

Products of Reaction Between *N,N'*-Bis(2-hydroxyethyl)urea and Ethylene Carbonate and their Application to Obtain Polyurethane Foams

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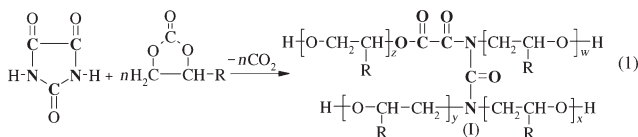
ABSTRACT: *N,N'*-Bis(2-hydroxyethyl)urea (BHEU) was hydroxyalkylated with ethylene carbonate (EC). The oligomeric products were obtained and analyzed by ¹H-NMR, IR, MALDI ToF, and GC methods. The polyols obtained from BHEU and EC in large excess have good thermal stability and possess suitable physical properties as substrates for foamed polyurethanes. The

rigid polyurethane foams obtained from the hydroxyethoxy derivatives of urea reveal enhanced thermal stability. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1141–1149, 2009

Key words: *N,N'*-Bis(2-hydroxyethyl)urea; ethylene carbonate; polyurethane foams; thermal stability

INTRODUCTION

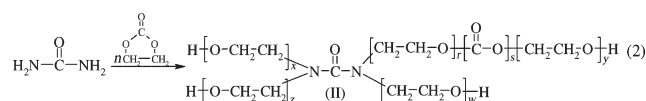
The reaction of parabanic acid with alkylene carbonates (ACs) results in the formation of products (I) possessing higher thermal stability (the temperature of maximum decomposition is 250–280°C),^{1–3} due to the presence of the structural fragment formed upon ring opening composed of oxalamidoester and carbamide units linked together via imide bond.



where: R = H—, CH₃—.

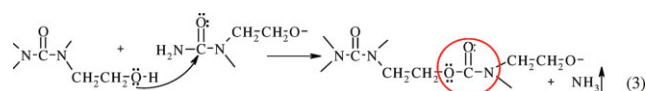
That conclusion was based on previous studies on the thermal stability of hydroxyalkyl derivatives of oxamic acid and those of urea containing oxalamidoester and carbamide groups, respectively.^{4–7} Oxamic acid was reacted with ACs to give products with oxalamidoester group; the products had maximum decomposition temperature in the 250–310°C^{4,5} range. Similarly the products obtained from urea with propylene carbonate (PC), with carbamide groups included in their structure, indicated the temperature of maximum decomposition in the 260–300°C range.⁶ The products of reaction between urea

and ethylene carbonate (EC) start to decompose at 220–240°C.⁷



where: $r \geq 0$.

In the reaction of urea with EC, partial release of carbon dioxide took place ((II), $s = 0$) with the carbonate partially preserved in the product ((II), $s = 1$). The carbonate groups were incorporated next to nitrogen atom ($r = 0$) or into oxyethylene chain ($r \geq 1$).⁷ The predominant product does not contain carbonate groups. In the course of reaction, the condensation of hydroxyethoxy derivatives of urea also occurred with the formation of carbamate group:



These groups are responsible for the decomposition of hydroxyethoxy derivatives, which began already about 220°C.^{7–9} It seemed that the replacement of urea with *N,N'*-Bis(2-hydroxyethyl)urea (BHEU) would allow to eliminate the condensation of hydroxyethoxy derivatives of urea, and/or the incorporation of carbonate into the product. These attempts are reported in this part of the project as well as attempts of application of obtained polyols for the preparation of foamed polyurethanes.

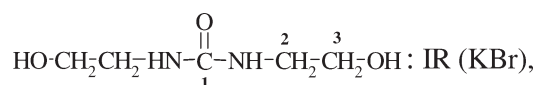
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EXPERIMENTAL

Synthesis

Synthesis of BHEU

Sixty grams (1 mol) of urea and 120.6 cm³ (122 g, 2 mol) of 2-aminoethanol were placed in a round-bottomed 250 cm³ flask equipped with reflux condenser. The mixture was magnetically stirred and heated on oil bath at 135°C for 2 h, then the temperature was raised to 140°C and the heating was continued for next 6 h. The ammonia evolved in the reaction was vacuum transferred to water trap. The crude oily product was formed upon cooling, which was dissolved in 50 cm³ cold methanol, kept in refrigerator until BHEU crystallized (after about 24 h). The precipitate was filtered off, the product was recrystallized from methanol, and dried in vacuum drier at 40°C under 0.09 MPa pressure. Melting point was 81–82°C.¹⁰



$\nu = 3500\text{--}3200$ (w, O—H and N—H valence), 2962 (w, —CH₂—, as. valence), 2865 (w, —CH₂—, sym. valence), 1628 (w, C=O, valence.), 1576 (w, C—N and N—H, deform.), 1420 (s, —CH₂—, scissoring), 1060 (w, C—O—H, valence), [cm⁻¹]; ¹H-NMR (500 MHz, d₆-DMSO), $\delta = 3.05$ (2 H, q, —N—CH₂—, J_{2,3} = 5.9 Hz), 3.36 (2H, q, —CH₂—O—, J_{2,3} = 5.6 Hz), 4.64 (1H, t, —O—H, J = 5.2 Hz), 6.0 (1 H, t, —NH—, J = 5.7 Hz); ¹³C-NMR (d₆-DMSO), $\delta = 158.4$ (C₁), 60.8 (C₃), 42.0 (C₂), [ppm]; MS, $m/z = 87$ (100%), 59 (42.6%), 42 (21.1%), 28 (36.3%); UV (methanol) = 204 [nm], EA: % N_{calc} = 18.90, % N_{exp} = 18.84, % C_{calc} = 40.54, % C_{exp} = 40.44, % H_{calc} = 8.17, % H_{exp} = 8.13.

Reactions of BHEU with EC

In a 100 cm³ three-necked round-bottomed flask, 3.7 g (0.025 mol) BHEU and the appropriate amount of EC (pure, Fluka, Switzerland) were placed to reach the molar ratio of reagents of 1 : 2 – 1 : 14 and 0.21–0.31 g potassium carbonate (8.4–12.6 g/mol BHEU, 0.06–0.09 mol/mol BHEU) or 0.17 g diazabicyclo[2.2.2]octane (DABCO) (6.2 g/mol BHEU, 0.06 mol/mol BHEU), or 0.37 g 57.5 wt % tetrabutylammonium hydroxide (TBAH) solution (14.8 g/mol BHEU, 0.06 mol/mol BHEU) was added. The reaction mixture was protected from moisture (with tube filled with magnesium sulfate) and stirred mechanically at 140 or 160°C with monitoring of progress of reaction by determining the unreacted EC.

Foam preparation

Attempts of foaming the reaction products of BHEU with EC were carried out in small 250 cm³ test cups at room temperature. To 5 g of hydroxyethoxy derivatives of urea, 0.1 g of surfactant (Silicon 5340, Houdry Hüls), 0.0–0.22 wt % of triethylamine (TEA) catalyst (pure, Avocado, Germany), and 2 wt % of water were added. After careful mixing of the components, a preweighed amount of 4,4'-diphenylmethane diisocyanate (pure, Merck, Germany) was added, the amount being calculated as described in Ref. 11. The amounts of diisocyanate and water were adjusted to give OH : NCO molar ratio varying from 1 : 1.7 to 1 : 2.0. Each mixture was vigorously mixed until it started to cream (see Table III). The samples for tests were cut out from the foams thus obtained after about 48 h.

Analytical methods

The reaction of BHEU with EC was monitored by the determination of EC.¹²

¹H-NMR spectra of products were recorded with BS-586A 80 MHz spectrometer (Tesla, Brno, Czechoslovakia) or with 500 MHz spectrometer (Bruker, Germany) in deuterated dimethyl sulfoxide (d₆-DMSO), and hexamethyldisiloxane (HMDS) or tetramethylsilan (TMS) reference.

¹³C-NMR spectra of BHEU were recorded with 500 MHz spectrometer (Bruker, Germany) in d₆-DMSO, and TMS reference.

IR spectra were recorded in capillary film or KBr pellets on a PARAGON 1000 FT spectrometer (Perkin-Elmer). Elemental analysis of BHEU was performed with EA 1108 (Carlo-Erba) analyzer.

The UV-vis spectra of methanol solutions in the region of 200–700 nm were obtained with Hewlett Packard 8943 spectrophotometer. All spectroscopic measurements were performed in quartz glass cells (1 cm).

GC-MS experiments were conducted with Hewlett Packard 6890N chromatograph equipped with 5973 Network mass detector, and HP-5MS 30 m × 0.25 mm column packed with film of 0.25 μm thickness. The samples were dissolved in acetonitrile.

Chromatographic analysis of byproducts, i.e., ethylene glycol (EG) and products of its consecutive reactions with EC were performed with gas chromatograph HP 4890A (Hewlett Packard, Ringoes, NJ, US) with FID detector, and HP1 30 m × 0.53 mm column packed with crosslinked methylsiloxane film of 1.5 μm thickness. Initial temperature was 50°C, heating rate 20°C/min, end temperature 220°C, time of heating at 220°C for 6 min, loader temperature 250°C, detector temperature 300°C. The samples were prepared as solution in methanol (0.01M).

TABLE I
Reaction Conditions of BHEU with EC

Synthesis	Initial molar ratio	Amount of K ₂ CO ₃ (mol/mol BHEU)	Temperature (°C)	Reaction time (h)
1	1 : 2	0.06	140	4.5
2	1 : 2	0.06	160	3
3	1 : 3	0.06	140	6
4	1 : 3.5	0.06	140	5
5	1 : 3.5	0.06 ^a	140	7.5
6	1 : 3.5	0.06 ^b	140	8
7	1 : 3.5	0.06	160	3
8	1 : 6	0.06	140	14.5
9	1 : 6	0.09	160	8
10	1 : 10	0.09	160	12.5
11	1 : 14	0.09	160	18

^a DABCO was used as catalyst.

^b TBAH was used as catalyst.

Internal reference was cyclohexanone. Percentage of diols and polyols were calculated according to calibration curves as described in Ref. 1.

MALDI ToF spectra of reaction products of BHEU with EC were obtained on Voyager-Elite Perceptive Biosystems (US) mass spectrometer, working at linear mode with delayed ion extraction, equipped with nitrogen laser working at 337 nm. The matrix was 2,5-hydroxybenzoic acid or matrix α -cyanocinnamic acid. The samples were diluted with methanol to 1 mg/cm³, followed by the addition of 10 mg/cm³ NaI in acetone. Therefore, in some cases, the molecular ion weights were increased by the mass of Na⁺, H⁺, and CH₃OH.

Thermal analyses (DTA, DTG, and TG) of hydroxyethyl derivatives of urea and polyurethane foams were performed in ceramic crucible at 20–1000°C temperature range, with 100 min registration time, 200 mg sample, under air atmosphere with Paulik-Paulik-Erdey derivatograph, MOM, Hungary.

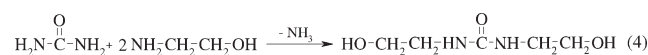
The following properties of hydroxyethoxy derivatives of urea have been determined: pycnometer density,¹³ refractive index, Höppler viscosity,¹⁴ and surface tension by ring detach method.¹⁵ All measurements were made in temperature range of 20–80°C.

The following properties of foams were determined: apparent density,¹⁶ water uptake,¹⁷ stability of dimension,¹⁸ glass transition temperature (by DSC), thermal stability as the weight loss after heating at 150, 175, and 200°C for a month, and the compressive strength.¹⁹

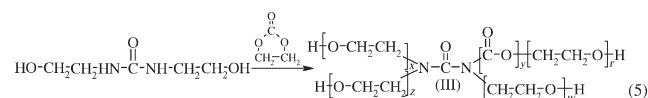
The differential scanning calorimetry (DSC) measurements were made using a DSC822^e Mettler Toledo instrument, in 20–200°C temperature range and 10deg/min heating rate under nitrogen atmosphere. The results were recorded as heat flow in [W/g] versus temperature.

RESULTS AND DISCUSSION

The BHEU was obtained by transamination of urea with 2-aminoethanol, and characterized by elemental analysis, IR, and NMR spectra (see Experimental).



BHEU was subjected to hydroxyalkylation with EC, in the presence of potassium carbonate (Table I). Mass balance and spectral analysis have shown that, similarly to the reaction of urea with EC,⁷ the mixture of products has been obtained, namely products without carbonate (III, $y = 0$) and another product, with preserved carbonate in its structure (III, $y = 1$).



where: $0 \leq y \leq 1$.

The ¹H-NMR spectra of products show the resonance at 4.2 ppm assigned to methylene protons in $-\text{CH}_2-\text{OCO}$ fragment²⁰ (Fig. 1), while in the IR spectra the intense bands at 1720 and 1250 cm⁻¹, attributed to valence vibrations of C=O and C–O(CO) of ester (carbamate) are present. The possible decomposition of EC into carbon dioxide and ethylene oxide²¹ was tested by careful examination of the spectra of the product formed in the reaction with 2-molar excess of EC and/or consecutive reaction of hydroxyl groups with EC. In the ¹H-NMR spectrum of the product, the resonance at 6.15 ppm belonging to unreacted secondary amide group protons of hydroxyethyl derivative of urea (III, where $x, y = 0, z, w, r \geq 1$) was found, as well as the resonance at about 7 ppm assigned to secondary amide

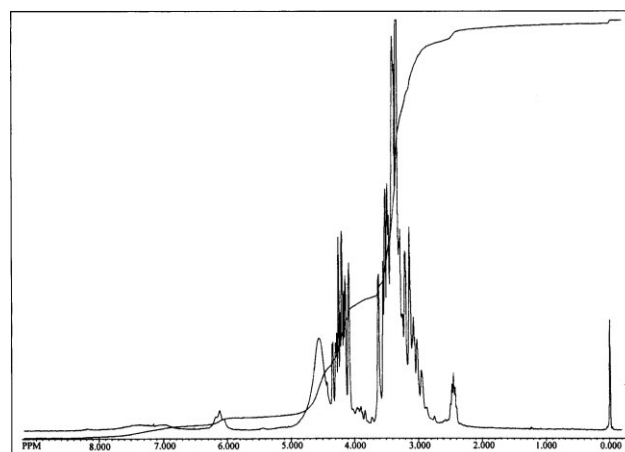


Figure 1 ¹H-NMR spectrum of product obtained from BHEU : EC (1 : 2) in the presence of 0.06 mol K₂CO₃/mol BHEU at 160°C.

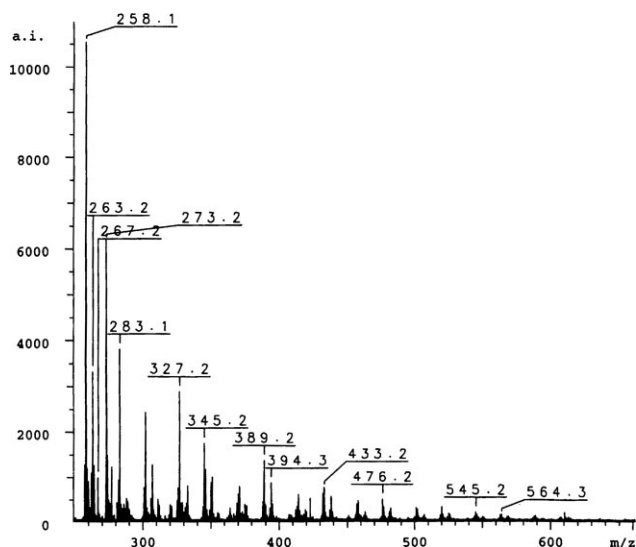
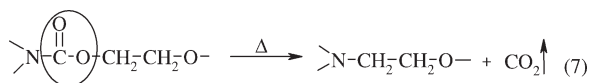


Figure 3 MALDI ToF spectrum of product obtained from BHEU : EC (1 : 6) in the presence of 0.09 mol K_2CO_3 /mol urea at 160°C (matrix 2,5-hydroxybenzoic acid).

(Table I, syntheses 4–6). When DABCO was used as catalyst, there were no secondary amide groups in the product (III, where $x, y = 0, z, w, r \geq 1$). However, the resonance at 7 ppm from secondary amide protons in III (where $x = 0, y = 1; z, w, r \geq 1$) was present [Fig. 2(b)]. When TBAH was used as catalyst, the product contained both mentioned secondary amide groups [resonances at 6.15 and 7 ppm; Fig. 2(c)]. Thus, DABCO as well as TBAH catalysts promote consecutive reaction of hydroxyl groups with EC, instead of amide group reaction with EC.

The condensation of hydroxyethyl derivatives of urea in the course of reaction (by presence of carbamate groups in product) was confirmed by 1H -NMR spectra of derivative obtained at 6-molar excess of BHEU (Table I, synthesis 8), recorded before and after heating of the sample at 200°C (the decomposition of carbonate and carbamate groups occurs in such condition^{8,9}). The heating of the product results in decrease of the intensity of the resonance at 4.2 ppm (from $-(CO)O-CH_2-$) after 4 h. At the same time, the resonance at 2.6 ppm from methylene protons in CH_2-N- appear, indicating the decomposition of carbamate groups.



After 10 h of heating, the changes in the spectrum are more pronounced. Moreover, the decomposition of carbonate groups in the product takes place.

The heating of the product obtained from urea and 8-molar excess of EC resulted in primary decomposition of carbonate groups (within first 4 h),

while the decomposition of carbamate groups took place later.⁷

Mass balance indicated the increase of the number of incorporated carbonate groups in the product, and MALDI ToF examination shows the decrease of carbamates in comparison with products of hydroxyalkylation of urea with EC (Figs. 3 and 4).

According to the MALDI ToF results, in the reaction between BHEU and 6- and 10-molar excess of EC (Table I, syntheses 9 and 10), mostly the hydroxyetoxy derivatives of urea are formed, containing 3 to 10 or 3 to 12 oxyethylene units per mole of urea, and the involvement of products of condensation (containing carbamate groups) is minor (Figs. 3 and 4). The derivatives obtained are oligomeric products with slightly lower number of oxyethylene units per mole of urea, than those obtained from urea and EC.⁷

The reactions of BHEU with EC are accompanied by the formation of minor amount of byproduct, i.e., tetraethylene glycol (TETRAEG), which was quantified by GC. This is formed in the reaction with TBAH as catalyst (about 10 wt %) or when 6- or larger molar excess of EC is used (about 4 wt %).

Thermal studies of products of reaction between BHEU and EC indicated enhanced thermal stability of them, similar to those obtained from urea and EC (Table II).⁷ Two peaks are observed at DTG curve, the first at 240°C due to decomposition of carbonate and carbamate groups,^{8,9} and the second one at 350°C related to total decomposition of compound (Fig. 5), which indicates slightly higher thermal stability in comparison with those products obtained from urea and EC.

The physical properties of the products obtained from BHEU and excess EC were studied (Fig. 6). It has been found that upon increasing the

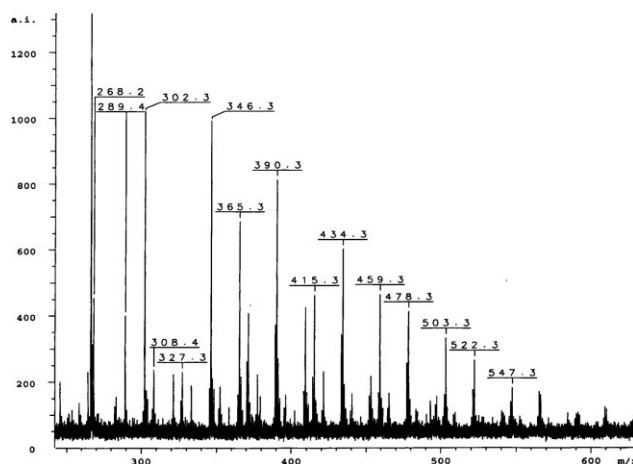


Figure 4 MALDI ToF spectrum of product obtained from BHEU : EC (1 : 10) in the presence of 0.09 mol K_2CO_3 /mol urea at 160°C (matrix α -cyanocinnamic acid).

TABLE II
Thermal Stability of Products

Entry	Initial molar ratio BHEU : EC	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$T_{20\%}$ (°C)	$T_{50\%}$ (°C)	Temperature at maximum decomposition (°C)
1	1 : 6	140	200	220	270	240 and 350
2	1 : 10	150	200	230	300	240 and 350
3	1 : 14	180	210	220	300	240 and 350
4 ^a	Composition 1	190	250	280	510	270

$T_{x\%}$, temperature at which the weight loss is $x\%$.

^a Thermal analysis of polyurethane foam Composition 1.

temperature, the refractive index, density, and surface tension decrease linearly, while viscosity decreases exponentially (Fig. 6). This behavior was typical for polyols traditionally used for the preparation of polyurethane foams.⁸

The products of hydroxyalkylation of BHEU with 6-, 10-, and 14-molar excess of EC were subjected to foaming with 4,4'-diphenylmethane diisocyanate and water as foaming agent at laboratory scale. The process was optimized for the amount of TEA, isocyanate, and water. It has been found that the best results were obtained for such an amount of isocyanate, that the ratio of hydroxyl groups to isocyanate groups in starting mixture was 1 : 1.7 – 1 : 2.0, while the water content should be kept at 2 wt % per mass of polyol (Table III).

The TEA was necessary only in case the polyol obtained from BHEU: EC, 1 : 6 system (BE6). In other cases the TEA was not necessary (Table III).

It has been observed that the time of creaming of compositions decreased together with the number of excessive ethoxy groups in polyol and varied within 7–11 s (Table III). Similarly the expanding time varied. All foams were dry immediately after expansion stage (Table III).

The apparent density of obtained polyurethane foams was in the range of 41–74 kg/m³ (Table IV). The water uptake was the lowest for those obtained from BE6 and did not exceed 8 wt % after 24 h exposition in water at room temperature (Table IV, Composition 1). The water uptake of other foams was considerably higher and after 24 h exposition it reached up to 40 wt %. The water uptake increased with the number of excessive EC in polyol used.

The foams obtained from BE6 polyol have also better dimension stability, which does not exceed 4.5 linear % (Table IV, Composition 1). In other cases the dimension changes are vast (Table IV).

The glass transition temperature (T_g) of obtained foams fall into 75–125°C region, which classifies them as rigid foams.⁸ It decreases with the increasing number of oxyethylene units in urea derivative.

Thermogravimetric analysis has shown the enhanced thermal stability of all obtained poly-

urethane foam. The 5 wt % weight loss occurred at least at 190°C, while temperature of maximum decomposition was 270°C (Table II, Composition 1).

Thermal stability of foams was also studied by static method, i.e., by measurements of weight loss upon heating sample for 30 days at 150, 175, and 200°C (Fig. 7). The constant weight was generally observed after about 10 days in temperature 150°C

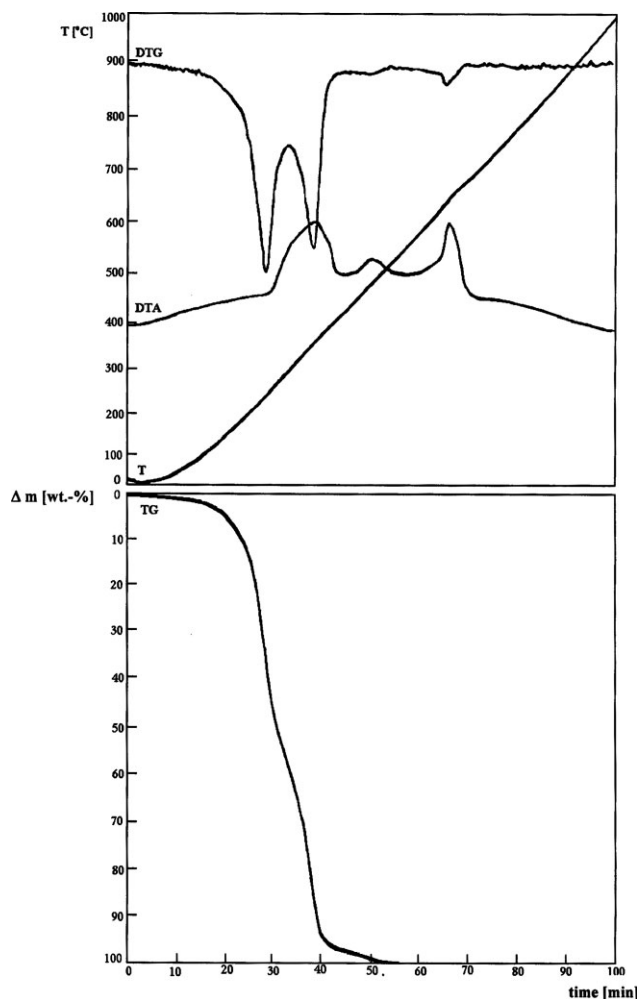


Figure 5 Thermal analysis of products of reaction BHEU : EC (1 : 6) in the presence of 0.06 mol K₂CO₃/mol urea at 160°C.

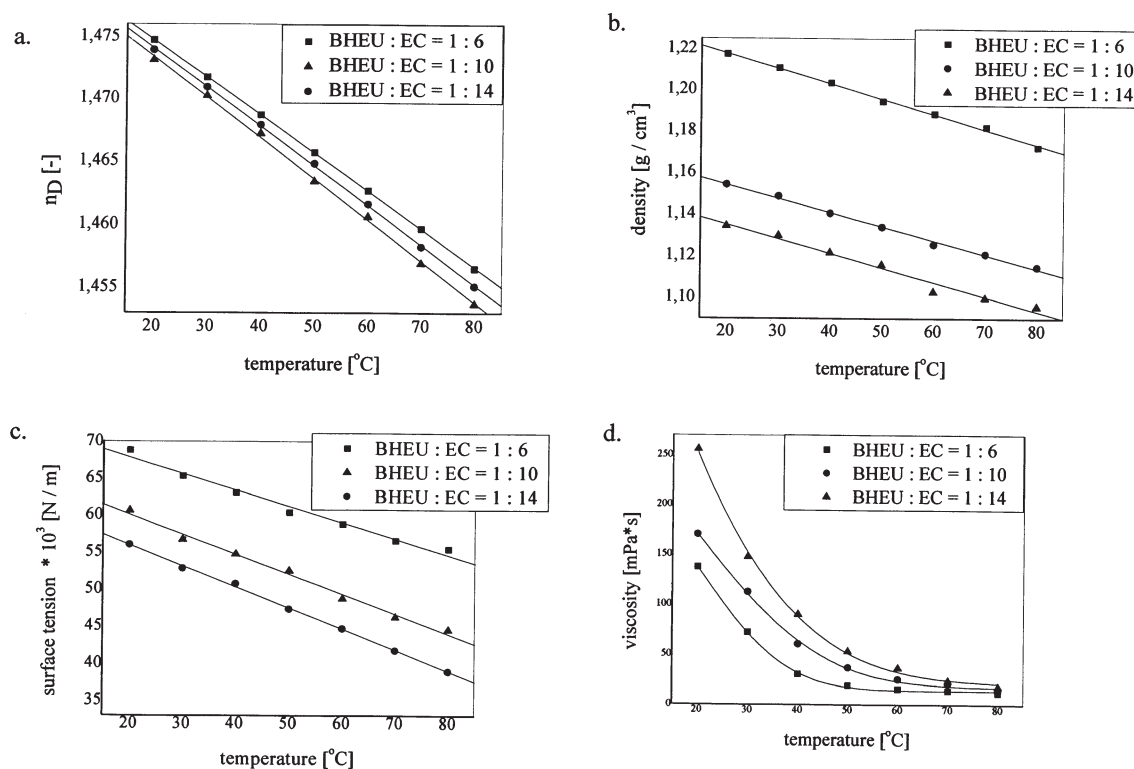


Figure 6 Physical properties of reaction products of BHEU with EC versus temperature.

and 20 days in temperature 175 and 200°C. All foams showed considerable weight loss; with the least weight loss after exposure at 150°C, while for the foams obtained from BE6 it was 25 wt % (Fig. 7).

The foam samples, both freshly prepared and after thermal treatment at 150, 175, and 200°C for 30 days, were tested for their compressive strength. The products obtained from BHEU and 6-molar excess of

EC had higher compressive strength (about 0.15 MPa) in comparison with classic polyurethane foams, for which the compressive strength value is at the level of 0.1 MPa.⁸ The foams obtained from the polyols synthesized at 10- and 14-molar excess of EC possess the compressive strength lower than 0.1 MPa. The compressive strength of the studied foams obtained from BE6 increased after high temperature exposure, and the biggest increase was

TABLE III
Parameters of Foaming Process

Initial molar ratio BHEU : EC in polyol	Composition no.	Composition (g/100 g of polyol)			Molar ratio OH/NCO	Foaming process			Properties of foams just prepared
		Isocyanate ^a	Water	Catalyst ^b		Time (s)			
						Creaming ^c	Expanding ^d	Drying ^e	
1 : 6	1	216	2	0.22	1 : 1.90	11	10	0	Rigid
	2	156	2	0.22	1 : 1.90	11	4	0	Semirigid
1 : 10	3	156	2	0	1 : 1.90	11	3	0	Semirigid
	4	132	2	0	1 : 1.71	11	3	0	Semirigid
1 : 14	5	128	2	0	1 : 2.00	8	4	0	Semirigid
	6	104	2	0	1 : 1.73	7	3	0	Semirigid

^a 4,4'-Diphenylmethane diisocyanate.

^b Triethylamine.

^c Time of creaming: the time elapsed from the moment of mixing to the start of volume expansion.

^d Time of expanding: the time from the start of expansion to the moment of reaching the sample final volume.

^e Time of drying: the time from reaching by the sample its final volume to the moment of losing its surface adhesion to powdered substances.

TABLE IV
Properties of Foams

Compound no. ^a	Density (kg/m ³)	Water uptake (wt %)			Linear dimension change after heating at 150°C (%)					
		After 5 min	After 3 h	After 24 h	Length		Width		Thickness	
					After 20 h	After 40 h	After 20 h	After 40 h	After 20 h	After 40 h
1	50.41	5.84	7.19	7.95	3.37	4.33	2.54	3.05	4.54	4.54
3	35.28	8.54	13.88	23.09	32.88	34.59	17.43	19.27	39.26	39.26
4	40.46	15.66	17.54	21.74	32.43	33.98	33.14	35.43	36.13	37.82
5	40.70	19.61	25.22	39.36	29.97	32.18	22.50	21.00	44.87	48.72

^a Compound no. according to Table III.

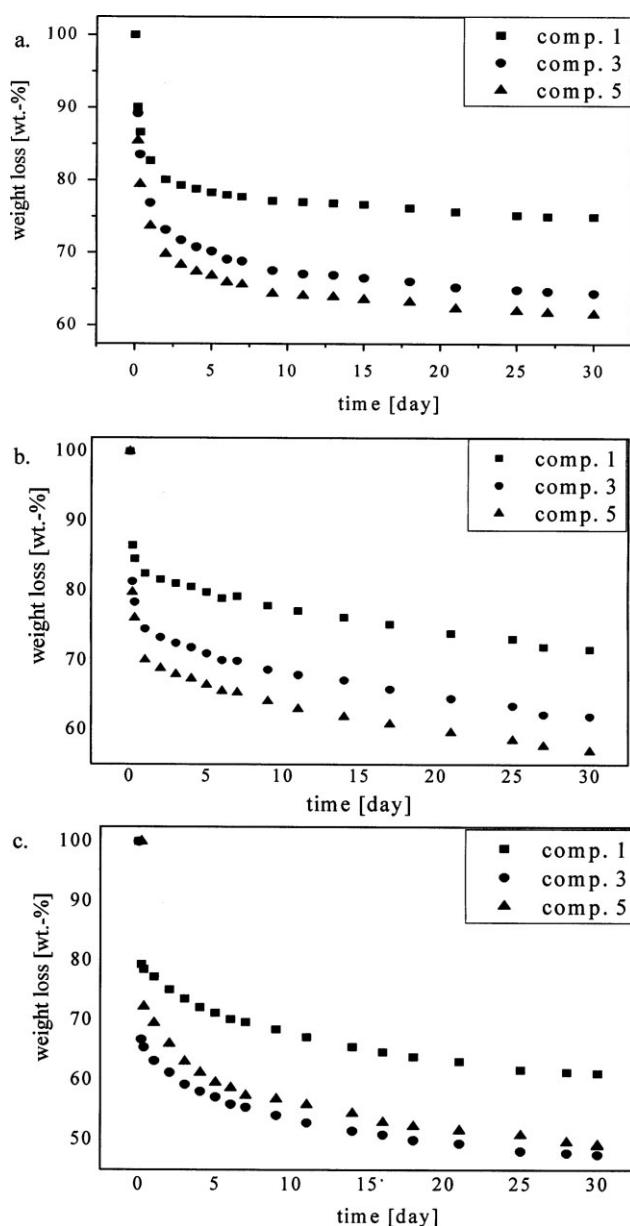


Figure 7 Thermal stability of polyurethane foams as the weight loss after heating at (a) 150°C, (b) 175°C, and (c) 200°C for a month.

observed for the samples heated at 150°C (up to 127% increase). The compressive strength increased further after heating at 175°C (up to 140% of initial value) and then (after exposure at 200°C) it decreased.

The properties of obtained foams were compared to the ones obtained from the products of reaction between urea and EC, although it should be emphasized that the products obtained from BHEU and EC had the same percentage of oxyethylene units. It has been noticed that the foams obtained from urea and EC had two times higher apparent density than those obtained from BHEU. Moreover, the foams obtained from urea and EC indicated higher water uptake and better dimension stability (Table IV). However, for the foams obtained from urea and 8-molar excess of EC (UE8) or from BHEU and 6-molar excess of EC (BE6) the results were similar.

Derivatographic investigations showed enhanced thermal stability of the foams, the larger improvement was found for the foams obtained from hydroxyethoxy derivatives of BHEM. The 30-day thermal exposure of the foams at 150, 175, and 200°C gave various results. The highest thermal stability showed that the foams were obtained from UE8. The differences are the most remarkable for the samples exposed to 150°C test.

The compressive strength was larger for the foams obtained from hydroxyethoxy derivatives of urea and increased upon increasing the exposure temperature; the trend was more visible for the foams obtained from BE6.

CONCLUSIONS

The BHEU was obtained by the reaction of urea with 2-aminoethanol. The product was characterized by spectral methods. The BHEU react with EC in similar way as urea with EC; however, in the product more carbonate groups remain preserved, while the condensation of hydroxyethyl derivatives of urea with the formation of carbamate groups occurs in less extent in comparison with the analogous reaction with urea. The obtained hydroxyethoxy

derivatives of urea possess higher thermal stability, and were used as polyol substrates for polyurethane foams. The rigid foams of enhanced thermal stability and compressive strength in comparison with classic foams were obtained. The foams obtained from the substrate synthesized from BHEU and 6-molar excess of EC have better properties, comparable to those obtained from urea and 8-molar excess of EC.

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