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Polyurethane foams with purine rings

RAPID COMMUNICATION

Summary — New group of foams can be obtained from isocyanates, water and polyetherols synthesized from uric acid and alkylene carbonates. Due to the presence of purine rings those polyurethanes are remarkably thermally stable and withstand prolonged heating at temperatures above 200 °C. The results of studies on influence of kind of polyetherol and composition subjected to foaming on the properties of polyurethane foams are presented. The thermal stability and mechanical properties of the foams were determined before and after thermal exposure.

Key words: polyetherols with purine rings, polyurethane foams, thermal stability, mechanical properties.

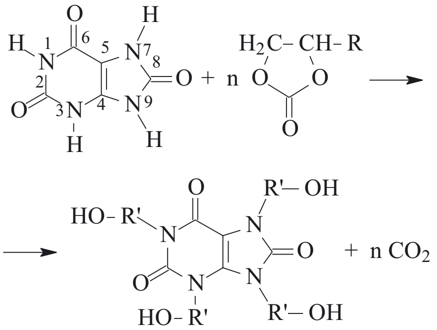
PIANKI POLIURETANOWE Z PIERŚCIENIAMI PURYNOWYMI

Streszczenie — W reakcjach polieteroli, uzyskanych z kwasu moczowego i typowych węglanów alkilenowych z izocyjanianami i wodą otrzymuje się nową grupę pianek poliuretanowych zawierających w swej strukturze pierścienie purynowe. Pianki te wytrzymują długotrwałe działanie wysokiej temperatury, wynoszącej nawet 200 °C. W pracy przedstawiono wyniki badań dotyczących wpływu rodzaju polieterolu i składu kompozycji spienianych na warunki otrzymywania i niektóre właściwości takich pianek poliuretanowych. Przeprowadzono badania ich odporności termicznej i wytrzymałości na ściskanie przed i po ekspozycji temperaturowej. Stwierdzono, że właściwości te są znacznie lepsze niż właściwości pianek uzyskiwanych z podobnych polieteroli, ale otrzymywanych z hydroksymetylowych pochodnych kwasu moczowego i oksiranów. Największą odpornością termiczną charakteryzują się pianki zawierające w swej strukturze zarówno grupy oksyetylenowe jak i oksypropylenowe. Ich wytrzymałość na ściskanie wyraźnie rośnie nawet po ekspozycji w temperaturze 200 °C. Inne właściwości tych pianek, takie jak gęstość pozorna, chłonność wody i skurcz polimeryzacyjny są zbliżone do właściwości klasycznych pianek poliuretanowych produkowanych na skalę przemysłową.

Słowa kluczowe: polieterole z pierścieniami purynowymi, pianki poliuretanowe, odporność termiczna, właściwości mechaniczne.

Thermal stability of polyurethane foams can be enhanced by application of azacyclic ring, like 1,3,5-triazine, perhydrotriazine or trioxoimidazoline [1—5] into the polymer structure. Recently the method of synthesis of polyetherols derived from hydroxymethyl derivative of uric acid (HMUA) and oxiranes [6] was reported. Later they were applied as components for the preparation of polyurethane foams with thermally stable purine rings [7]. The foams possessed oxymethylene groups originating from formaldehyde, which was used for synthesis of polyetherols. However, the thermal stability of those foams was lower than expected, probably because of the presence of oxymethylene groups. Furthermore, the lower molar ratio of oxirane and HMUA was used for synthesis of polyetherols, the weaker bound formaldehyde was observed in the product. The weakly bound formaldehyde was present as *O*-hydroxymethyl groups. Those groups were released from the polyurethane foams resulting in non—controlled foaming [7]. Additionally, the polyetherols were obtained in two-step synthesis, *i.e.* synthesis of HMUA and then the reaction of the latter with oxiranes like ethylene or propylene oxide in excess [8].

Therefore simpler method for synthesis of polyetherols containing purine rings, without oxymethylene groups was desired. Eventually, the one-step protocol was designed, in which the uric acid (UA) was condensed with neat ethylene or propylene carbonates (EC or PC), respectively according to the reaction scheme [8, 9]:



(1)

where: R = —H,—CH_3, R' = oxyalkylene groups

The matter of the choice was the use of such polyetherols in order to enhance the thermal stability of polyurethane foams. Here the attempts to reach the target is described based on practical parameters like thermal resistance and some physical properties.

EXPERIMENTAL

Materials

The following materials were used in this work:

— uric acid (UA) (pure, Avocado, Germany),

— ethylene carbonate (EC) and propylene carbonate (PC) (pure, Fluka, Switzerland),

— Silicon 5340 as a surfactant (pure, Houdry Hülls, USA),

— triethylamine (TEA) as a catalyst (pure, Fluka, Switzerland),

— diphenylmethane-4,4′-diisocyanate (MDI) [in form of mixture of di- (65 wt. %) and triisocyanate (30 wt. %), Merck, Germany].

Syntheses of polyetherols

Polyetherols with purine rings were obtained by reaction of UA with excess of EC or PC according to described procedure [8, 9] to get the products with 12 or 16 oxyethylene groups or 6.6, 9, 13 or 16 oxypropylene groups per mole of UA. Some syntheses of polyetherols containing both oxyethylene and oxypropylene groups at the level of 8 and 6 moles per mole of UA were performed. In this procedure EC and PC were reacted with UA subsequently.

Foam preparation

Laboratory scale foaming of polyetherols was performed in the cups of 250 cm^3 volume at room temperature. To 10 g of a polyetherol, 0.1 g of surfactant Silicon 5340, triethylamine as a catalyst, and 0.1—0.3 g of water were added. After careful mixing of the components, a pre-weighed amount of MDI was added. The amounts of diisocyanate and water were adjusted to have NCO/OH molar ratio of 1.0—2.3. The composition was vigorously mixed until it started creaming. The times elapsed from the moments of mixing to the begining of wolume espansion (named time of creaning) for samples with different compositions are listed in Table 1 together with the times of expanding (the time of beginning of expansion to the moment of reaching the sample final volume) and times of drying (the time from reaching by the sample its final volume to the moment of loosing its surfface adhesion to powdered substances). From the foams thus obtained the samples for testing were cut out after *ca.* 48 hrs.

Method of testing

The progress of reaction between UA and alkylene carbonates was monitored by measuring of the content of unreacted ethylene carbonate using barium hydroxide as was described previously [8, 9].

The following properties of polyetherols have been determined using methods described in literature: hydroxyl number by xylene method [10], density (pyknometrically), refractive index, Höppler viscosity, surface tension by ring detach method [11].

Prepared foams were investigated to determine following properties:

— apparent density according to standard EN ISO 845:1995,

— water uptake according to ISO 2896:1987,

— linear shrinkage in agreement with standard ISO 2796:1986, including determination of changes in linear dimensions before and after heating at 100 °C for 4 and 24 hrs,

— flammability according to ASTM 635-56T,

— thermal stability as the weight loss after heating at 150, 175, and 200 °C in air atmosphere for 25 days,

— compression strength in accordance to ISO 844: 1978.

The preliminary selection of foam samples has been made by analyzing the changes in their shapes after heating at 200 °C for 14 hrs.

RESULTS AND DISCUSSION

The properties of polyetherols used here for the formation of polyurethane foams are comparable with those used regularly for the same purpose (Table 2). It has been found the decrease in viscosity, surface tension, refractivity, and density of polyetherols with increase in percentage of oxyalkylene units per UA in the product.

The foaming process was optimized by changing the amount of isocyanate, TEA as the catalyst, foaming agent (water) and the length of polyetherol chains. The optimization of foaming conditions and starting composition aimed at formation of the rigid (R) or semirigid foams (SR), resistant to mechanical deformation after 14 hours of thermal exposure at 200 °C (see Table 1). It has been noticed, that the best foams were formed from

T a b l e 1. The compositions, parameters of foaming process and characteristics of products

Alkylene carbonate	Oxyalkylene units per UA molecule	Symbol of sample	Composition, g/100 g of polyetherol				Foaming process			Characteristics		
			MDI	water	TEA	NCO/OH molar ratio	time of creaming, s	time of expanding, s	time of drying, s	of mixture[a]	of foams	
											just prepared[b]	after heating at 200 °C for 14 hrs[c]
EC	12	1	140	2	1,6	1.2	30	15	90	inh	R	+
		2	160	2	1,0	1.5	30	35	60	inh	R	+
		3	160	2	1,2	1.5	30	20	20	inh	R	+
		4	160	2	1,4	1.5	30	20	90	inh	F, R	—
		5	160	2	2,0	1.5	13	15	30	inh	R	—
		6	160	2	1,6	1.5	26	30	30	inh	R	+
		7	196	2	1,6	1.9	34	23	300	inh	R	+
		8	220	2	1,0	2.3	50	60	300	inh, lfd	R	+
	16	9	142	2	1,4	1.5	17	7	9		SR	—
		10	144	2	1,4	1.6	16	10	2		SR	—
		11	158	2	1,4	1.8	20	15	10		SR	—
		12	142	2	0,6	1.5	26	19	7	inh	R	—
		13	158	2	1,4	1.8	16	14	5	inh, lfd	R	—
		14	166	2	0,6	1.9	30	30	10	inh, lfd	R	—
		15	166	2	0,8	1.9	21	25	12		R	—
		16	166	3	0,8	1.4	22	24	6		R	—
		17	140	3	0,8	1.0	19	14	2	lfd	R	—
		18	166	3	0,8	1.4	25	27	5		R	—
		19	168	3	0,8	1.5	26	20	21		R	+
		20	190	3	0,8	1.9	27	23	31	lfd	R	+
PC	6.6	21	222	2	1.4	1.8	30	45	20	lfd	R	+
		22	222	1	1.4	2.1	10	60	10	lfd	R	+
	9	23	184	—	1.4	2.0	27	55	20	lfd	R	+
		24	184	1	1.4	1.7	20	30	15	lfd	R	+
		25	184	2	1.4	1.4	17	17	20		R	+
	13	26	130	2	1.4	1.4	17	29	11		F, R	—
		27	144	2	1.4	1.6	17	34	21		F, R	—
		28	160	2	1.4	1.9	17	30	27		R	+
		29	160	2	1.0	1.9	23	35	30		R	+
	16	30	120	2	1.0	1.4	15	40	22	lfd	R	+
		31	134	2	1.0	1.7	20	39	26		F, R	—
		32	110	2	0.8	1.2	24	38	55		F, R	—
		33	124	2	0.8	1.8	18	40	25		F, R	—
		34	150	2	0.8	2.1	23	43	18		F, R	—
EC/PC	8/6	35	140	2	1.4	1.5	19	86	87		R	+
		36	140	2	1.8	1.5	16	80	66		R	+
		37	140	2	2.2	1.5	15	76	76		R	+
		38	158	2	1.0	1.8	23	130	119		R	+
		39	160	2	2.2	1.8	17	79	116		R	+

[a] inh — initially the inhomogeneous mixture; [b] SR — semirigid foam, R — rigid foam, F — fragile foam, lfd — low foaming degree; [c] + — no deformation of foam, — — sample deformed.

T a b l e 2. Physical properties of polyetherols used in the preparation of polyurethane foams

Alkylene carbonate	Oxyalkylene units per UA molecule	Refractive index n_D^{20}	Density g/cm^3	Viscosity $N \cdot s/m^2$	Surface tension N/m	Hydroxyl number	
						calculated	found
EC	12	1.5120	1.2471	35.482	0.03891	322	345
	16	1.5002	1.2144	3.033	0.03704	257	277
PC	6.6	1.4878	1.4446	3.597	0.03069	407	412
	9	1.4837	1.1139	1.906	0.02718	325	320
	13	1.4788	1.0946	0.855	0.02696	243	245
	16	1.4718	1.0785	0.225	0.02652	205	194
EC/PC	8/6	1.4888	1.1372	0.653	0.02632	259	264

polyetherols with oxypropylene groups (*i.e.* synthesized from PC) or both oxyethylene and oxypropylene (*i.e.* synthesized from polyetherols obtained by subsequent reaction of UA with EC and PC (corresponding to the samples 21—25, 28—30 and 35—39 in Table 1). The foams formed on the basis of polyetherol obtained form UA and EC in most cases underwent deformation upon heating in 200 °C for 14 hours. The mixture of polyetherols with short chains (not more than 12 oxyethylene groups or less than 9 oxypropylene groups per one UA) with other reactants used for foaming were inhomogeneous due to high viscosity of polyetherols and therefore the foaming was not well controlled process. The homogenity of mixtures was better for the longer chains of polyetherols and eventually the completely homogeneous mixtures were obtained with polyetherols containing 16 oxyethylene or 9 oxypropylene groups or more. Optimization of the amount of isocyanate used for foaming with studied polyetherols evidenced that NCO/OH index should be at the level of 1.4—1.5 (Table 1, samples 19, 25, 30 and 35—37). In the compositions containing polyetherols with oxyethylene and oxypropylene groups this index can reach even 1.8 (Table 1, samples 38 and 39). The optimized water content in the foaming mixture should be 2—3 wt. % in relation to the mass of polyetherol. The amount of catalyst is crucial; the best foams were obtained when 1.4 g of TEA per 100 g of polyetherol obtained from PC or 1.0—2.2 g of TEA per 100 g of polyetherol obtained from EC and PC were used. When other conditons of foaming were used different than those optimized here, the foams were either too soft, or too dense with irregular pores. The time of creaming, time of expanding and time of drying of polyurethane composites were within tenths of seconds. Accordingly to those properties, the obtained polyurethane composites can be applied for fabrication by spraying.

Table 3. Some properties of the foams obtained

Alkylene carbonate	Symbol of sample	Density kg/m^3	Absorption of water, wt. %		Linear post-shrink-age, %
			after 4 h	after 24 h	
EC	9	51.00	2.15	3.25	0.0
	10	56.55	1.60	3.30	0.0
	11	56.20	1.30	2.95	0.0
	16	61.50	0.70	1.45	0.0
	19	55.50	1.00	2.00	0.0
PC	25	51.4	0.96	2.36	0.0
	26	48.2	0.60	1.90	—d)
	27	44.8	1.57	1.76	—d)
	28	54.8	1.01	1.29	0.2
	29	46.4	0.21	0.30	0.0
	30	49.1	0.08	0.79	0.0
	31	45.6	0.33	0.74	—d)
	32	50.1	1.51	1.62	0.0
	33	47.6	0.42	0.88	—d)
	34	48.8	0.91	1.46	0.0
EC/PC	35	38.00	0.30	0.70	0.0
	36	34.60	0.90	3.50	0.0
	37	40.15	0.55	4.50	0.0
	38	43.25	0.35	0.85	0.0
	39	39.30	0.55	4.50	0.0

d) Sample deformed.

All foams are flammable. Their apparent density is within 35—61.5 kg/m^3 (Table 3), *i.e.* it is lower in comparison with the foams obtained from polyetherols synthesized from HMUA and oxiranes (50—90 kg/m^3) [7]. Thus, the obtained foams can be regarded as semirigid

Table 4. Weight loss and changes in compression strength after thermal exposure of foams

Alkylene carbonate	Oxyalkylene units per UA molecule	Symbol of sample	Weight loss (in wt. %) after exposure to temperature			Compression strength, MPa				Increase in compressive strength, %		
						before exposure	after exposure to temperature			after exposure to temperature		
			150 °C	175 °C	200 °C		150 °C	175 °C	200 °C	150 °C	175 °C	200 °C
EC	16	9	8.5	26.0	41.0	0.394	0.246	0.306	—d)	-37.6	-22.3	—d)
		10	9.4	26.0	41.0	0.315	0.368	0.469	—d)	+16.8	+48.9	—d)
		11	7.0	23.0	37.0	0.326	0.318	0.402	—d)	-2.5	+23.3	—d)
		16	5.6	23.0	36.0	0.372	0.485	0.534	—d)	+30.4	+43.5	—d)
		19	6.2	22.0	35.0	0.308	0.399	0.483	0.401	+29.5	+56.8	+30.2
PC	9	25	6.2	20.0	34.0	0.287	0.331	0.208	0.205	+15.3	-27.5	-28.6
	13	26	14.0	30.0	45.0	0.320	0.404	0.321	—d)	+26.3	+0.3	—d)
		27	11.5	27.5	40.0	0.336	0.322	0.230	—d)	-4.2	-31.5	—d)
		28	7.2	22.5	35.0	0.286	0.397	0.242	0.235	+38.8	-15.4	-17.8
		29	6.8	22.6	36.0	0.307	0.346	0.262	0.206	+12.7	-14.7	-32.9
EC/PC	8/6	35	8.7	22.0	36.0	0.190	0.226	0.267	0.268	+18.9	+40.5	+41.1
		36	9.2	23.0	37.5	0.205	0.206	0.232	0.244	+0.5	+13.2	+19.0
		37	9.2	23.0	36.0	0.205	0.229	0.288	0.261	+11.7	+40.5	+27.3
		38	7.1	18.0	33.0	0.229	0.226	0.301	0.347	-1.3	+31.4	+51.5
		39	8.4	22.5	35.5	0.268	0.296	0.280	0.304	+8.2	+4.5	+13.4

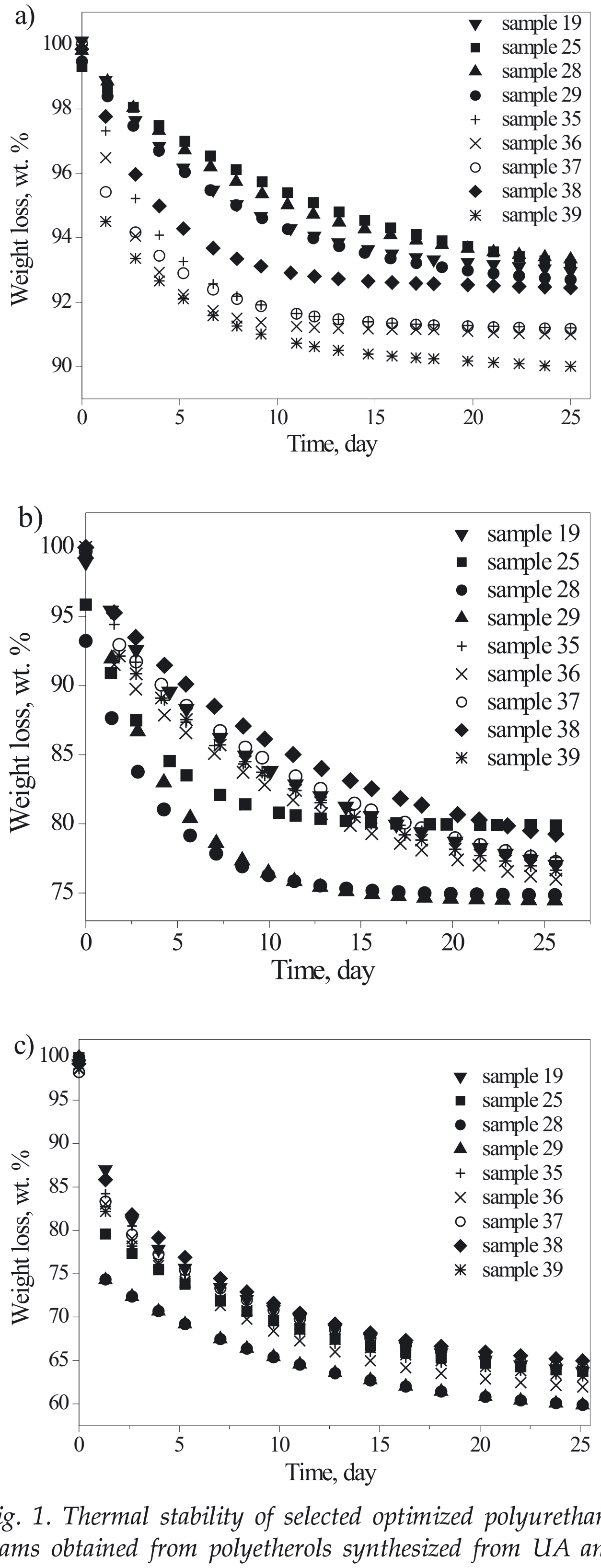


Fig. 1. Thermal stability of selected optimized polyurethane foams obtained from polyetherols synthesized from UA and alkylene carbonates, measured as weight loss of the sample at: a) 150 °C, b) 175 °C, c) 200 °C; (the number of foam in accordance to the composition in Table 1)

and rigid. Water absorption is small (0.3—4.5%, Table 3). The smallest values of water absorption were observed for the foams obtained from polyetherols containing high number of oxypropylene groups (Table 3, samples 29—31). The foams did not show linear shrinkage (Table 3). On the other hand some of the foams underwent deformation upon thermal exposure (samples 26, 27, 31 and 33).

Thermal stability was estimated by measuring the weight loss and determination of mechanical properties after thermal exposure of the samples at 150, 175 or 200 °C for one month almost. The lowest weight loss was observed for the foams with oxypropylene groups (Table 4, samples 25, 28 and 29), both oxyethylene and oxypropylene groups (Table 4, samples 35—39) and also for polyetherols obtained from EC (Table 4, sample 19). The weight loss results for those foams were 6.2—8.7, 18.0—22.5 and 33.0—37.5 wt. % at 150, 175 and 200 °C, respectively. For comparison, the lowest weight loss for polyetherols obtained from HMUA and oxiranes were 23—26, 30—47 and 52—55 wt. %, respectively [7].

The values of compression strength for the samples before and after thermal exposure are listed in Table 4. Definitely the best mechanical properties considering thermal history of samples demonstrated the foams obtained from polyetherols containing both oxyethylene and oxypropylene units and for sample 19. The value of compression strength increases after heating at 200 °C. This behavior is related to thermal crosslinking. The foams obtained here showed remarkable improvement in comparison with those obtained from HMUA and oxiranes [7], for which the decrease in compression strength or deformation occurred. The weight loss versus time for the foams showing the best thermal properties observed at temperatures 150, 175 and 200 °C is given in Figure 1.

CONCLUSIONS

Polyetherols obtained from UA and EC and/or PC, containing purine rings are usefull candidates for the preparation of polyurethane foams of enhanced thermal stability. Their thermal stability and mechanical properties are much better than those of foams obtained from polyetherols synthesized from HMUA and oxiranes. The best foams are obtained from polyetherols containing both oxyethylene and oxypropylene groups. The compression strength of these foams increases even after thermal exposure at 200 °C. Other properties of the foams, like apparent density, water absorption and polymerization shrinkage are as those for commercial polyurethane foams.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— Glikoliza odpadów poliuretanowych. Cz. II. Oczyszczanie oraz wykorzystanie glikolizatów

— Laserowe modyfikowanie materiałów polimerowych. Cz. III. Ablacja laserowa i zmiany struktury geometrycznej powierzchni

— Dyspersja napełniacza w matrycy kauczuku. Cz. II. Metody oceny stopnia dyspersji

— Silnie rozgałęzione poli(hydroksyetery) na podstawie biscyklicznego węglanu z grupą fenolową

— Zmiany struktury chemicznej estrów metylowych kwasów tłuszczowych oleju rzepakowego podczas katalitycznego utleniania w temp. 200 ^oC

— Napięcie powierzchniowe tworzyw polimerowych

— Polimery szczepione nanocząstkami tlenków metali w celu kontrolowanych zmian współczynnika załamania światła (*j. ang.*)

— Wpływ grzania strefowego na strukturę włókien PET i na dynamikę procesu przędzenia ze stanu stopionego. Cz. II. Model matematyczny