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Polyurethane foams with pyrimidine rings in polymer molecules

RAPID COMMUNICATION

Summary — New polyurethane foams were obtained by reaction of oligoetherols synthesized from hydroxymethyl derivative of barbituric acid (HMBA) and propylene oxide (PO) with methylenediphenyl 4,4'-diisocyanate (MDI) and water. Thermal stability of the polyurethane foams containing pyrimidine rings in polymer molecules were investigated. They are stable at 150–200 °C for long time. The influence of oligoetherol chain length and composition on properties of foams were studied in details. The studies of mechanical properties before and after thermal exposition were studied in order to optimize the compositions of polyurethane foams to ensure good thermal stability.

Key words: oligoetherols with pyrimidine ring, polyurethane foam, thermal stability.

PIANKI POLIURETANOWE Z PIERŚCIENIAMI PIRYMIDYNOWYMI W CZĄSTECZKACH POLIMERU

Streszczenie — W reakcjach oligoeteroli, uzyskanych z hydroksymetylowych pochodnych kwasu barbiturowego (HMBA) i tlenku propylenu (PO), z 4,4'-diizocyjanianem difenylometanu (MDI) i wodą otrzymano nową grupę pianek poliuretanowych zawierających w cząsteczkach pierścienie pirymidynowe. Badano wpływ rodzaju oligoeterolu i składu spienianych kompozycji na niektóre właściwości otrzymanych pianek. W celu optymalizacji składu pianek zapewniającego im dobrą odporność termiczną wyznaczono wytrzymałość na ściskanie przed i po ekspozycji na działanie wysokiej temperatury. Stwierdzono, że pianki te są odporne na długotrwałe działanie temperatury wynoszącej nawet 200 °C. Inne właściwości badanych pianek, takie jak: gęstość pozorną, absorpcja wody czy skurcz polimeryzacyjny mają wartości zbliżone do analogicznych wartości charakteryzujących typowe pianki poliuretanowe produkowane na skalę przemysłową.

Słowa kluczowe: oligoeterole z pierścieniami pirymidynowymi, pianka poliuretanowa, odporność termiczna.

Thermal stability of polyurethane foams can be improved by introduction of azacycles like perhydro-1,3,5-triazine ring present in isocyanuric acid (IA) [1, 2]. Barbituric acid (BA) has similar structure to IA except one NH group which is replaced with CH₂ group. We have expected that polymers with BA included should reveal similar thermal stability like those with perhydro-1,3,5-triazine ring obtained from IA, especially because BA itself has high temperature of decomposition, above 250 °C. Moreover, BA is much better soluble in organic solvents than IA enabling synthesis of BA derivatives. Recently methods of oligoetherols synthesis from hydroxymethyl derivative of barbituric acid (HMBA) and oxiranes were developed [3, 4]. Here we report the

use of mentioned oligoetherols to obtain polyurethane foams thermal stability. Other properties of this foams were also determined.

EXPERIMENTAL

Materials

The following materials were used in this work:

- propylene oxide (PO, pure, Fluka, Switzerland);
- triethylamine (TEA, pure, Fluka, Switzerland);
- diphenylmethane 4,4'-diisocyanate (MDI, mixture of 70 % of di- and 30 % of triisocyanate, Merck, Germany);
- Silicon 5340 (pure, Houdry H, USA);
- hydroxymethyl derivative of barbituric acid (HMBA) prepared as it was described in [3].

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Syntheses

Oligoetherols with pyrimidine ring were obtained by reaction of HMBA with an excess of PO according to the procedure described in [3] to get products with 10, 12 or 18 oxypropylene units per mole of HMBA.

Foam preparation

Laboratory scale foaming of oligoetherols was performed in cups of 250 cm³ volume at room temperature. To 10 g of oligoetherol and 0.1 g of surfactant Silicon 5340, certain amount of TEA (catalyst) and 0.1–0.3 g of water were added. After careful mixing of the components for 10 s, a pre-weighted amount of MDI was added. The amount of diisocyanate and water was adjusted to get the NCO/OH molar ratio of 1.5–2.0. The composition was vigorously mixed until it started creaming *i.e.* volume expansion was noticed. Samples for testing were cut out from the obtained foams after *ca.* 48 h.

Methods of testing

Physicochemical properties of oligoetherols have been determined according to published standard methods:

- hydroxylic number (established by xylene method [5]),
- density (measured pycnometrically),
- refractive index (n_D^{20}),

Table 2. The influence of composition on foaming process

HMBA:PO molar ratio	Sample number	Isocyanate content, g	TEA content, g	OH/NCO molar ratio	Time of creaming ^{*)} , s	Time of expanding ^{**)} , s	Time of drying ^{***)} , s
1:10	1	10.8	0.08	1.51	4	21	2
	2	12.0	0.08	1.68	4	19	2
1:12	3	9.8	0.10	1.50	4	21	2
	4	11.2	0.10	1.72	4	18	3
1:18	5	10.2	0.16	1.98	4	35	5

^{*)} Time of creaming — the time elapsed from the moment of mixing to the start of volume expansion.

^{**)} Time of expanding — the time from the start of expansion to the moment of reaching the sample final volume.

^{***)} Time of drying — the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

- Höppler viscosity,
- surface tension (determined by ring detach method [6]).

Foams were characterized by following properties:

- apparent density (PN-EN ISO 845),
- water absorption (PN-EN ISO 2896),
- linear shrinkage (PN-EN ISO 2796) including determination of changes in linear dimensions before and after heating at 100 °C for 4 h,
- heat transfer coefficient (PN-EN ISO 4897),
- flammability (ASTR 635-56T),

- thermal stability as the mass loss after heating at 150, 175, and 200 °C in air atmosphere for a month,
- compression strength (PN-EN ISO 844).

RESULTS AND DISCUSSION

The properties of oligoetherols used to prepare polyurethane foams are listed in Table 1. With increasing number of connected oxirane molecules, the refraction index, density and viscosity decrease. These parameters do not vary from those of typical oligoetherols used for preparation of polyurethane foams [7].

Table 1. Physical properties of oligoetherols used for preparation of polyurethane foams

HMBA:PO molar ratio	n_D^{20}	Density g/cm ³	Viscosity N s/m ²	Surface tension N/m	Hydroxyl number	
					calculated	found
1:10	1.4680	1.0936	1.099	0.03906	258	184
1:12	1.4665	1.0903	0.8321	0.03402	228	173
1:18	1.4581	1.0680	0.3117	0.03752	168	135

The obtained foams are rigid. The best foams were obtained when initial ratio of hydroxyl groups to isocyanate groups (isocyanate index) was 1.5–2.0 (Table 2). The optimized amount of water was 2 g per 100 g of oligoetherol

mass. The amount of catalyst used was essential; the optimized amount was 0.8–1.6 g per 100 g of oligoetherol. As it can be seen in Table 2, the time of foam expansion was between 18 and 35 s.

It has been found that all foams were flammable. Some properties of obtained foams are listed in Table 3. Apparent density of these rigid foams was within 44–48 kg/m³. Water absorption was *ca.* 9 wt. %. Some foams have quite large linear shrinkage. Their heat transfer coefficient was *ca.* 0.062 J/(K · m · s), *i.e.* considerably higher than that of industrial polyurethane foams and close to

that of foamed polystyrene [0.026 J/(K · m · s) and 0.053 J/(K · m · s), respectively] [1].

Table 3. Some properties of obtained foams

Sample number	Apparent density, kg/m ³	Absorption of water, wt. %	Post-shrinkage linear, %
1	46.01	8.76	2.1
2	44.57	8.97	10.2
3	47.88	9.07	2.3
4	44.66	8.48	14.6
5	48.38	7.83	4.2

Table 4. Thermal stability and compressive strength of foams

Sample number	Mass loss after exposure to high temperature, wt. %			Compressive strength, MPa			
	150 °C	175 °C	200 °C	before exposure to high temperature	after exposure at		
					150 °C	175 °C	200 °C
1	32.66	42.57	49.43	0.1200	0.1468	0.1486	0.2338
2	29.03	40.25	47.36	0.1053	0.1398	0.1285	0.1428
3	36.52	45.13	51.82	0.1669	0.1665	0.2569	0.1036
4	31.25	41.38	48.47	0.1414	0.1731	0.1989	0.2206
5	31.00	41.84	49.57	0.1750	0.2380	0.2070	0.2074

The results of thermal stability investigations at 150, 175 and 200 °C are listed in Table 4 and presented in Fig. 1. The continuous mass loss of polyurethane foams was noticed within the first 24 hours of test (Fig. 1). The lowest final mass loss was observed at 150 °C (Fig. 1a), and mass plateau was reached after 10–15 days. Mechanical properties of all foams were studied after one month of thermal exposure at 150, 175 and 200 °C. All foams were more rigid and had higher compressive strength after exposure to high temperature than before (Table 4). The mass loss profiles were similar to those found for foams obtained from oligoetherols synthesized from melamine or IA with oxiranes [8, 9]. Foams obtained in this work had some advantage in comparison with foams obtained from oligoetherols synthesized from melamine or IA; they were considerably more rigid and had generally higher compressive strength after thermal exposition at 150–200 °C. Only the samples obtained from oligoetherol, in which HMBA:PO molar ratio was 1:12, revealed decrease of compressive strength after one-month exposition at 200 °C (Table 4, sample 3). The lowest mass loss was noticed for the foams obtained from oligoetherols, in which HMBA:PO molar ratio was 1:10 *i.e.* those containing the highest percentage of pyrimidine rings in the structure of the polymer.

CONCLUSION

Oligoetherols obtained from HMBA and PO containing pyrimidine ring are useful substrates for polyurethane foams of enhanced thermal stability. The foams

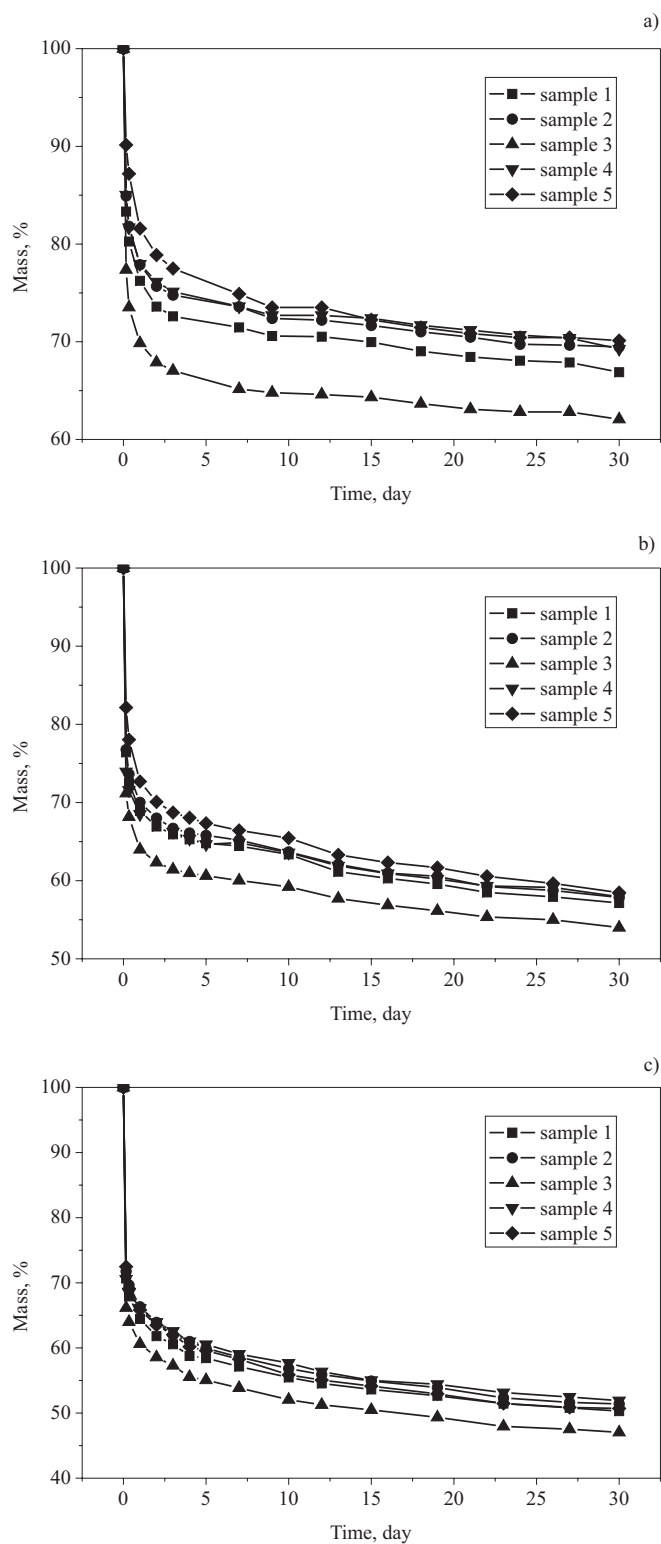


Fig. 1. Thermal stability of foams measured as mass loss after one-month exposure to temperature: a) 150 °C, b) 175 °C, c) 200 °C

have increased compression strength even after thermal exposition at 200 °C. Other physical properties, like apparent density, water absorption and polymerization shrinkage are close to those of typical commercially available polyurethane foams.

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