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Polyurethane foams based on oligoetherols obtained from 6-aminouracil and alkylene carbonates

Summary — The method of synthesis of polyurethane foams with good thermal stability, containing a 1,3-pyrimidine ring is presented. Oligoetherols obtained in reactions of 6-aminouracil (6-AU) with excess of ethylene carbonate (EC) and propylene carbonate (PC) were used as polyol substrates for synthesis of these foams. Properties of the foams, such as apparent density, water absorption, dimensional stability, thermal stability and compression strength were studied. The obtained foams show a good thermal stability up to 200 °C for a long time.

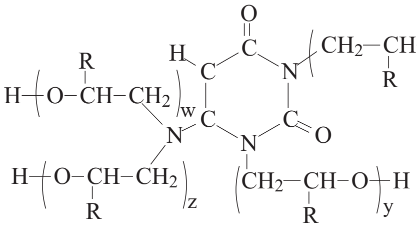
Keywords: 6-aminouracil, ethylene carbonate, propylene carbonate, polyurethane foams, thermal stability.

PIANKI POLIURETANOWE OTRZYMYWANE Z OLIGOETEROLI UZYSKANYCH Z 6-AMINOURACYLU I WĘGLANÓW ALKILENOWYCH

Streszczenie — W pracy przedstawiono metodę syntezy pianek poliuretanowych zawierających w swej strukturze pierścień 1,3-pirymidynowy (tabela 1). Jako składniki poliolowe zastosowano oligoeterole otrzymane w reakcjach 6-aminouracylu (6-AU) z nadmiarem węglanu etylenu (EC) i węglanu propylenu (PC). Zbadano gęstość pozorną, absorpcję wody, stabilność wymiarów, odporność termiczną i wytrzymałość na ściskanie uzyskanych pianek (rys. 1—5, tabele 2—4). Stwierdzono, że pianki te, zawierające w cząsteczkach polimeru pierścienie pirymidynowe, charakteryzują się zwiększoną, w porównaniu z klasycznymi piankami poliuretanowymi, stabilnością termiczną, są odporne na długotrwałe działanie temperatury dochodzącej nawet do 200 °C. Pozostałe właściwości pianek są zbliżone do właściwości klasycznych pianek poliuretanowych.

Słowa kluczowe: 6-aminouracyl, węglan etylenu, węglan propylenu, pianki poliuretanowe, stabilność termiczna.

Foams with good thermal stability can be obtained from oligoetherols containing a heterocyclic ring with high stability as a polyol component. So far, the polyetherols and oligoetherols with perhydro-1,3,5-triazine [1—4], 1,3,5-triazine [5—8], purine [9—11] or 1,3-pyrimidine [12] rings were applied with a successful result for synthesis of the foams. The foams containing 1,3-pyrimidine rings [12] were prepared by using oligoetherols [formula (I), where: $R = \text{-H}, \text{-CH}_3$, and $6.9 \le x + y + z \le 10.7$, and $w = 0$] obtained from 6-aminouracil (6-AU) and excess of oxiranes, such as ethylene oxide (EO) and propylene oxide (PO).



(I)

The method of synthesis of oligoetherols from 6-AU and oxiranes [13] has some disadvantages, namely: a long time of reaction, necessity to use a high pressure reactor, necessity to distilate off at reduced pressure solvent and catalyst from products after the reaction is completed. Synthesis of oligoetherols with a 1,3-pyrimidine ring from 6-AU and excess of alkylene carbonates, such as ethylene carbonate (EC) [14] and propylene carbonate (PC) [15] is substantially more convenient. Carbonates, unlike oxiranes, are non-flammable and non-toxic. They can be used as both the solvent and reagent. Physical properties and thermal stability of the products can be related to the properties and stability of oligoetherols obtained from 6-AU and oxiranes.

In this work, attempts to obtain polyurethane foams with good thermal stability from some oligoetherols with a 1,3-pyrimidine ring obtained from 6-AU and alkylene carbonates [14, 15] [formula (I), where: R = -H, -CH_3, and $3.7 \leq x + y + z + w \leq 8.3$] are described.

EXPERIMENTAL

Materials

The following materials were used in this work:

— 6-aminouracil (6-AU, pure, Sigma-Aldrich, Steinheim, Germany);

— ethylene carbonate (EC, pure, Fluka, Buchs, Switzerland);

— propylene carbonate (PC, pure, Fluka, Buchs, Switzerland);

— Silicon 5340 (Houdry Hülls);

— triethylamine (TEA, pure, Fluka, Buchs, Switzerland);

— 4,4'-diphenylmethane diisocyanate (MDI, mixture of 70 % of di- and 30 % of triisocyanates for synthesis, Merck-Schuchardt, Hohenbrunn, Germany).

Oligoetherols preparation

Oligoetherols were obtained in reactions of 1 mol of 6-AU with 6, 8 or 12 moles of EC or 6, 8 or 12 moles of PC, according to the procedure described in [14] and [15].

Foams preparation

Attempts to foam oligoetherols were carried out in small 250 cm^3 test cups at the room temperature. To 10 g of a oligoetherol 0.04—0.08 g of surfactant (Silicon 5340), 0.2 g of water and 0.05-0.16 g of TEA (catalyst) were added. After mixing of the components for 10 s, a pre-weighed amount of MDI was added. The mixture was vigorously stirred until it started creaming. The amount of MDI was adjusted to maintain the molar ratio of hydroxy to isocyanate groups (OH:NCO) in the mixture between 1.06 and 1.87. From thus obtained foams, test samples were cut out after *ca.* 48 h.

Methods of testing

The content of oxyalkylene groups in obtained oligoetherols was determined on the basis of mass balance [14, 15]. Propylene carbonate in reaction with 6-AU decomposes partially with release of CO_2 and PO. Hence the content of oxypropylene groups in the product is smaller than calculated from initial molar ratio of substrates [15].

The following properties of foams were determined: apparent density (PN-EN ISO 845:2009), water absorption capacity (PN-EN ISO 2896:1987), dimensional stability (PN-EN ISO 2796:1986), thermal stability as the mass loss after heating at 150, 175, 200 °C for a month, and compression strength (PN-EN ISO 844:2009).

The thermal analysis of products was carried out using a thermogravimetric analysis apparatus (MOM, Hungary) working under nitrogen atmosphere regime. A sample (100 mg) was heated in a china crucible in the temperature range 20—1000 °C. The sensitivity of the instrument was 1/10 for DTA and 1/10 for DTG. Thermal investigations of the foams were also made using differential scanning calorimeter (DSC) type 822^e with the software Stare^e system (Mettler Toledo, Spain) according to the PN-EN ISO 11357-1:2002 standard. Measurements are carried out for sample mass of 6—9 mg in the temperature range 25—175 °C at the heating rate of 10 °C/min under the nitrogen atmosphere.

RESULTS AND DISCUSSION

Oligoetherols with a 1,3-pyrimidine ring, obtained in reactions of 1 mol of 6-AU with 6, 8 or 12 moles of alkylene carbonates were used to prepare polyurethane foams. At first the optimal amount of isocyanate, amount of catalyst and influence of length of oligoether chain on the foaming course were determined to obtain rigid foams of regular pores. The results of these investigation are presented in Table 1. It has been found that the best results were obtained when the molar ratio of OH:NCO groups in the mixture was within the range 1.06—1.5. The optimal amounts of water used as the foaming agent (2 g/100 g of oligoetherol) and Silicon 5340 (0.8 g/100 g of oligoetherol) were determined based on the work described in [12]. The amount of TEA, used as catalyst was in the range of 0.5—1.6 g per 100 g oligoetherol. The rigid foams with regular pores were obtained using 1.3—1.6 g of TEA. When oligoetherols obtained from PC were used, the amount of catalyst was 1.6 g/100 g of oligoetherol.

The foams of small, regular pores were obtained from oligoetherols with shorter oligoether chains. Foams obtained from product of reaction of 1 mol of 6-AU with 12 moles of EC were cracking during expanding and they had large, irregular pores. When product of reaction of 1 mol 6-AU with 12 moles of PC was used, the foams were fragile and showed large polymerization shrinkage (Table 1). This effect was not observed when oligoetherols were synthesized from 1 mol of 6-AU and 12 moles of oxiranes as polyol substrates [12]. Some properties of the investigated foams are listed in Table 2.

All foams are rigid. Their apparent density was found in the range of 30—60 kg/m^3 and was insignificantly smaller than the density of foams based on oligoetherols obtained from 6-AU and oxiranes [12].

Water absorption after 24 h of exposition was within 3.1—15.2 wt. % (Table 2) and in comparison with absorption of water for foams obtained from oligoetherols synthesized from 6-AU and oxiranes (5.8—32.5 wt. %) was not large [12]. The foams prepared from oligoetherols obtained in reactions of 6-AU with PC show smaller absorption of water, up to 5.2 wt. %.

T a b l e 1. Parameters of oligoetherol synthesis and foaming process*)

Sample number	Oligoetherol synthesis			Composition of foams g/100 g of oligoetherol			Molar ratio of OH:NCO in foams	Parameters of foaming process			Characteristics of the foams
	type of alkylene carbonate	6-AU:EC or 6-AU:PC molar ratio	content of oxyalkylene groups in the product mol	MDI	TEA	Silicon 5340		creaming time, s	expanding time s	dryling time, s	
1	EC	1:6	6	212	1.1	0.8	1.49	40	39	35	not fully cured
2				160	1.6	0.8	1.41	36	29	12	rigid
3				150	1.6	0.8	1.06	27	12	3	rigid
4				160	1.6	0.4	1.13	43	25	7	rigid
5		1:8	8	132	1.1	0.8	1.12	34	20	5	rigid
6				156	1.1	0.8	1.32	33	33	23	rigid
7				140	1.3	0.8	1.18	30	13	3	rigid
8				140	1.1	0.4	1.19	37	22	10	fragile, irregular pores
9				132	1.3	0.8	1.12	23	10	3	rigid
10				142	1.3	0.8	1.20	25	13	3	rigid
11		1:12	12	100	1.1	0.8	1.11	20	30	1	large pores, crack**)
12				136	1.1	0.8	1.51	20	8	1	large pores**)
13				136	0.5	0.8	1.51	20	10	1	large pores, crack**)
14				168	1.1	0.8	1.87	25	8	1	large pores, crack**)
15				168	0.5	0.8	1.87	22	16	1	large pores, crack**)
16	PC	1:6	5.2	144	1.6	0.8	1.10	18	15	2	rigid
17				184	1.6	0.8	1.41	20	18	2	rigid
18		1:8	6.5	172	1.6	0.8	1.51	15	15	1	rigid
19				148	1.6	0.8	1.30	14	16	1	rigid
20		1:12	9.1	136	1.6	0.8	1.51	13	24	1	little shrink
21				118	1.6	0.8	1.31	13	19	7	shrink, fragile
22				122	1.6	0.8	1.36	12	20	4	shrink, fragile

*) Creaming time — the time elapsed from the moment of mixing to the start of volume expansion; expanding time — the time from the start of expansion to the moment of reaching the sample final volume; drying time — the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

**) Samples not used for later investigations.

The foams revealed both positive (a volume of a sample grows) and negative dimension changes after thermal treatment at temperature 150 °C (Table 2). The smaller dimension changes showed foams obtained from oligoetherols with shorter oligoether chains based on EC (compositions No 1—6, Table 2).

Thermal conductivity coefficient of obtained foams was 0.036 J/(m·s·K). Its value is the same as thermal conductivity coefficient of the foams obtained from oligoetherols based on 6-AU and oxiranes [12] and was comparable to ones for classic polyurethane foams [0.025—0.03 J/(m·s·K)] [16, 17].

The thermal stability measurements of polyurethane foams were performed at temperatures 150 °C, 175 °C and 200 °C by registering the loss of mass. Results of these investigations are presented in Figs. 1—5. The samples were exposed to the thermal treatment for one month. The gradual loss of mass has been observed. The highest loss of mass was always observed after the first day of exposition. After heating all foams showed larger rigidity. Polyurethane foams based on oligoetherols containing oxypropylene groups showed small distortion of their shape after 1 day of thermal treatment at temperature 150 °C (samples No 21 and 22), large distortion of their shape after 1 day of thermal treatment at temperature 175 °C (samples No 16, 20—22) and relatively large one at temperature 200 °C (samples No 16, 18—22). Only the sample No 17 changed its shape insignificantly after thermal treatment at temperature 200 °C. Among polyurethane foams based on oligoetherols containing oxyethylene groups, only samples No 3—5 and 7 show small distortion of their shape, after 4 day of thermal treatment at temperature 200 °C.

There was observed, that the kind of oxyalkylene groups included in oligoetherol has no influence on thermal stability of foams. It depends on the length of oligoether chain. The shorter chain in oligoetherol the less was the mass lost of obtained foam (content of pyrimidine

T a b l e 2. Selected properties of polyurethane foams

Sample number	Density kg/m^3	Water absorption, wt. %			Linear dimensional stability at temperature 150 °C					
					length increase, %		width increase, %		depth increase, %	
		after 5 min	after 3 h	after 24 h	after 20 h	after 40 h	after 20 h	after 40 h	after 20 h	after 40 h
1	42.20	4.8	6.4	9.9	0.66	0.66	3.15	3.15	0.00	0.00
2	46.75	8.5	11.6	15.2	0.00	0.00	0.67	1.33	0.00	0.00
3	30.50	4.6	7.5	11.6	0.00	-0.81	-0.57	-0.46	-1.43	-1.92
4	31.70	4.45	6.4	8.7	0.17	0.34	-0.61	-0.31	2.23	2.68
5	44.50	4.4	7.0	12.9	-0.55	-0.55	-1.06	-1.06	0.00	1.14
6	59.90	5.7	7.0	10.0	-0.99	-0.99	0.00	0.00	0.00	0.00
7	41.80	4.9	6.9	8.6	-0.34	-0.57	-1.04	-1.04	13.64	14.49
8	32.20	5.9	7.2	8.1	0.00	0.00	-0.61	-3.03	3.23	6.45
9	38.60	2.6	4.6	6.4	-1.14	-0.23	0.00	-0.68	0.95	0.95
10	43.90	3.7	6.2	9.4	-0.81	-1.40	-0.64	-1.28	6.81	6.87
16	29.05	2.8	4.0	5.0	-3.76	-5.55	-6.59	-8.06	-1.90	-4.48
17	32.85	2.4	4.1	5.3	-0.87	-1.20	-1.00	-1.00	-0.36	-1.07
18	31.75	1.8	2.4	4.0	0.12	-0.84	1.07	0.00	0.56	0.19
19	31.05	2.6	3.7	5.2	-6.75	-7.42	-7.26	-9.50	-6.57	-9.04
20	35.80	2.4	2.6	3.1	-4.08	-6.31	-0.88	-5.24	-0.25	-4.78
21	36.90	2.2	2.7	4.0	-7.14	-8.49	-12.89	-15.25	-9.24	-17.44
22	36.70	1.3	2.1	3.2	-8.76	-11.78	-3.06	-5.49	-16.77	-21.74

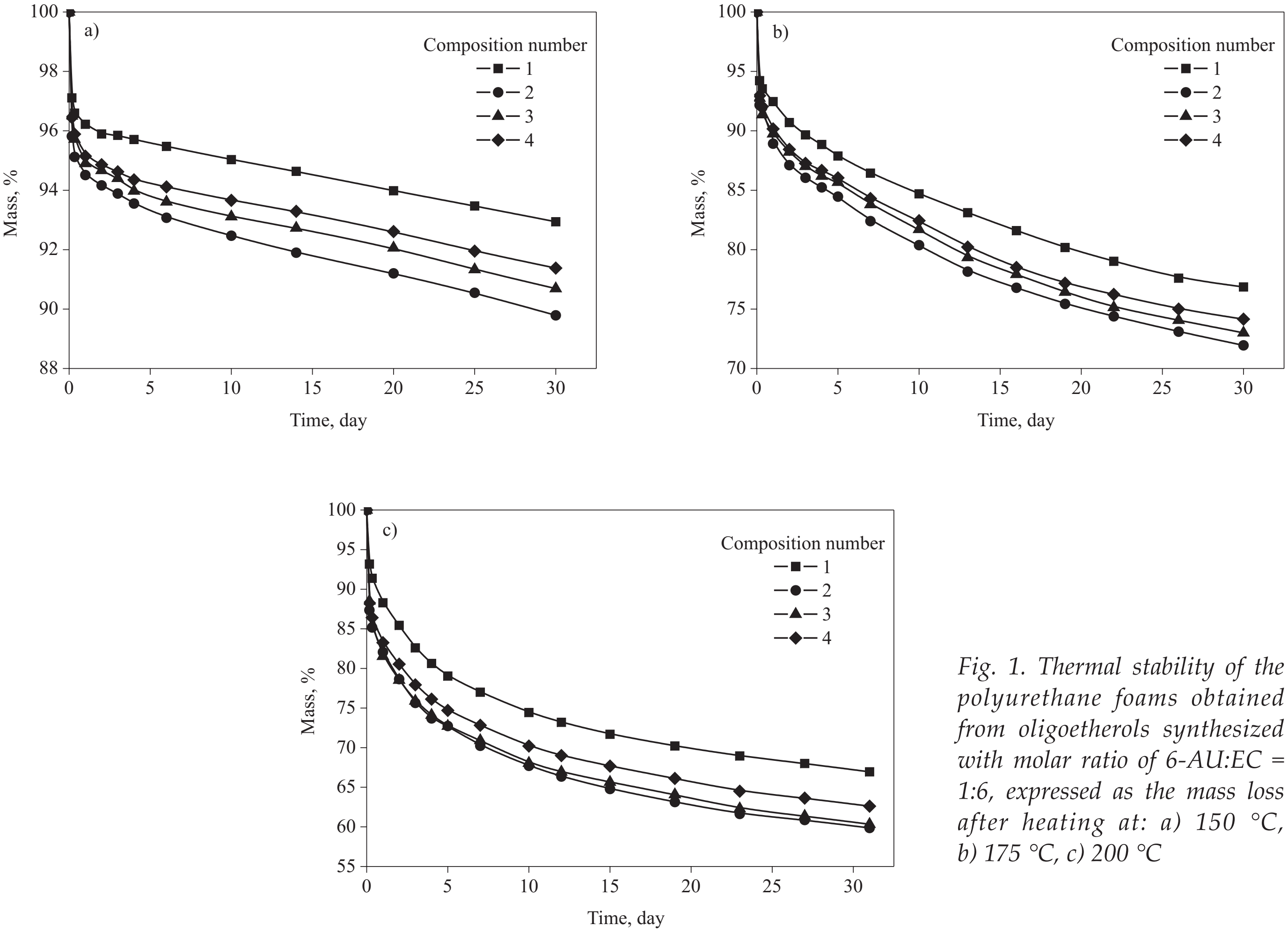


Fig. 1. Thermal stability of the polyurethane foams obtained from oligoetherols synthesized with molar ratio of 6-AU:EC = 1:6, expressed as the mass loss after heating at: a) 150 °C, b) 175 °C, c) 200 °C

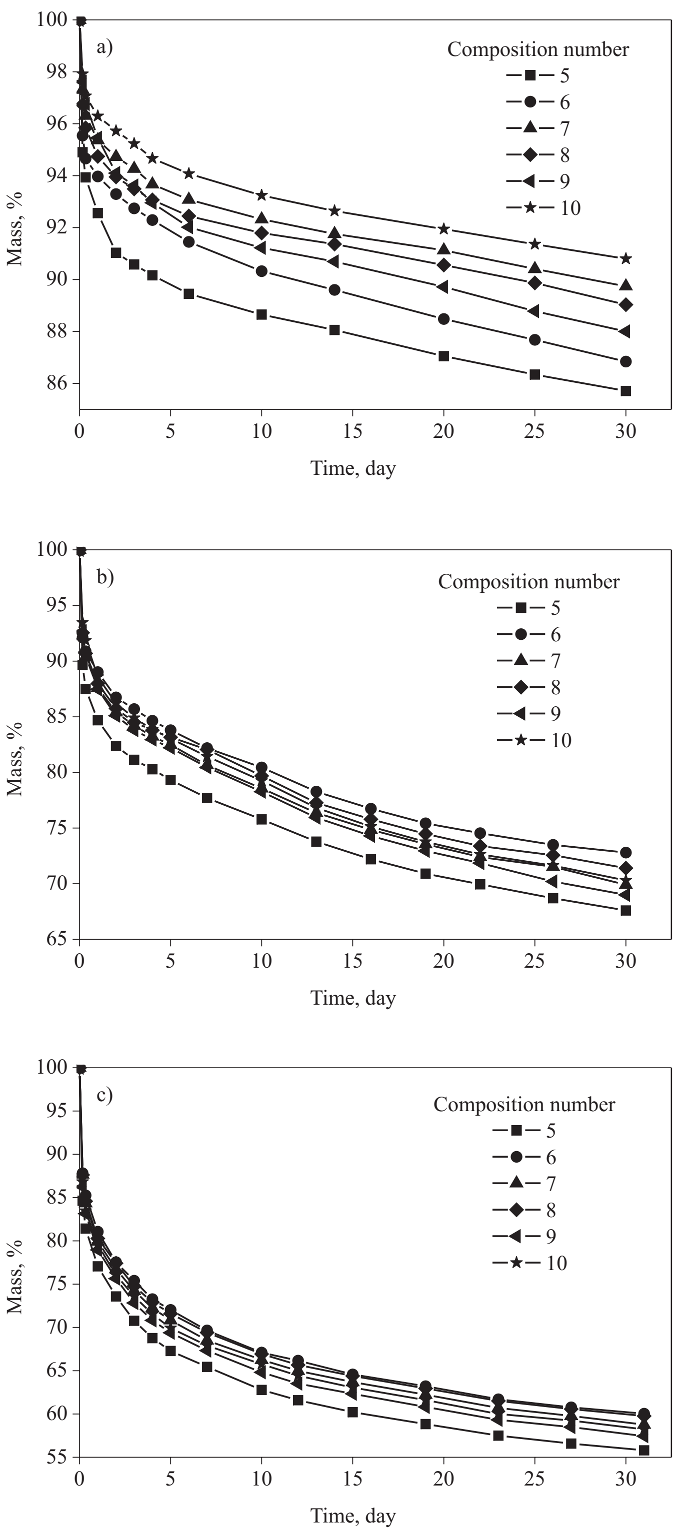


Fig. 2. Thermal stability of the polyurethane foams obtained from oligoetherols synthesized with molar ratio of 6-AU:EC = 1:8, expressed as the mass loss after heating at: a) 150 °C, b) 175 °C, c) 200 °C

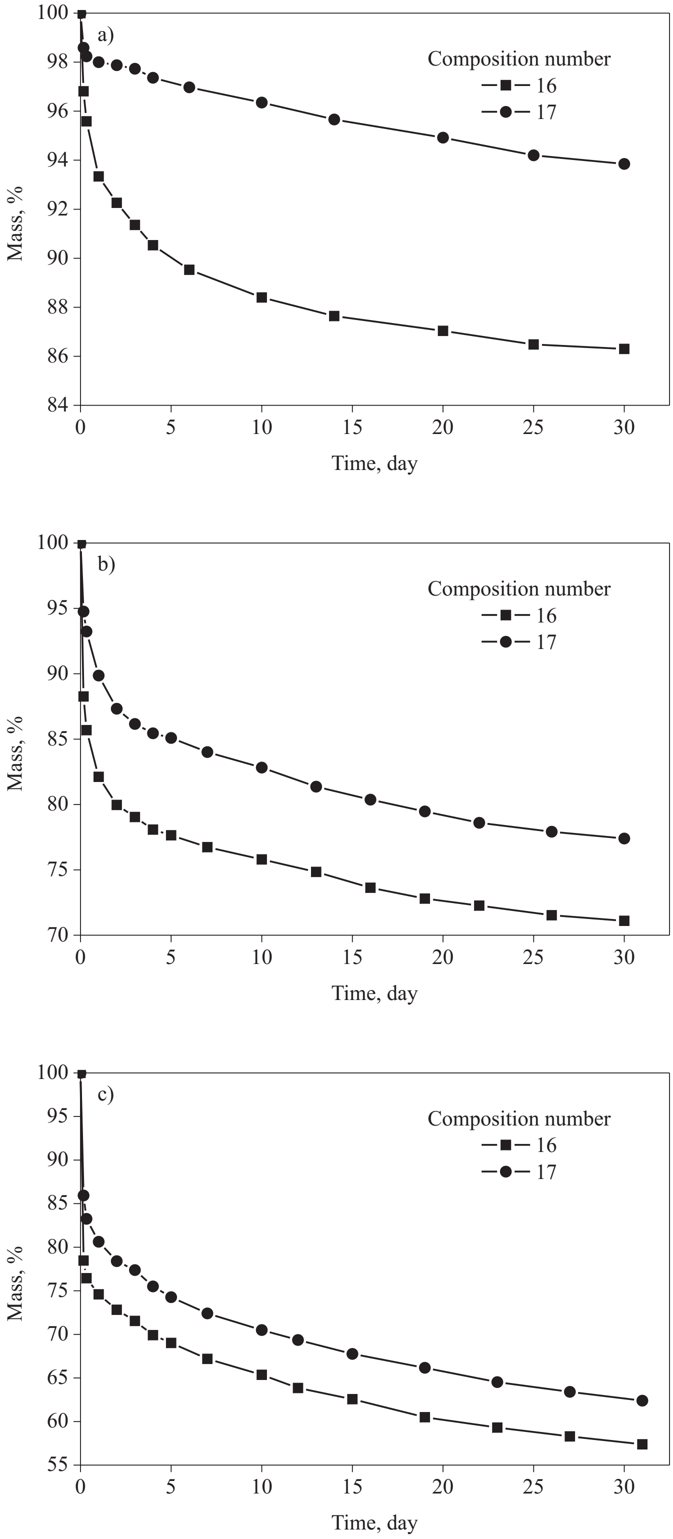


Fig. 3. Thermal stability of the polyurethane foams obtained from oligoetherols synthesized with molar ratio of 6-AU:PC = 1:6, expressed as the mass loss after heating at: a) 150 °C, b) 175 °C, c) 200 °C

rings is larger). The foams obtained from oligoetherol with initial molar ratio of 6-AU:EC or PC equal to 1:6 showed the lowest mass loss; *i.e.*: 6.9 wt. % at 150 °C, 23.1 wt. % at 175 °C and 33.1 wt. % at 200 °C — sample No 1 (Fig. 1); 8.8 wt. % at 150 °C, 25.8 wt. % at 175 °C and 37.4 wt. % at 200 °C — sample No 4 (Fig. 1). Similar mass losses are observed for sample No 17 (Fig. 3) obtained from oligoetherol with initial molar ratio 6-AU:PC equal to 1:6 — 6.1 wt. % at 150 °C, 23.3 wt. % at 175 °C and 37.6 wt. % at 200 °C. In other cases the loss of mass was

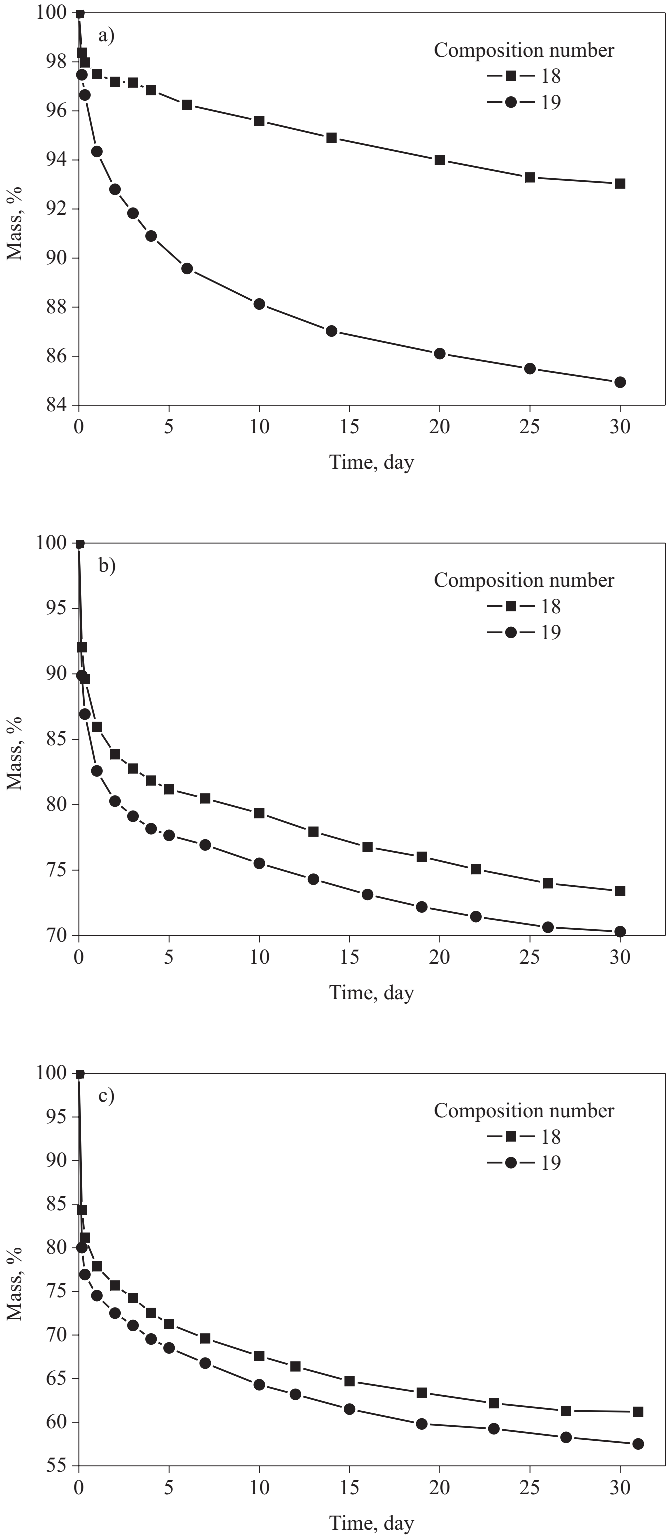


Fig. 4. Thermal stability of the polyurethane foams obtained from oligoetherols synthesized with molar ratio of 6-AU:PC = 1:8, expressed as the mass loss after heating at: a) 150 °C, b) 175 °C, c) 200 °C

much bigger — up to 49.5 wt. % at temperature 200 °C for sample No 21 (Fig. 5).

The foams based on oligoetherols obtained from 6-AU and carbonates show slightly better thermal stability than those based on oligoetherols obtained from 6-AU and

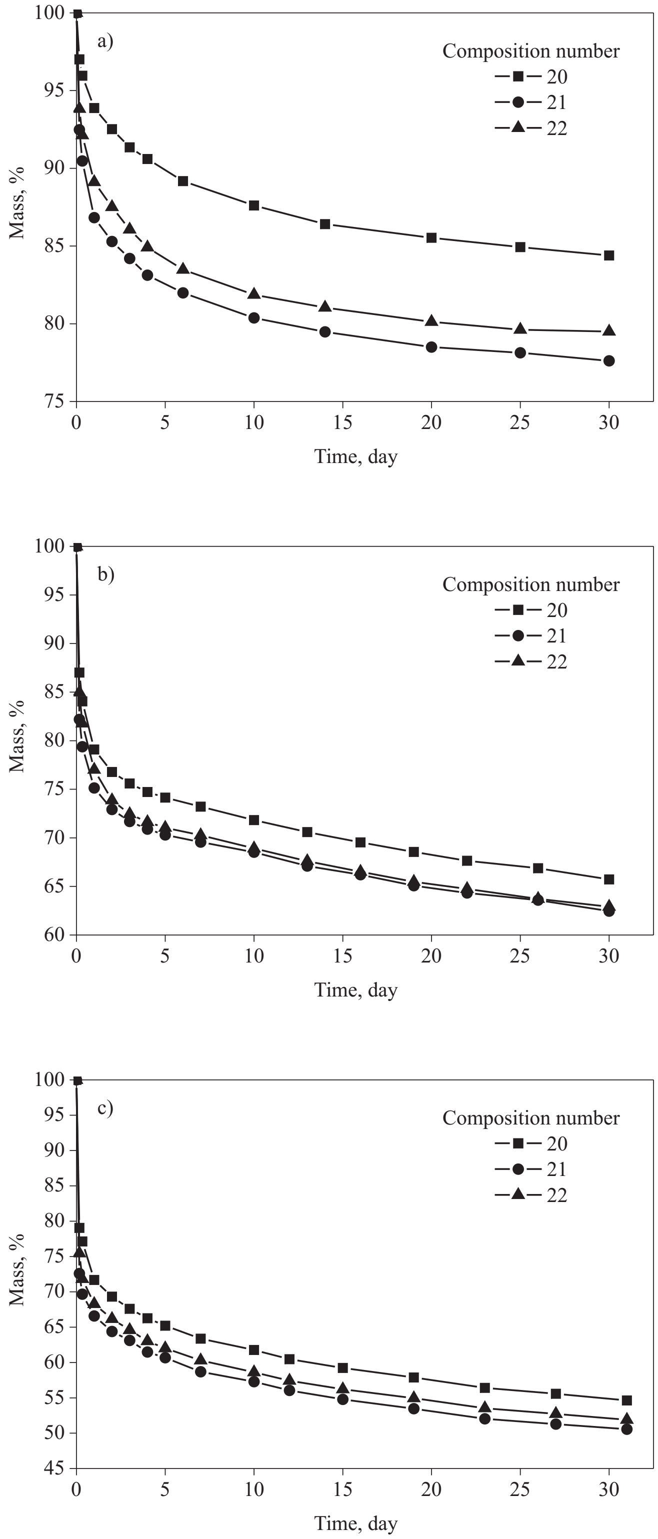


Fig. 5. Thermal stability of the polyurethane foams obtained from oligoetherols synthesized with molar ratio of 6-AU:PC = 1:12, expressed as the mass loss after heating at a) 150 °C, b) 175 °C, c) 200 °C

oxiranes [12] and better than stability of foams containing perhydro-1,3,5-triazine [4], 1,3,5-triazine [7] or purine [9, 11] ring.

The results of DSC investigations presented in Table 3 confirmed good thermal stability of obtained polyurethane foams. The analysis of some foams showed that 5 % mass loss occurred at temperature $T_{5\ \%}$ = 190—210 °C, while 50 % mass loss at much higher temperature $T_{50\ \%}$ = 410—550 °C.

T a b e l a 3. Thermal resistance and thermal stability of some polyurethane foams based on thermogravimetric analysis and DSC

Sample number	$T_{5\ \%}$, °C	$T_{10\ \%}$, °C	$T_{25\ \%}$, °C	$T_{50\ \%}$, °C	T_g, °C
1	210	260	320	550	100
4	200	240	300	430	104
17	190	220	280	420	159
18	190	220	270	410	147

Glass transition temperatures (T_g) of some polyurethane foams, as determined by the DSC method are included in the range 100—159 °C (Table 3) what shows that the obtained foams are rigid.

T a b l e 4. Compression strength properties*) of polyurethane foams before and after exposition at high temperature

Sample number	Before exposition	After exposition at									Percentage increase of compression strength after exposition at		
	σ_{10} MPa	150 °C			175 °C			200 °C			150 °C	175 °C	200 °C
		σ_{10}, MPa	σ_M, MPa	ε_M, %	σ_{10}, MPa	σ_M, MPa	ε_M, %	σ_{10}, MPa	σ_M, MPa	ε_M, %			
1	0.14	0.06	—	—	—	0.09	9.71	0.08	—	—	-57.1	—	-42.9
2	0.10	0.13	—	—	0.09	—	—	0.11	—	—	30.0	-10.0	10.0
3	0.05	0.07	—	—	0.05	—	—	0.07	—	—	40.0	0.0	40.0
4	0.07	0.09	—	—	0.06	—	—	0.06	—	—	28.6	-14.3	-14.3
5	0.05	0.08	—	—	0.13	—	—	0.15	—	—	60.0	160.0	200.0
6	0.07	0.19	—	—	0.16	—	—	0.12		—	171.4	128.6	71.4
7	0.07	0.10	—	—	0.08	—	—	0.12	—	—	42.9	14.3	71.4
8	0.07	0.10	—	—	0.07	—	—	—	0.05	6.78	42.9	0.0	—
9	0.10	0.18	—	—	0.14	—	—	0.12	—	—	80.0	40.0	20.0
10	0.12	0.18	—	—	0.18	—	—	0.13	—	—	50.0	50.0	8.3
16	0.12	0.13	—	—	0.23	—	—	—	—	—	8.3	91.7	—
17	0.14	—	0.14	9.4	—	0.12	8.89	0.38	—	—	—	—	171.4
18	0.18	0.14	—	—	0.13	—	—	0.24	—	—	-22.2	-27.8	33.3
19	0.16	0.20	—	—	—	0.10	6.71	0.17	—	—	25.0	—	6.3
20	0.16	0.21	—	—	0.26	—	—	—	0.16	5.75	31.3	62.5	—
21	0.05	0.19	—	—	0.28	—	—	0.36	—	—	280.0	460.0	620.0
22	0.04	0.22	—	—	0.20	—	—	0.51	—	—	450.0	400.0	1175.0

*) σ_{10} — compression strength at 10 % strain; σ_M — compression strength; ε_M — strain.

Mechanical properties evaluated on the basis of compression strength measurements are listed in Table 4. The compression strength (σ_M) was tested for samples both before and after thermal exposure. The foams obtained from oligoetherols based on PC indicated higher compression strength than those obtained from oligoetherols based on EC. The compression strength of the foams increases after one month of heat exposition at 150 and 175 °C with exception of samples No 1 and 18 (Table 4). The compression strength of the foams obtained from oligoetherols based on PC increased even after their exposition to 200 °C (compositions No 22 about 1175 %, No 21 about 620 %, No 17 about 171.4 %, Table 4).

CONCLUSIONS

Oligoetherols containing 1,3-pyrimidine ring, obtained in reactions of 6-AU with alkylene carbonate can be used for synthesis of polyurethane foams with good thermal stability. The other properties of foams, such as apparent density, water absorption, dimensional stability, thermal conductivity and compression strength were similar related to the properties of classical polyurethane foams. Because expanding time of obtained foams is short, they are suitable for spraying.

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