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Sorbitol/glycerin/water ternary system as a novel glycolysis agent for flexible polyurethane foam in the chemical recycling using microvawe radiation

Summary — An eco-friendly and convenient method was performed for recycling of flexible polyurethane foams. Glycerin/sorbitol/water mixture was used as destroying solvent and sodium hydroxide as a catalyst. In all reactions phase separation appeared after complete foam digestion. The upper phase contained recycled polyol and lower phase was a brown liquid that applied in rigid polyurethane foam formulations. The mechanical properties of formulated foams were compared with virgin polyol formulated sample. Reactions were studied using various glycerin/sorbitol/water ratios and the recovered polyols were characterized by spectroscopic methods and data compared with a virgin sample.

Key words: PUR foams, hydroglycolysis, sorbitol, microwave, polyol recovery.

TRÓJSKŁADNIKOWY UKŁAD SORBITOL/GLICEROL/WODA JAKO NOWY CZYNNIK GLIKOLIZUJĄCY W CHEMICZNYM, WSPOMAGANYM MIKROFALAMI RECYKLINGU ELASTYCZNEJ PIANKI POLIURETANOWEJ

Streszczenie — Zbadano wpływ składu wymienionej w tytule mieszaniny na przebieg wspomaganej mikrofalami hydroglikolizy, otrzymywanej we własnym zakresie elastycznej pianki poliuretanowej (PUR) (tabele 1—3). Metodami FT-IR, ^{1}H NMR i ^{13}C NMR (rys. 1—3) scharakteryzowano odzyskany w wyniku glikolizy poliol stanowiący fazę górną glikolizatu. Pozostałość zawierającą sorbitol — fazę dolną glikolizatu — wykorzystywano w mieszaninach ze świeżym poliolem do wytwarzania sztywnych pianek PUR (tabele 4—6). Oceniono wpływ udziału tej fazy na przebieg procesów spieniania (tabela 7) i właściwości mechaniczne uzyskiwanych w ten sposób pianek (tabela 8); stwierdzono, że wraz ze zwiększaniem zawartości omawianej fazy w mieszaninie reakcyjnej następuje wzrost ich modułu sztywności i zmniejszenie wydłużenia przy zerwaniu. Świadczy to o wzroście gęstości usieciowania wynikającym z obecności sześciofunkcyjnego sorbitolu w zastosowanej do syntezy pianek dolnej fazie glikolizatu.

Słowa kluczowe: pianki poliuretanowe, hydroglikoliza, sorbitol, mikrofale, odzyskiwany poliol.

In the recent years, polyurethane (PUR) materials have been used in diverse areas and formed one of the most important groups of plastics because of their versatility [1]. Among them, flexible foams are of great importance and they has reached 29 % of the total PUR production. They are widely used *e.g.* in furniture mattresses and automotive seats [2]. Nowadays PUR recycling is an urgent task and categorized into physical or chemical recycling.

In the chemical recycling the urethane bonds can be broken down by means of a suitable destroying solvent. The general purpose of PUR chemical recycling is to obtain its original initial raw materials, especially polyols.

Chemical recycling include glycolysis [3, 4], hydrolysis [5—7], hydroglycolysis [8] and aminolysis [9, 10]. Many researchers have investigated the glycolysis and hydroglycolysis of PUR wastes. Datta and his *co*-workers investigated the recycling of PUR foams by using monomeric and polymeric diols and polyols [11]. Simioni and his *co*-workers investigated the glycolysis of flexible PUR foams at 190 °C by use of ethylene glycol (EG) at high polymer/glycol ratio (up to 4:1) [12]. Borda *et al.* studied the glycolysis of flexible PUR foam and elastomers in the temperature range of 170—180 °C with use of diethanolamine (DEA) and glycols [EG, 1,2-propylene glycol, triethylene glycol, poly(ethylene glycol)] [13]. Troev *et al.* observed the chemical degradation of flexible PUR foam under the influence of triethyl phosphate at 190 °C [14]. Kanaya and Takahashi reported the

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decomposition of flexible PUR foam in the presence of alkanolamines without a catalyst at 150 °C [15].

There are some advantages of microwave (MW) assisted reactions in comparison to conventional heating methods. For example, MW enhances the reaction rates and increases the yields by limiting of side reactions. While some authors believe that these results can be explained through thermal influences, the others argue that additional nonthermal or specific MW effects play a role. The exact source of reaction improvement under the influence of MW is the subject of controversy [16].

There are some reports concerning polymer chain degradation by use of MW radiation. For example, it appeared that poly(ethylene terephthalate) (PET) solvolysis occured in the shorter reaction times in comparison with the processes of glycolysis and hydroglycolysis of flexible PUR foam wastes investigated by us [17—20]. To continue our previously reported experiments, we decided to examine the performance of glycerin/sorbitol/water system combined with NaOH as a new "green" destroying agent in the flexible PUR foam hydroglycolysis reactions. In order to save energy consumption and enhance the reaction rates all reactions were performed using a commercial microwave (MW) oven.

EXPERIMENTAL

Preparation of initial flexible foams

Flexible PUR foam samples were received from flexible foam polyol Daltoflex EC 20240 (Table 1) and diphenylmethanediisocyanate (MDI) Suprasec® 5005 (Table 2), both purchased from Huntsman. Formulation and mold conditions were as follows: Daltoflex EC 20240 — 100 parts by weight, Suprasec 5005 — 65 parts, recommended mold temp. 40—45 °C, demolding time 5 min (molding density 42—47 kg/m^3).

Table 1. Daltoflex EC 20240 specification

M_w	1900
Viscosity (Pa · s at 20 °C)	1.250
Density (g · cm^{-3} at 20 °C)	1.035
Functionality	2.0
Hydroxyl number (mg KOH/g)	59
Fire point (°C)	240

Table 2. MDI (Suprasec® 5005) specification

Color	Dark brown liquid
Viscosity (Pa · s at 25 °C)	0.22
Density (g · cm^{-3} at 25 °C)	1.23
Practical NCO value (% by wt. of NCO groups)[*)]	30.9
Average functionality	2.7
Flash point (°C)	233
Fire point (°C)	245

[*)] Group weight: 42 g · mol^{-1}.

Hydroglycolysis

The scraps of flexible PUR foam (5 g) (segmented into small sizes), NaOH (1 % w/w) and various systems in which glycolysis reactions were running, were placed in a two necked flask and then put into microwave oven (Milestone MicroSYNTH, NP Ethos 1600) at atmospheric pressure at 180 °C and 800 W in various reaction times (Table 3). When foam digestion was completed, the mixture was removed from microwave oven and was left to separate two distinguishable phases. The upper phase (recycled polyol) was decanted carefully and centrifuged for 20 min and then characterized by spectroscopic methods.

Table 3. Effect of the composition of the system causing hydroglycolysis on its course

Sample	Glycerol % w/w	Sorbitol[*)] %	Water %	Time min	Upper phase %	Lower phase %
GSF1	95	3.5	1.5	1.5	54	45
GSF2	90	7.0	3.0	1.7	58	42
GSF3	85	10.5	4.5	2.0	68	32
GSF4	80	14.0	6.0	4.0	54	46
GSF5	75	17.0	7.5	4.0	70	30
GSF6	70	21.0	9.0	6.0	78	22
GSF7	65	24.5	10.5	7.0	27	73
GSF8	60	28.0	12.0	8.0	42	58

[*)] Sorbitol solution (70 %) purchased from Roquette (France) was used as received without further purification.

Preparation of new rigid PUR foam using lower recycled phase

In order to use the lower phase in PUR rigid foam formulations, this phase which contained unreacted destroying solvents and some recovered amines (*e.g.* 4,4′-diaminediphenylmethane, MDA) [21—23], was directly mixed in different ratios with virgin polyol (Daltofoam TA 14066, purchased from Huntsman Company, Table 4), aliphatic amines, catalysts surfactant and water. The virgin polyol in a blend with lower phase and mentioned additives were mixed with MDI (Suprasec 5005) in a free rise conditions for production of rigid foam. All data are collected in Table 5.

Table 4. Virgin polyol (Daltofoam® TA 14066) specification

Color	Viscous yellow liquid
Viscosity (Pa · s at 25 °C)	5.263
Density (g · cm^{-3} at 25 °C)	1.06
Water content (%)	2.3
pH	9.45
Practical OH number (mg KOH · g^{-1})	20 ÷ 430

For comparison, a sample of rigid PUR foam made of virgin polyol Daltofoam TA 14066 (100 parts) and MDI — Suprasec 5005 (133 parts) (sample 0) was prepared.

Table 5. Preparation of new rigid PUR foams using lower recyclate phase

Sample	MDI (133 weight parts), %	Polyol reagent (100 weight parts)	
		lower phase, %/sample	virgin polyol, %
1	100	5/GSF1	95
2	100	10/GSF2	90
3	100	15/GSF3	85
4	100	20/GSF4	80
5	100	25/GSF5	75
6	100	30/GSF6	70
7	100	35/GSF7	65

Methods of testing

— FT-IR spectra were registered using a Bruker Tensor 27 spectrometer.

— ^{1}H NMR and ^{13}C NMR spectra were registered using a Bruker CRX 300 instrument, deuterated $CDCl_3$ as a solvent and TMS (tetramethylsilane) as an internal standard.

— Tensile properties were determined using an Instron 1122 tensometer (5 kN), at a cross head speed of 5 mm · min^{-1} at room temperature, according to ASTM D-638. Three specimens of each sample were tested. In these samples, the tensile trend was linear according to the performed force and thus the *E*-modulus results were obtained from the slope of stress-strain curves.

RESULTS AND DISCUSSION

Recovered polyol characterization

According to our previously reported paper [20], dissolution of PUR foam in destroying solvents without catalysts was extremely difficult and basic catalysts, namely KOH or NaOH, were the suitable catalysts from the points of view of reaction rates as well as economic considerations. For this reasons we used now NaOH as the catalyst. In order to investige the sorbitol effect on the recycling of flexible PUR foam, we examined the dependence of reaction time versus sorbitol content according to Table 3.

We found out that with the increasing sorbitol content, reaction time increased. This was possibly due to increasing viscosity of the reaction media as well as difficulties in nucleophilic attack of destroying agent to the polyurethane bonds. The increase in sorbitol part over 50 % of destroying agent deteriorated reaction times.

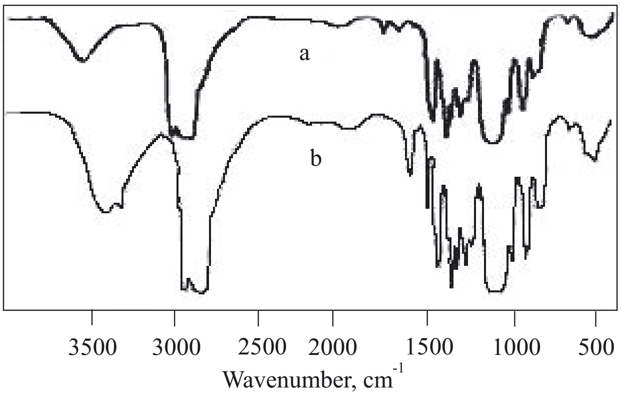

Fig. 1. FT-IR spectra of virgin (a) and recycled (b) polyols

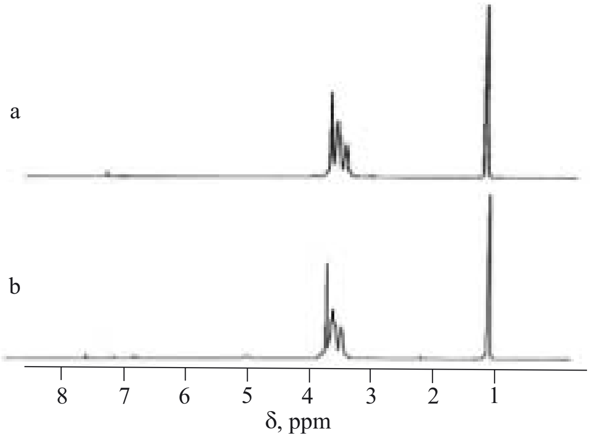

Fig. 2. ^{1}H NMR spectra of virgin (a) and recycled (b) polyols

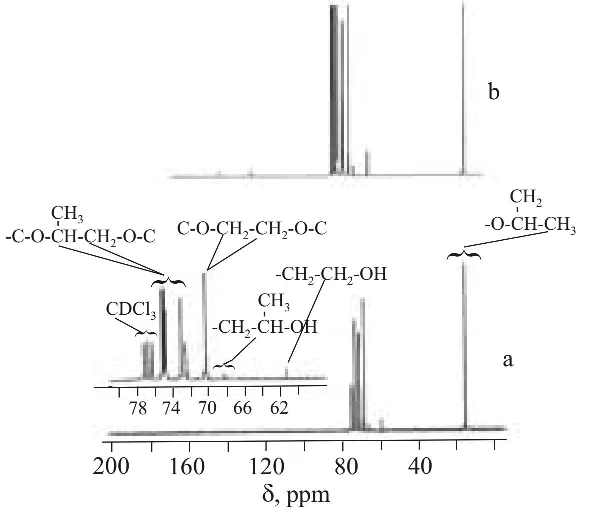

Fig. 3. ^{13}C NMR spectra of virgin (a) and recycled (b) polyols

For characterization of recovered polyol, we used spectroscopy techniques. Figure 1 shows FT-IR spectra of virgin and recycled polyols. The absorption band at 1115 cm^{-1} related to aliphatic ether group of polyether polyol. Bending vibrations of methylene groups appear in the polyol chain at 1374 and 1456 cm^{-1}, stretching vibrations of CH bonds in aliphatic carbons are found at 2970—2868 cm^{-1} and stretching vibrations of OH groups are found at 3482 cm^{-1}.

Figure 2 shows typical ^{1}H NMR spectra of recovered polyol in comparison with virgin one. There are four characteristic peaks — at 1.1 ppm (3H, $-CH_3$) and 3.3—3.6 ppm (6H, $-CH_2-O-$ and 1H, $-CH-O-$) — in ^{1}H NMR spectra of recovered and virgin polyols that indicate their structural similarity. The weak peak near to 5.0 ppm relates to water.

In ^{13}C NMR spectra the characteristic peaks consist of: 17.3 ppm [-OCH(CH_2)-**C**H_3], 61.1 ppm (-CH_2-**C**H_2-OH), 68.5 ppm [-CH_2-**C**H(CH_3)-OH], 70.2—70.7 ppm (C-O-CH_2-CH_2-O-C), and 72.5—75.3 ppm [C-O-**C**H(CH_3)-**C**H_2-O-C] (Fig. 3). The presence of contaminant in the recovered polyol has been appeared in ^{13}C NMR spectra comparison, namely the peaks in the spectral regions 40, 114.5, 129, 130.5 and 146 ppm in ^{13}C NMR spectrum of recovered polyol (Fig. 3b) are corresponding to the carbons originated from MDA as contaminant and we assigned all peaks in our recently published paper [19].

Rigid PUR foams preparation and characterization

An important observation in the reactions of rigid foams preparation from virgin polyol and lower recyclate phase is the compatibility of these two products what makes them useful in a similar formulation for production of new rigid PUR foam. According to the Tables 5 and 6, increase in the lower phase content up to 20 % (samples 1—4) causes increasing density of PUR foams prepared. An increase in lower phase content over 20 % in a blend with virgin polyol (samples 5 and 6) is not suitable due to failing in high quality PUR foam formation; in these conditions it was impossible to determine some foaming process factors.

Table 6. Foaming process parameters, density and foam quality of PUR rigid foam samples

Sample	Foam quality	Density g/cm^3	Tack free time, s	String time, s	Rising time, s	Cream time, s
0	OK	0.052	112.0	65.0	60.0	25.5
1	OK	0.118	107.0	56.0	55.0	53.3
2	OK	0.130	53.1	40.0	50.2	37.4
3	OK	0.160	16.5	13.5	47.0	40.0
4	OK	0.161	7.0	10.3	39.0	43.3
5	Failed	0.095	—	—	35.0	45.0
6	Failed	0.063	—	—	32.0	48.6

As it is shown in Table 6, the foaming process parameters (tack free, string and rising times) are diminished when lower recycled phase content in the polyol blend increased. On the other hand, the foaming process of blends containing higher contents of this phase is more exothermic, so the heat release during foaming process is enhanced by increase in the recyclate content in the polyol blend.

According to Table 7, tensile strength and elongation at break of formulated foams decrease by increasing content of lower phase containing sorbitol. As shown in Table 7, comparison of the mechanical properties of formulated foams made with use of virgin or lower phase from recycled foam confirms that the foams prepared with use of residue (lower phase) of glycolysis process (samples 1—4) are approximately similar to the one prepared with virgin polyol (sample 0). It is worth to mention that all the samples prepared with use of lower phase of glycolysis product are more rigid (lower elongation, bigger *E*-modulus values) than the one prepared from virgin polyol exclusively (of functionality = 2). This is due to increments in crosslinking densities dependent on sorbitol (functionality = 6) content. Additionally unreacted sorbitol physically dense the foam and causes *E*-modulus enhancement.

Table 7. Mechanical properties of formulated foams

Sample	Tensile strength MPa	Elongation at break, %	*E*-modulus MPa
0	0.38	14.0	2.7
1	0.29	6.8	3.7
2	0.27	5.3	3.9
3	0.20	4.5	4.5
4	0.12	4.3	4.8

CONCLUSION

Hydroglycolysis of flexible PUR foam has been studied under the microwave radiation. Glycerol/sorbitol/water mixtures, differing in compositions, and NaOH were used as glycolysis agents and the catalyst respectively. An increase in sorbitol part in the mixture being glycolysis agent prolongs the glycolysis process.

Our observations showed that increasing part of lower recyclate phase in polyol reagent caused decrease in elongation at break and increase in *E*-modulus of PUR foam.

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