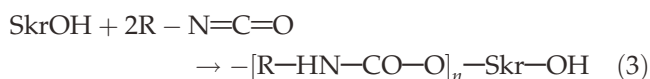
Polyurethane with built-in starch molecule was obtained in reaction of polyisocyanate with polyol and starch [eq. (4)]:

$$\begin{array}{cccc} 2R{-}N{=}C{=}O & + & R'OH + SkrOH \rightarrow R - NH - CO - OR' + \\ \text{polyisocyanate} & \text{polyol} & \text{starch} & \text{polyurethane} \end{array}$$

$$\begin{array}{c} \text{-[R-NH-CO-O-R'-O-CO-NH-R-NH-CO-O-Skr-O-]}_n\text{-} \\ \text{Polyurethane with build-in starch molecule} \end{array} \quad (4)$$

where: Skr—starch

The fact that the starch molecule incorporated in the polyurethane bond derivative of amylose and amylopectin can provide vibrations in IR spectra, e.g., -OH bending vibrations enhanced by the -CH

TABLE IV
Composition of Polyols (Original and "New" Obtained by Glycolysis) Applied to Synthesize Foams

Name of material	Unit	Symbol of foam		
		GS10 (0.1)	GS10 (0.2)	GS10 (0.3)
Rokopol RF55	Gramme (chemical equivalent)	54.0 (0.9)	44.5 (0.8)	38.9 (0.7)
Glycolysate of foam S10	Gramme (chemical equivalent)	19.4 (0.1)	38.7 (0.2)	58.1 (0.3)

TABLE V
Methods for Testing the PUR-PIR Foams Produced

Methods for testing	Metod description
Structure	Eclipse 400 POL microscope, Canon, Japanese, transmitting light, magnification 5 times and 10 times
Compression strength	Tira Test 2200 testing machine, ISO 844 : 1993: DIN 53420
Brittleness	ASTM C-421-61
Thermal resistance (softening point)	Vicat apparatus, DIN 53424
Density	ISO 845-1988
Change of mass	Thermostating in drier for 6 hours
Change of volume	Thermostating in drier for 6 hours
Thermal conductance	"FOX 200" apparatus of Lasercomp
Content of closed cells	PN-ISO 4590 : 1994
Absorptivity of water	DIN 53433
Flammability, horizontal test	PN-78 C-05012
Flammability, shorten chimney test (vertical – Butler's)	ASTM D3014-73
Analysis by IR method	spectrophotometer Vector firmy Brücker

bending vibrations 1209 cm^{-1}, 1260–1000 cm^{-1} oscillation of CO, 1046 cm^{-1} symmetric bond vibration – C—O—C-, 745 cm^{-1} -CH bending vibrations of aromatic, the methylene bond of 2940–2860 cm^{-1}.

The respective parameters of S10 foam processing were as follow: start time—17 s, time of expansion—54 s, and time of gelation 50 s.

Biodegradation of S10 foam

The results show that saturation of foams by water and molecules of sand occurs for the first 50 days, which is demonstrated by the growth of foam mass (Fig. 1). Loss in mass begins already after about 100 days. Foam sample containing 10% wt of starch changes its shape (there are losses.) There are also color changes from yellow foam to brown.

It was found that degradation in gravel proceeded less intensively. Rather intensive gain in weight from 0.9682 g to 1.1210 g was observed until about 50 days. During next 150 days, a slight loss in weight to 1.082 g (250 days) occurred. It can be due to the high permeability of material (gravel), which causes the water to penetrate inside the samples and simultaneously it evaporates.

Degradation in meadow soil progresses more intensively, what can result from different composition of bacteria responsible for degradation. A slight gain in weight from 1.0864 g to 1.0880 g (50 days) occurs in the first 50 days. After 100 days high reduction in weight to 0.9420 g (250 days) was observed.
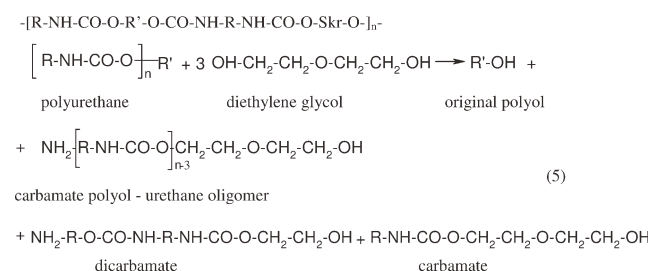
Natural polymers such as starch are sensitive to the action of microorganisms and they are regarded as fully biodegradable (decomposition to CO_2, H_2O, and biomass), therefore their addition promotes degradation. Chemical structure of polyurethane group (similarly as ester, carboxyl, ether, and hydroxyl group) is susceptible to hydrolytic attack of microorganisms (bacteria, moulds), to moisture, and to access

of oxygen. Therefore, higher reduction of sample mass is observed in meadow soil than in gravel.

Glycolysis of S10 foam

Course of glycolysis with diethylene glycol

Diethylene glycol probably partially reacts with polyurethane and original (initial) polyol and carbamate polyol and carbamate and dicarbamate [eq. (5)] are formed:

-[R-NH-CO-O-R'-O-CO-NH-R-NH-CO-O-Skr-O-]$_n$-

$$\left[\text{R-NH-CO-O} \right]_n \text{R'} + 3 \text{ OH-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH} \longrightarrow \text{R'-OH} +$$

polyurethane   diethylene glycol   original polyol

$$+ \text{ NH}_2 \left[\text{R-NH-CO-O} \right]_{n-3} \text{CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-OH}$$

carbamate polyol - urethane oligomer

(5)

+ NH$_2$-R-O-CO-NH-R-NH-CO-O-CH$_2$-CH$_2$-OH + R-NH-CO-O-CH$_2$-CH$_2$-O-CH$_2$-CH$_2$-OH

dicarbamate   carbamate

Reaction of polyurethane with ethanolamine

Aromatic amines, polyols, short-chain carbamate urethanes, and urea are formed as a result of degradation by alkanolamines.
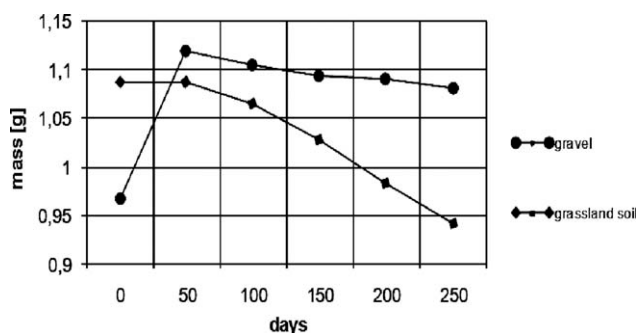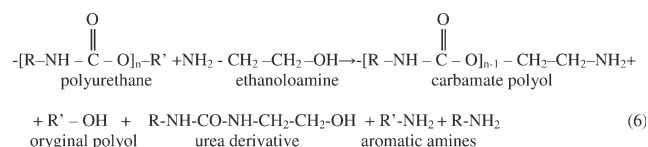

Figure 1 Change in mass of S10 foams placed in soil material during 250 days.

TABLE VI
Properties of Liquid Products from Decomposition of Polyurethane–Polyisocyanurate Foams
(I, II, III, IV—Stages of Glycolysis)

Symbol of foam	Viscosity at temp. of 20°C (mPa s)	Density at temp. of 20°C (kg/m³)	Hydroxyl number (mgKOH/g)	Acid number (mgKOH/g)	Form of the product obtained	pH
S10 I	100.2	1048.0	420.1	26.1	Liquid	8.2
S10 II	205.0	1072.0	388.7	25.2	Liquid	8.0
S10 III	390.9	1102.0	228.9	23.4	Liquid	7.8
S10 IV	2584.8	1170.0	144.6	22.6	Liquid	5.2

In reaction of polyurethane with ethanolamine, carbamate polyol, original polyol, urea derivative and aromatic amines are formed [eq. (6)]:

$$-[R-NH-\overset{\overset{\text{O}}{\parallel}}{C}-O]_n-R' +NH_2-CH_2-CH_2-OH \rightarrow -[R-NH-\overset{\overset{\text{O}}{\parallel}}{C}-O]_{n-1}-CH_2-CH_2-NH_2+$$

polyurethane   ethanoloamine   carbamate polyol

$$+ R'-OH + R-NH-CO-NH-CH_2-CH_2-OH + R'-NH_2 + R-NH_2 \qquad (6)$$

oryginal polyol   urea derivative   aromatic amines

As the amount of foam waste S10W introduced into flask was increased, viscosity of glycolysate violently increased from 100.2 mPa s (product S10I—content of waste foam in solution—10 g) to 2584.8 (product S10IV—content of waste foam 68 g). Moreover, density increased (Table VI), whereas, hydroxyl number, acid number, and pH of solution (from 8.2 for S10I to 5.2 for S10IV) decreased.

In order to apply product of alcoholysis to the synthesis of foams, it should be dissolved in polyols commonly used to obtain foams. Solubility of glycolysates in common dissolvent is presented in Table VII.

Content of unreacted glycol in the product of glycolysis decreases as the amount of waste foam in so-lution is increased from 51.36% (S10I) to 35.23% (S10IV)—Table VIII.

Content of water was also determined in the products of glycolysis since it is a significant parameter affecting density of PUR-PIR foams. Results are presented in Table VIII. As the amount of foam in the product of glycolysis was increased, content of water increased from 0.70% to 0.85%.

Presence of wide band (1) and narrow (7) characteristic for hydroxyl groups OH within the range from 3500 to 3250 cm^{-1} and 1120 cm^{-1} was observed in IR spectra (Fig. 2). In Figure 2, vibrations at 1741 cm^{-1} can also be observed (marked as 2). They are attributed to ether group C=O. Appearance of amide -NH- and amine -NH$_2$ groups at wavelength of 1500 cm^{-1} was marked by symbol 3. Urea groups –NH—CO—NH- wavelength of 1630–1670 cm^{-1} (4) and bands characteristic for saturated hydrocarbons C—H (2890 cm^{-1}, symbol 5) also appear in the product of glycolysis. A weak band at 1941 cm^{-1} proves about appearance of aromatic rings with substituent (symbol 6). It is probably attributed to aromatic amines.

Properties of PUR-PIR foams

The linear dimensions and volume of foams containing products of glycolysis were unchanged after 48 h of thermostating. The exception was foam S10 in which the volume increased by 20%. The increase in the volume of foam could be caused by swelling of starch in the foam.

Parameters of processing for foams containing product of glycolysis were shorter by almost twice in comparison with these parameters for "original" foam S10 (start time 17 s, rise time 56 s, gelation time 45 s) and at the same time twice longer

TABLE VII
Solubility of Glycolysaties

Solvent	Solubility
Toluene	No
Ksylene	No
Acetic anhydride	No
Water	No
Ethanol	No
Methanol	Yes
Turpentine wood	No
Pyridine	No
Ekstraction naphta	Yes
n-hexane	No
Diethylene glycol DEG	No
Ethanediol	Yes
1,2-propanediol	Yes
1,3-propanediol	Yes
Rokopol RF55	Yes
Rokopol TG 500	Yes
Chloroform	Yes
Triethanoloamine TEA	Yes
Ethanoloamine	Yes
Acetone	Yes
Etyl acetate	Weakly

TABLE VIII
Determination of Water and Unconverted Glycol
Contents in the Products of Glycolysis

Symbol of foam	Content of DEG (%)	Content of water (%)
S10I	51.36	0.70
S10II	46.12	0.76
S10III	40.99	0.81
S10IV	35.23	0.85
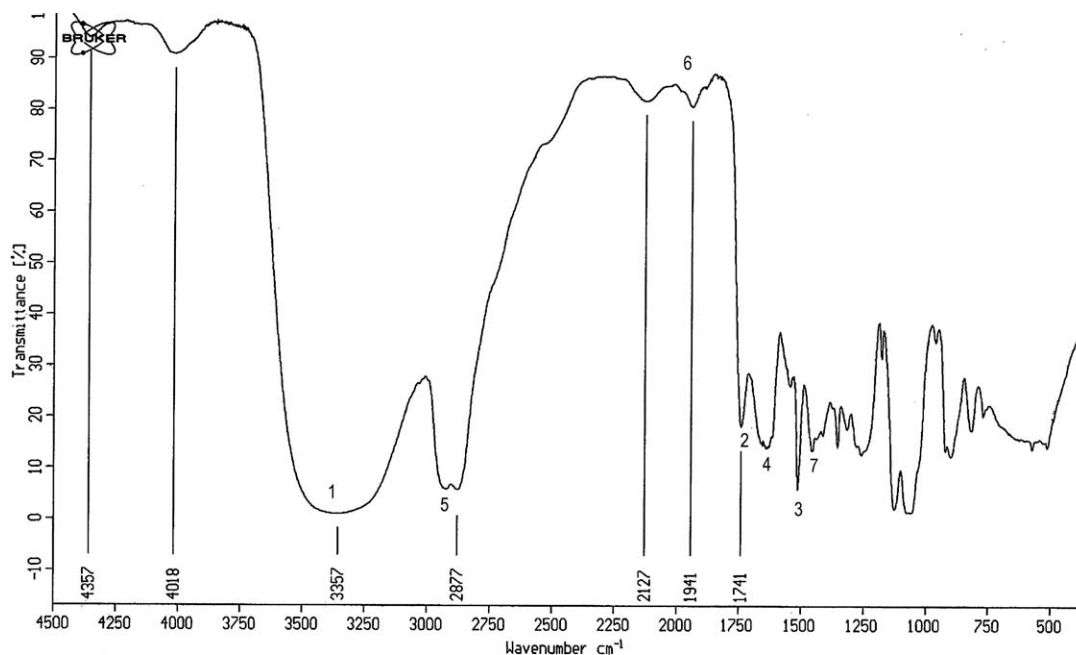
Figure 2 IR spectrum of the glycolysate (GS10-0.1): 1, 7-hydroxyl group OH; 2, ether group C=O; 3, amide NH and amino NH$_2$ group; 4, group of urea NH—CO—NH; 5, saturated C—H; 6, substytuted aromatic ring.

compared to the foam without filler W (start time 17 s, rise time 18 s, gelation time 37 s). However, time of gelation and time of expansion were slightly prolonged: from 24 s (foam with 0.1 of ch. eq. of glycolysate) to 37 s (foam with 0.3 of ch. eq. of glycolysate) and from 30 s (foam GS10 with 0.1 of ch. eq. of glycolysate) to 45 s (foam GS10 with 0.3 of ch. eq. of glycolysate), respectively, as the content of glycolysate in foam was increased. The foam processing parameters were 17 s (start time), 18 s (rise time), 37 s (gelation time). Extending the time of the foam processing S10 in relation to the other may be due to the addition of starch to the premix polyol.

Addition of starch can have generally a negative effect on strength of material since change in this filler structure occurs during processing. Lower strength can result partial decomposition of starch (hydrolysis during oryginal S10 foam glycolysis). It is due to lower ordering of starch chains. Small quantity of glycolysis product (0.1 of ch. eq.) in foam causes increase in compressive strength by over twice (Fig. 3). Increase in amount of glycolysate have an effect on decrease in compressive strength from 311 kPa (foam with glycolysate GS10-0.1) to 240.5 kPa (foam GS10-0.3), however these values are higher than these obtained for "original" foam containing 10% w/w of starch (152.1 kPa—foam S10) and reference foam W (221.7 kPa). The reason may be the structure of foam stickers (chapter "structure of foams"). Densely packed structure of the foam GS-0.1, and equal-sized cells make the value of the compressive strength of this foam the highest.

A sharp reduction of brittleness from 19.9% (foam S10) to 4.5% (foam GS10-0.3) was observed in the case of foams obtained—Table IX.

Thermal conductivity ranged in a narrow interval from 33 to 35 mW/m K independently of the amount of product of glycolysis and shows no strict correlation with the contents of the closed cells.

Content of closed cells varied from 87.8% to 95% with the amount of glycolysate used. For the foam W it is 91.5%.

Absorbability of water decreased within the range from 1.8% (W) and 1.60% (S10) to 1.52% v/v (GS10-0.1). Reduction of water absorption is due to the increasing amount of closed cells in the foam with the increase in glycolysate.
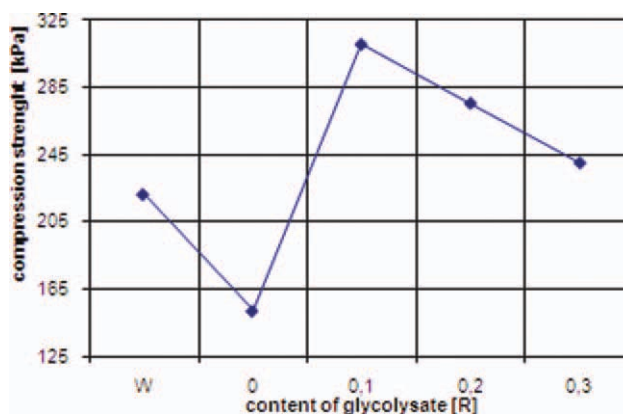
Figure 3 Effect of the glycolysis product addition on the compression strength. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IX
Properties of the PUR-PIR Rigid Foams

Symbol of foam	Apparent density (kg/m^3)	Brittleness (%)	Content of closed cells (pores) (% volume)	Absorptivity of water (% volume)	Retention residue (% after combustion)
W	36.9	41.1	91.5	1.8	76.6
S10	34.9	19.9	87.8	1.6	80.0
GS10-0.1	49.9	17.3	91.1	1.59	89.9
GS10-0.2	70.3	9.3	94.2	1.57	93.1
GS10-0.3	84.7	4.5	95.0	1.52	96.4

Retention (residue after combustion) increased to 96.4% (foam GS10-0.3 of ch. eq.) in comparison with "original" foam S10 (80%) and foam W (79.9%). The results show that glycolysis contributed to reduce the flammability of foam by 16%. Perhaps stickers structure has resulted in reduced access of air to the interior of cells and thus decreased the flammability of the foams. Softening point of foams increased from 182°C (foam S10) to 216°C (foam GS10-0.3) as the amount of glycolysate was increased in foam composition but it decreased in comparison with W foam (230°C)—Figure 4. Addition of both starch and glycolysis product with starch foam lowers the softening temperature of the foams.

The bands characteristic for isocyanurate marked as 2 and 3 (1690 cm^{-1} and 1410 cm^{-1}) and urethane marked as 1 (1720 cm^{-1}) bonds were recorded in IR spectra of standard foam and foam containing starch—Figure 5. Moreover, vibration band at wavelength of 3360 cm^{-1} was recorded which proves about appearance of hydroxide group –OH (marked as 4).

Structure of foams

Foam S10 is characterized by regular, branched, and fine-cell structure (Fig. 6). Only singular inclusions of larger cells were observed. For comparison, the fo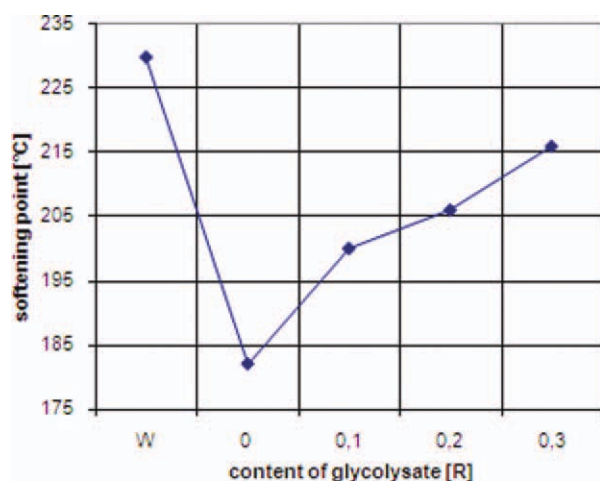am W structure is less strict, the cells are larger and are regular, and they are of equal size. Appendix glycolysis (GS10 foam) gives rise to agglomerates and veneers the structure of the foams. Glycolysis, the more the structure is more veneered. An increasing number of glycolysis positive impact on closing the cells. On photography glycolysis (GlyS10) shows the two structures. Product of glycolysis does not separated into layers. It was homogeneous.

Foam structure reflects some of its properties, such as foam strength S10 is the lowest, as well as the content of closed cells. Large and thin foam W cells in the cause that it absorbs the most water, because these cells has larger surface then other foams.

CONCLUSIONS

The "original" rigid PUR-PIR modified with starch (10% w/w) was produced.

On the basis of the properties, glycolysate was accepted as a product useful for synthesis of PUR-PIR foams (viscosity—2584.8 mPa s, density—1170.0 kg/m^3, and hydroxyl number 144.6 mgKOH/g).

Addition of product of glycolysis into foam composition causes increase in compressive strength by twice (at glycolysate content of 0.1 of ch. eq.), high reduction of brittleness from 19.9% (S10; foam no content of glycolysate) to 4.5% (GS10-0.3; foam content 0.3 of ch.eq) and increase in softening point by 34°C (at glycolysate content of 0.3 of ch. eq.-GS10-
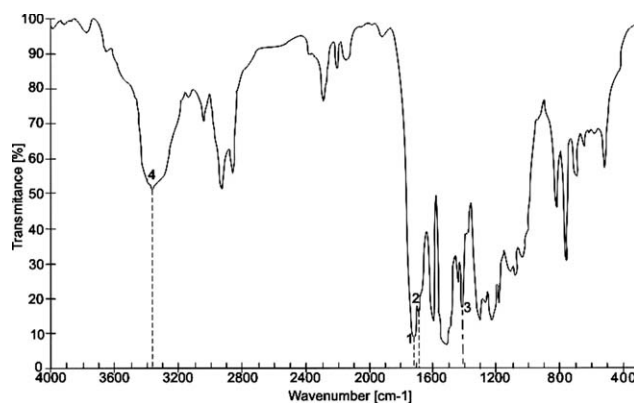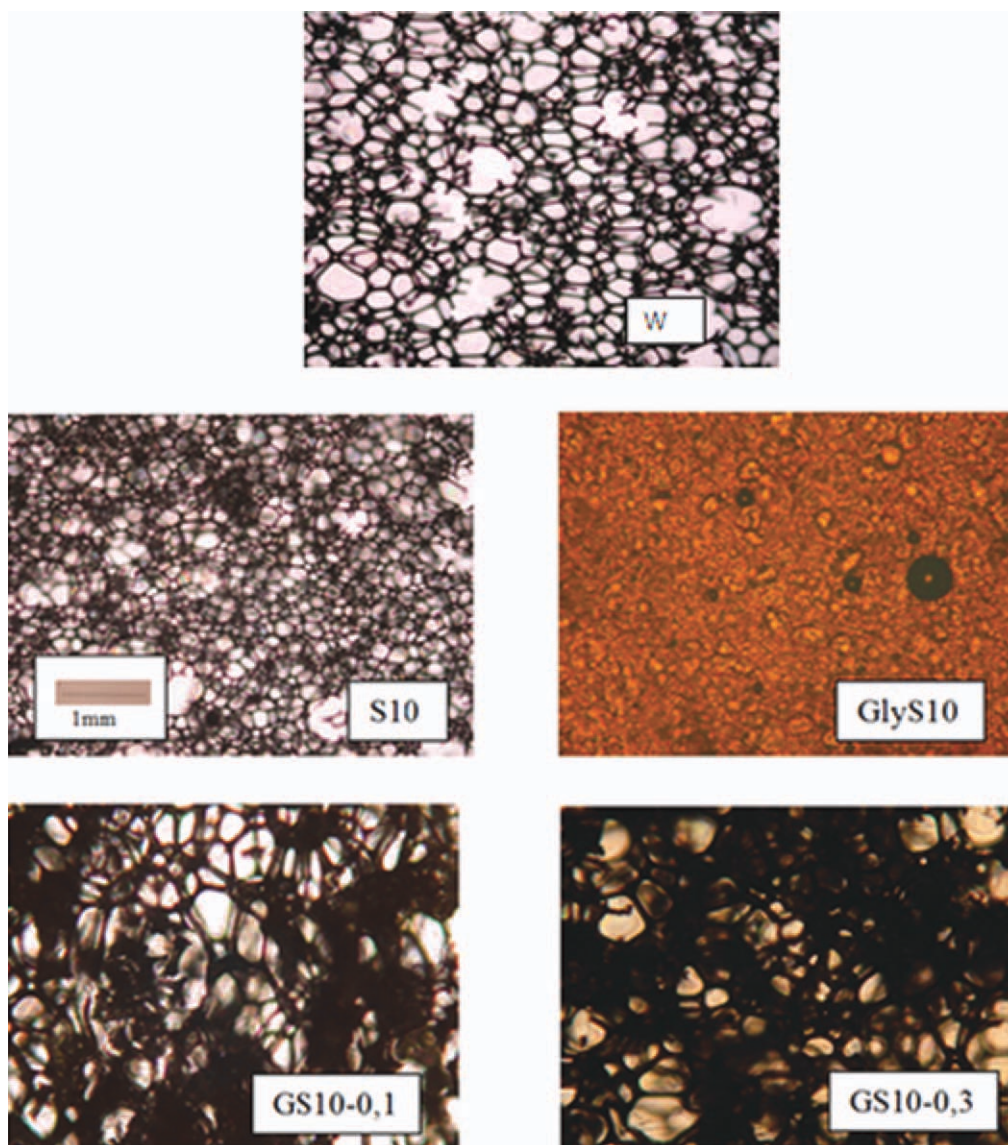

Figure 4   Effect of the glycolysis product addition on the softening point. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5   IR spectrum of PUR-PIR foam (S10): 1, urethane group (1720 cm^{-1}); 2,3, isocyanurate group (1690 cm^{-1} and 1410 cm^{-1}); 4, hydroxyl group OH (3360 cm^{-1}).

Figure 6 Structure of reference foam (W), "primary" foam (S10, magnification 5×) and glycolysis (GlyS10, magnification 10×) and "new" foams with 0.1 and 0.3 of chemical equivalent of glycolysate (GS10-0.1 and GS10-0.3, magnification 5×).[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

0.3) in comparison with "original" foam S10. Content of closed cells increased by 7.2% and thus, absorbability of water range from 1.6% v/v (S10 foam) to 1.52% v/v (GS10-0.3 foam). Formation of more and more stickers in the structure of foam, as the amount of glycolysate is increased in the foam composition, results in reduction of water absorptivity (Fig. 6).

It is worth noticing that pores in foams obtained are practically of the same dimensions that proves about proper selection of surfactant and porophor as well as about no effect of glycolysate amount on this characteristic. Only small percentage of inclusions of cells with larger dimensions was recorded.

In summary, it was found that addition of product of glycolysis of waste foam modified with starch improved some characteristics of the "new" foams. Glicolysate can be applied for synthesis of rigid PUR-PIR

foams in amount from 0.1 to 0.3 of chemical equivalent in relation to the industrial polyol; however, the most favourable amount is 0.1 of chemical equivalent.

Foams containing glycolysate (new) are suitable as constructional foams similarly as the "original" foam without glycolysate.

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