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Od Redakcji

Niniejszy zeszyt „Polimerów" jest poświęcony tematyce poliuretanów.

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Supermolecular structure, morphology and physical properties of urea-urethane elastomers

Summary — Urea-urethane elastomers from polyesterdiol, 4,4'-diphenylmethane diisocyanate (MDI) and dicyandiamide were examined. Their structure was analysed using atomic force microscopy, and the obtained images underwent quantitative analysis. FT-IR spectroscopic analyses were performed, and the phase separation degree was calculated using the results. The structure was also estimated *via* indirect methods with the use of thermal analysis DSC and TGA. Mechanical and abrasive wear properties were also tested. As a result of the analyses, a linear dependence was found between the size of the hard domain agglomerates and the analysed properties of PUR materials, such as the glass transition temperature of the soft phase, the temperature of the maximum speed of the hard phase's degradation, density, hardness, tensile strength and strain.

Keywords: polyurethanes, elastomers, polyurea-urethanes, phase structure, morphology, atomic force microscopy, quantitative image analysis.

STRUKTURA NADCZĄSTECZKOWA, MORFOLOGIA I WŁAŚCIWOŚCI FIZYCZNE ELASTOMERÓW URETANOWO-MOCZNIKOWYCH

Streszczenie — Badano elastomery uretanowo-mocznikowe wytworzone z poliestrodiolu, 4,4'-difenylometanodiizocyjanianu (MDI) i dicyjanodiamidu. Z zastosowaniem mikroskopii sił atomowych oceniano ich struktury nadcząsteczkowe a otrzymane obrazy poddano analizie ilościowej. Zarejestrowano widma FT-IR, a na ich podstawie obliczono stopień separacji fazowej. Strukturę oceniano też metodami pośrednimi wykorzystując analizę termiczną DSC i TGA. Określono właściwości wytrzymałościowe i zużycie ścierne otrzymywanych elastomerów. Stwierdzono liniową zależność pomiędzy rozmiarem aglomeratów domen twardych a temperaturą zeszklenia fazy miękkiej, temperaturą maksymalnej szybkości degradacji fazy twardej, gęstością, twardością, wytrzymałością na rozciąganie i odkształceniem trwałym.

Słowa kluczowe: poliuretany, elastomery, poliuretanomoczniki, struktura nadcząsteczkowa, morfologia, mikroskopia sił atomowych, analiza ilościowa obrazów.

Physical properties of numerous polymer groups depend on their phase structure. Polyurethanes belong to the polymer group. Polyurethane elastomers, specifically multi-block copolymers such as segmented polyurethanes, provide a unique template for the design of synthetic materials with hierarchical microstructures.

Polyurethane macromolecules are built of flexible and rigid segments, from which (as a result of the phase separation process) hard and soft domains are formed; then, two phases (*i.e.* soft and hard) are formed from the said domains. Polyurethane properties depend on the presence of rigid segments, their chemical constitution and the phase separation process. In both polyurethane phases, different phase structures can be formed *e.g.* globules, spherulites or bands [1—3].

An examination of the molecular architecture of these polymers has offered a new perspective to the development of these materials.

Many researchers have focused on the effect of the soft segment (SS) type and length, the rigid segment (HS) type and length, the domain crystallinity and the extent of microphase segregation on the structure–function relationships in segmented polyurethanes [4—28]. Young's modulus of the polyurethanes in which rigid segments were formed from hydrogenated MDI (HMDI) and 1,4-butanediol increases, regardless of the type of polyol, from several dozen up to approximately 200 MPa. The rigid segments' content also increases in the range between 20 and 70 %, while the modulus differences among polyurethanes from different polyols do not exceed 20 % [29—31]. However, the chemical constitution of polyol considerably affects the tensile strength of polyurethanes with similar structures, involving rigid segments and may differ even by *ca*. 80 % [29, 30]. The tensile strength of polyurethanes can also be affected by the type of chain-extending factor. When a bi-functional diol is applied, together with an increase in the number of rigid segments, the strength can grow by *ca*. 75 % in PUR containing 60 % rigid segments. In the case in which a mixture of chain extenders — diols and triols — was applied (with HS content equal to 60 %), the strength dropped by *ca*. 30 %.

A number of experimental studies have been conducted to investigate the relationship between physical properties and material morphology of polyurethanes [6, 9, 32—36].

Skarja and Woodhouse suggested that the crystalline soft phase leads to enhanced mechanical behavior, including tensile strength, tensile modulus and elongation at break [34]. Similar behavior has also been reported by Yen and Cheng [35]. Sonnenschein *et al*. concluded that crystalline soft segments reinforce the hard phase according to the continuous reinforcement model [36].

The author [37] stated that the properties of urea-nitrile-urethanes obtained from crystalline prepolymers change together with the change in the diameter of spherulites formed in the soft phase. The diversity of spherulite sizes was achieved through prepolymer crystallisation at temperatures ranging between –20 °C and 18 °C. The soft phase of the analysed urea-nitrile-urethanes contained 32± 2 % of the crystalline phase. The increase in spherulite diameter by 20 % led to a decrease in tensile strength by *ca*. 40 %, an increase in Young's modulus of the analysed urea-nitrile-urethanes by *ca*. 50 % and an increase in abrasive wear by *ca*. 30 %.

In the works of many authors, we found analyses of the influence of hard domain size on the properties of polyurethanes [6, 9, 30, 31]. However, in the literature, there is a lack of information on the influence of the size of the supermolecular structures formed in the hard phase on the properties of polyurethanes.

The subject of this study was polyurea-nitrile-urethanes obtained by the reaction of polyesterdiol, 4,4'-diphenylmethane diisocyanate and dicyandiamide (used as an extender).

The length of rigid segments is one of the elements affecting the properties of polyurethanes. In the investigated urea-urethane elastomers, the hard segments are the result of the reaction of the isocyanate (-NCO) groups of diisocyanate and the amino (-NH_2) groups of dicyandiamide (DYDI) [38]. In the macromolecules of this polymer there is a strong polar aminonitryle group. Owing to the structure of the macromolecules, these polymers possess numerous functional features; they are self-extinguishing and their oxygen index can reach up to 36 % without using flame retardants or other modifiers. Their favourable strength properties and high wear resistance allowed them to be applied in the manufacture of a wide range of elements used in natural resources mining [39]. Such features as the mechanical properties, abrasion wear resistance and thermal characteristics are essential for this type of application.

Within the framework of the study, the author analysed the structure of prepared materials and the influence of the size of hard domain agglomerates on the properties of the materials.

EXPERIMENTAL

Materials

Polyurethane was synthesised by the one-shot polymerisation approach with 17—39 wt. % hard segments formed by 4,4'-diphenylmethane diisocyanate [MDI — Isonate M 125 (Dow Chemical) and dicyandiamide DYDI (POCH Gliwice)]. The soft segment consisted of a polydiol formed by poly(ethylene adipate) — PEA with a mol. wt. of 2000 g/mol (Alfaster T620, Alfa Systems). An ester copolymer with acid groups Disperbyk 111 (Byk Chemie) was used as a modifier.

Syntheses of PUR

Two series of PUR were prepared—one with the addition of a modifier (PUxM) and the other without the mentioned modifier (PUx). The PUxM series—PEA, DYDI and modifier (10 % of DYDI mass)—and the PUx series—PEA with DYDI—were dried in a vacuum reactor for 2 h at the temperature of 150±5 °C under the pressure of 2—5 hPa while being intensely stirred. The anhydrous mixture was cooled to approximately 70±3 °C, and MDI was added. The curing reaction was conducted by 16 hours at the temp. of 110±5 °C. The samples were cooled to room temperature and conditioned for two weeks.

Table 1. Summary of the prepared PUR chemical composition and the reactants' molar ratio

PUR samples	Modifier	MDI:PAE:DYDI	Wt. % of rigid segment
PU1	–	3:2:1	17.6
PU1M	M		
PU2	–	7:4:3	20.4
PU2M	M		
PU3	–	5:2:3	27.8
PU3M	M		
PU4	–	3:1:2	32.0
PU4M	M		
PU5	–	4:1:3	39.1
PU5M	M		

A description of the produced PUR is listed in Table 1. The rigid segment content by weight was calculated with formula (1) and content by volume with formula (2).

$$wt(\%)\mathrm{HS} = \frac{(n+1)M_{\mathrm{MDI}} + nM_{\mathrm{DYDI}}}{(n+1)M_{\mathrm{MDI}} + nM_{\mathrm{DYDI}} + M_{\mathrm{SS}}} \quad (1)$$

where: n — *mole number of DYDI*, M_i — *molecular weight.*

$$v(\%)\mathrm{HS} = wt(\%)\mathrm{HS}\cdot\rho \quad (2)$$

where: ρ — *experimental density of HS [37].*

METHODS OF TESTING

Differential scanning calorimetry (DSC)

The thermal phase behavior of these elastomeric polyurethanes was investigated using a TA Instruments Q1000 differential scanning calorimeter, operating at the heating and cooling rate of 10 °C/min under the nitrogen atmosphere. As-precipitated, unannealed polymer samples were subjected to heating and cooling cycles between -90 and 250 °C.

Atomic Force Microscopy (AFM)

AFM images were recorded in air using a Digital Instrument Multimode Nanoscope V (Digital Instruments, Santa Barbara, CA) operating in the tapping and force modulation modes using antimony-doped silicon cantilever tips (POL-15, 130 do 250 kHz, 48 N/m). The scanner was used with scan rates between 0.5 and 1 Hz. All images were subjected to the first-order plane-fitting procedure to compensate for sample tilt. The microstructure of polyurethane was investigated on microsections. These were prepared using a rotary microtom RM 2165 (Leica) with an LN 21 cooling device working at -60 °C.

Image analysis

Binary images revealing hard domain agglomerates were produced via digital processing of AFM images. The size and volume fractions of the hard domain agglomerates in polyurethane were determined by measurements of the sections [40]. The image was transferred to MicroMeter software and a quantitative analysis was performed. The diameters were randomly determined on 5 microphotographs.

Fourier transform infrared (FT-IR) spectroscopy

Infrared spectra of PURs were collected using an FT-IR spectrophotometer (Thermo Electron Corporation model Nicolet 6700). Measurements were carried out using the attenuated total reflectance (ATR) technique. Each sample was scanned 64 times at the resolution of 4 cm^{-1} over the frequency range of 4000—400 cm^{-1}. Analysis of the FT-IR data made it possible to determine the carbonyl hydrogen-bonding index (*R*). A straight baseline was drawn in the spectrum between 1780 cm^{-1} and 1640 cm^{-1}, and the carbonyl stretching zone was corrected by subtracting the baseline. To estimate the signal strengths, peak modeling of the infrared active carbonyl bands was carried out using the Gaussian curve-fitting method software OMNIC 7.3. The carbonyl absorption bands were deconvoluted into component bands, the peak areas of these bands were measured and the carbonyl hydrogen-bonding index R was calculated using Eq. (3) [41—43]:

$$R = \frac{A_1z + A_2z}{A_1w + A_2w} \quad (3)$$

where: A_1z, A_2z — *the respective surface areas of bands from vibrations bounded with the hydrogen bond of the carbonyl groups of urea (1) and urethane (2) bonding.*

A_1w, A_2w — *the respective surface areas of bands from vibrations unbounded with the hydrogen bond of the carbonyl groups of urea (1) and urethane (2) bonding.*

Moreover, the degree of phase separation (*DPS*) was obtained through Eq. (4):

$$DPS = \frac{R}{R+1} \tag{4}$$

On the basis of the phase separation degree (*DPS*) and the volume share of hard segments (V_{HS}), the percentage by volume was calculated for hard segments linked with hydrogen bonds ($V_{FTIR\text{-}HS}$).

$$V_{FTIR\text{-}HS} = V_{HS} \cdot DPS \tag{5}$$

Tensile testing

The tensile properties of these polyurethanes were determined using an Instron 1115 testing machine. The samples were elongated at the rate of 500 mm/min according to ISO 527.

Hardness was measured using an indentation hardness tester according to ASTM D2240-75.

Abrasion resistance

The abrasion resistance of test samples was measured with a Schopper–Schlobach instrument with an APGi circulating roller from Heckert, and the procedure complied with PN-ISO 4649 standard. The test pieces were in the form of a roll (16 ± 0.2 in diameter and 2 mm high). Standard rubber from The Institute for Engineering of Polymer Materials and Dyes, Elastomer and Rubber Technology Division (Piastów, Poland), was used as a reference material (PN-ISO 2781+AC1). The abrasion resistance index (ΔV) was calculated with the following relation:

$$\Delta V = \frac{\Delta m_t \cdot 0.2}{\Delta m_s \cdot \rho} \tag{6}$$

where: Δm_s — *the arithmetic mean of the mass loss of three standard rubber samples (g);* Δm_t — *the mass loss of the analyzed sample (g); 0.2 — the required mass loss of the standard rubber sample (g);* ρ — *the density of the analyzed material (g/cm*^{3}*).*

Determination of the **density** was performed according to ISO 2781.

A **thermogravimetric analysis** (TGA 500, TA Instruments) was carried out using samples of 5 mg in an alumina crucible under the heating rate of 10 °C/min under N_2.

RESULTS AND DISCUSSION

Selection of urea-nitrile-urethanes intended for the manufacture of machine elements should be based on the knowledge of the relationship between their morphology and properties, which is why a detailed examination was carried out on the morphology of phases formed during the phase separation process in these materials.

The DSC curves of unmodified PUR samples are shown in Fig 1. On the curves, the glass transition temperature of the soft phase was observed at –35 °C to –25 °C, and the endothermic peak connected with the change in the order in the hard phase appeared at ca. 180—220 °C. When the soft phase occurs in the amorphous form, then the hard phase can form the structure shown as a model in Fig. 2.

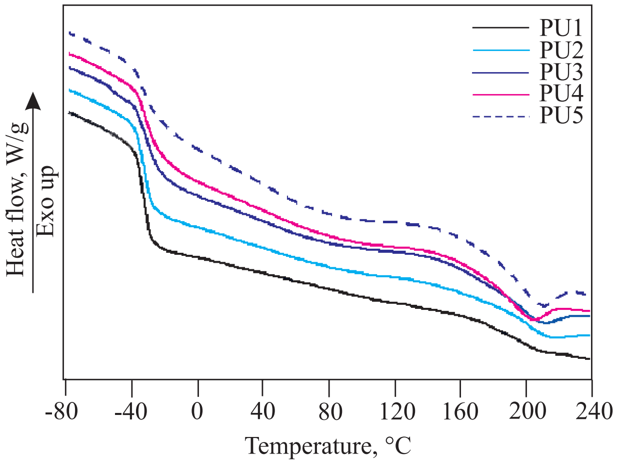

Fig. 1. DSC curves for unmodified PUR

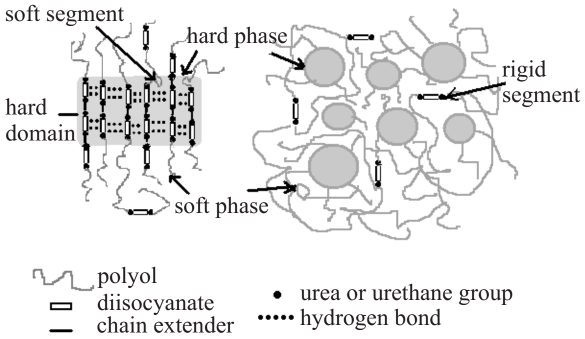

Fig. 2. The structural model of polyurethanes with 15—40 wt. % of rigid segment

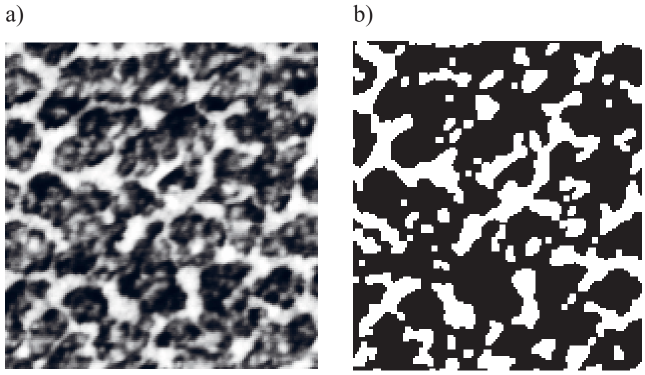

Fig. 3. Force modulation AFM 2D image of the cross-sectional structure of PU4 and a binary image of PU 4. Scan 4 × 4 μm

To confirm that the produced polyurethanes form the structures presented in the proposed model, there was conducted a phase structure analysis of urea-urethane elastomers using atomic force microscopy. Fig. 3 shows an exemplary image of the surface of a PUR section performed in Force Modulation (FM) mode and a binary image of the structure.

A qualitative analysis of the structural images of urea-urethane elastomers revealed that these are isotropic structures whose elements are isolated in space. In the soft phase, different-sized agglomerates of hard domains are present in the shape of ovals and ellipsoids. The size of ovals grows together with the increase in the rigid segment content caused by the change in the molar composition of the substrate. The results of the quantitative analysis of the PUR phase image structures are listed in Table 2.

Table 2. Phase structure of PUR parameters from the AFM images analysis

PUR materials	Volume % hard segment	$\bar{d}_2$, µm	STD($\bar{d}_2$) µm	CV($\bar{d}_2$)	$V_{\text{HS AFM}}$ %
PU 1	14.2	0.4	0.23	0.58	8
PU1M		0.7	0.63	0.90	27
PU2	16.5	0.8	0.85	1.06	11
PU2M		0.9	0.45	0.50	29
PU3	22.4	1.1	0.64	0.58	14
PU3M		1.3	0.71	0.55	31
PU4	25.8	1.2	0.28	0.23	17
PU4M		1.6	0.89	0.56	35
PU5	31.5	1.5	0.51	0.34	21
PU5M		2.4	0.96	0.40	55

$\bar{d}_2$ — equivalent diameter of hard domain aggregate, STD — standard deviation CV($\bar{d}_2$) variability coefficient of $\bar{d}_2$ and $V_{HS\ AFM}$ — volume fraction of hard domain aggregate calculated basing on AFM images.

An increase in the participation of rigid segments brings about an increase in the size and percentage per volume of hard domain agglomerates. A comparison between urea-urethane elastomers of the same molar composition with or without the addition of a modifier makes it possible to state that the introduction of this type of modification favors the phase separation process, resulting in an increased size of the hard domain agglomerates of the materials.

The change in the size and volume of the hard domain agglomerates of urea-urethane elastomers can be explained based on the analysis of the phase separation degree in the materials. For this reason, infra-red spectroscopy was performed, and the respective spectra are shown in Fig. 4.

Bands from the stretching vibrations of carbonyl groups present in urea and urethane bonds were used to analyze the phase separation degree. In Fig. 5, the band sections are shown, including the so-called multiplet bands from the stretching vibrations of carbonyl groups of urea-urethane elastomers. In the range between 1800 and 1570 cm^{-1} there are several separate signals.

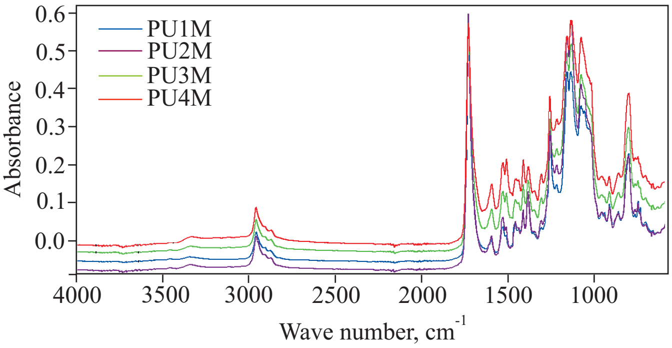

Fig. 4. FT-IR spectra of PUR with a modifier and different rigid segment contents

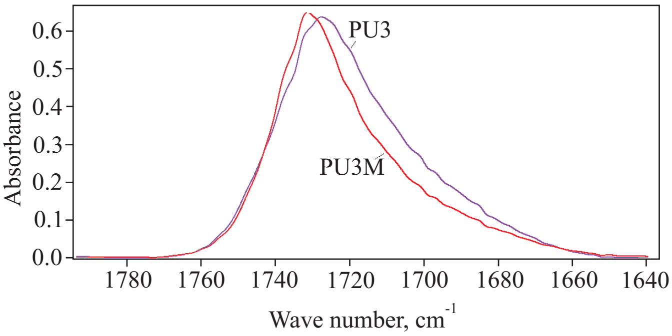

Fig. 5. FT-IR spectrum of PU3 and PU3M in the range between 1760 and 1680 cm^{-1}

The information on storage bands from which multiplet bands were formed (in the range between 1800 and 1640 cm^{-1}) was obtained on the basis of these bands' distribution using the Gauss function used to describe solid materials. The analysis was carried out with the use of the OMNIC 7.3 program. Within the multiplet bands there are bands originating from the vibrations of C=O urea bonding groups bounded with hydrogen bonds occurring in the range between 1630 and 1686 cm^{-1} and bands from unbounded groups ranging between 1700 and 1691 cm^{-1}. The second group constitutes bands originating from the vibrations of C=O urethane bonding groups bounded with hydrogen bonds in the range between 1726 and 1706 cm^{-1} and from unbounded groups ranging between 1738 and 1729 cm^{-1}.

Phase separation degree (*DPS*), determined by the participation of hydrogen bonding in the hard phase, was calculated with formula (4). Moreover, the percentage per volume of hard segment vibrations bounded with hydrogen bonds was calculated with formula (5).

The calculation results are listed in Table 3.

Phase separation degree describes the share of hard segments mutually bounded with hydrogen bonds. In urea-urethane elastomers from groups PUx and PUxM, the phase separation degree decreases together with the growth of the rigid segments' participation in their macromolecules. The greater the share of rigid segments, the lower the participation of the hydrogen bonding linking urea and the urethane groups. The dependence of the change of the phase separation degree (*DPS*) and the average equivalent diameter of hard domain agglomerates, calculated based on AFM images of PUR sections, are presented in Fig. 6. The presented relationships can be described with linear functions; the larger the agglomerates of hard domains, the lower the degree of hard phase separation. In the PUxM series with a modifier, the degree of phase separation is higher than in PUx.

Table 3. Calculation results of carbonyl hydrogen-bonding index (*R*), phase separation degree (*DPS*) and hydrogen bounded hard segments volume ($V_{FTIR\ HS}$)

PUR materials	*R*	*DPS*, %	$V_{FTIR\ HS}$, %
PU1	1.53	60	8.5
PU1M	4.19	81	11.4
PU2	1.34	57	9.5
PU2M	3.52	78	12.9
PU3	1.14	53	11.9
PU3M	2.70	73	16.4
PU4	1.07	52	13.4
PU4M	2.55	72	18.6
PU5	1.02	45	14.2
PU5M	2.23	69	21.7

The dependence between the average equivalent diameter of the hard domain agglomerates, calculated basing on AFM images of PUR and the volume percentage of the agglomerates, calculated on the basis of the infra-red spectroscopy results, is shown in Fig. 7. The higher volume percentage of hydrogen-bounded rigid segments in the PUxM series with a modifier is the result of differences within the *DPS*. The observed differences in the size between agglomerates of the hard domains of both PUR groups result from the change of the pH environment of the reaction with the acid groups caused by the introduction of a modifier in the form of an ester copolymer. In the case of PU5M, to which a modifier was added, a phase inversion took place, which is indicated by the volume percentage of hard domain agglomerates, calculated based on AFM images of the morphology of these materials.

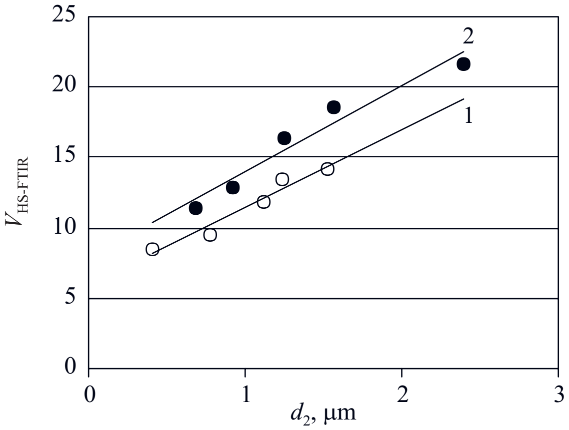

Fig. 7. Relationship between the volume of hydrogen-bounded rigid segments ($V_{HS\text{-}FTIR}$) and the average equivalent diameter of hard domain agglomerates, calculated based on AFM images of PUR: 1) without modifier and 2) with modifier

The selection of polyurethanes intended for specific applications requires a profound knowledge of the relationships between their chemical constitution, molecular structure and properties; that is why these relationships are analyzed in many studies. In most studies, the relationships between the mass and volume content of the hard segments are studied. More rarely, the relationships between the sizes of hard domains and different properties of the materials are studied. On occasion, the size of the hard domains was determined on the basis of the results of a SAXS analysis [44—56]. The obtained relationships between the properties and the size of the hard domains changed in a non-monotonic way, which made difficult to estimate the properties of new materials. How-

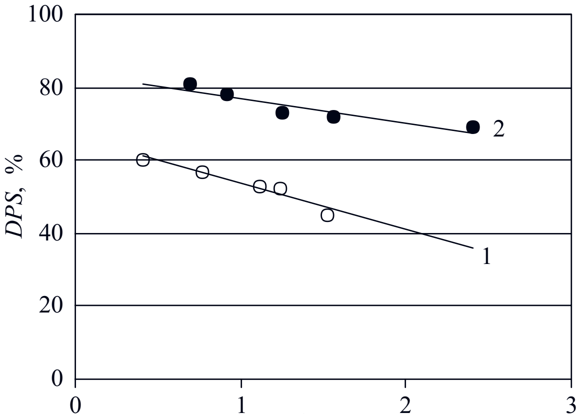

Fig. 6. Relationship between the phase separation degree (DPS) and the average equivalent diameter of the hard domain agglomerates of PUR: 1) with modifier and 2) without modifier

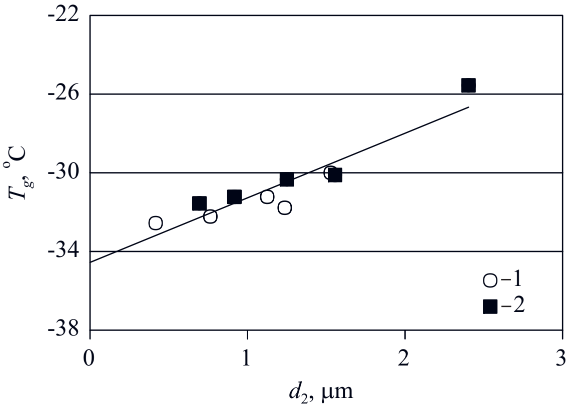

Fig. 8. Relationship between the average equivalent diameter of the hard domain agglomerates and the glass transition temperature of the soft phase in PUR: 1) without modifier and 2) with modifier

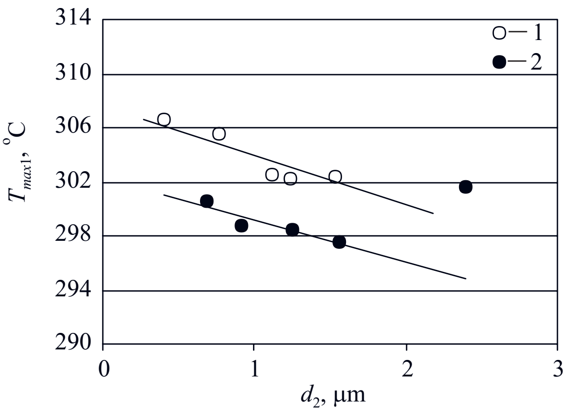

Fig. 9. Relationship between the average equivalent diameter of the hard domain agglomerates and the temperature of the maximum degradation temperature of the rigid segments in PUR: 1) without modifier and 2) with modifier

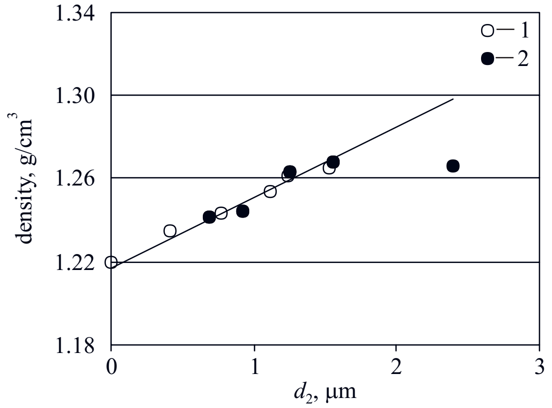

Fig. 10. Influence of the equivalent diameter of hard domain agglomerates on density in PUR: 1) without modifier and 2) with modifier

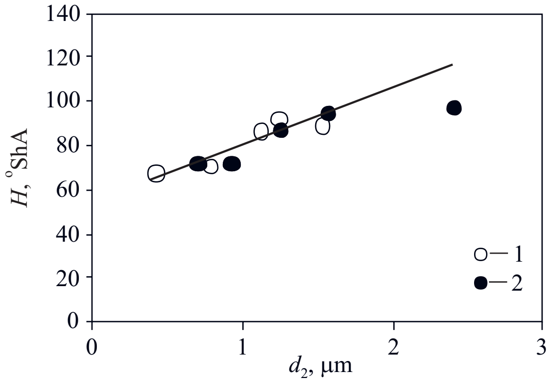

Fig. 11. Influence of the equivalent diameter of the hard domain agglomerates on the hardness (H) in PUR: 1) without modifier and 2) with modifier

ever, sometimes neither the change of the percentage per volume participation of the rigid segments nor the change of the size of the hard domains provides any explanation of the changes in the polyurethanes' properties.

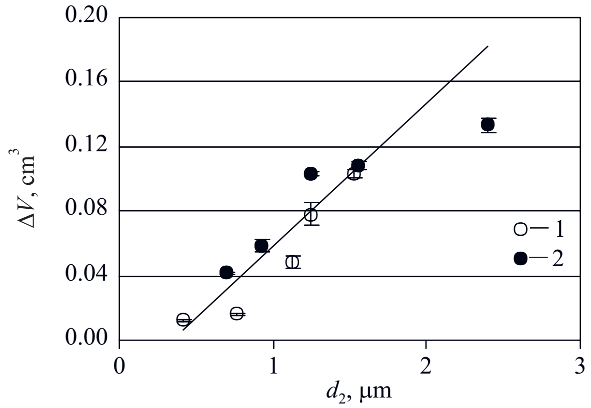

Fig. 12. Influence of the equivalent diameter of the hard domain agglomerates on the abrasion wear (ΔV) in PUR: 1) without modifier and 2) with modifier

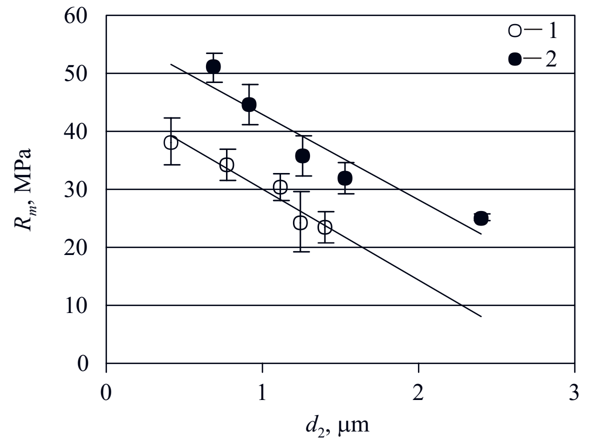

Fig. 13. Influence of the equivalent diameter of the hard domain agglomerates on the tensile strength (R_m) in PUR: 1) without modifier and 2) with modifier

For this reason, a relationship analysis was proposed between the average equivalent diameter of the hard domain agglomerates and selected properties of polyurethanes. Among the analyzed properties are parameters describing the structure indirectly, *i.e.* the glass transition temperature of the soft phase (Fig. 8) and the maximum degradation temperature of the rigid segments of the analyzed PUR (Fig. 9), as well as physico-mechanical properties such as density (Fig. 10), hardness (Fig. 11), abrasion wear (Fig. 12), tensile strength (Fig. 13) and strain (Fig. 14). The selected examination methods for the two groups of urea-nitrile polyurethanes helped to estimate their usability for applications in various elements of industrial machines.

There is no doubt that the important features of PUR, including hardness, abrasion wear, tensile strength, permanent strain at break, glass transition temperature of the soft phase, temperature of maximum degradation speed of the hard phase and density depend in a linear way on the average equivalent diameter of the hard domain agglomerates. Only in the case of abrasion wear

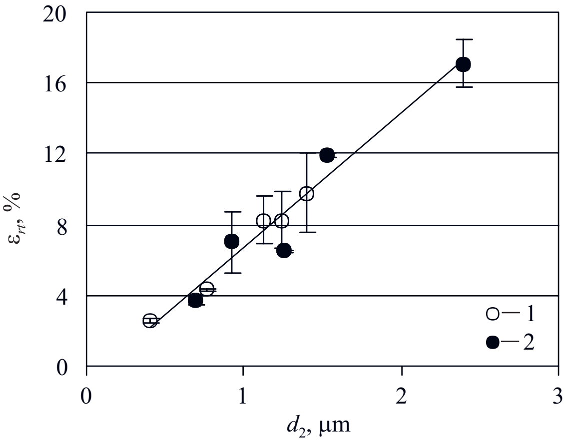

Fig. 14 Influence of the equivalent diameter of the hard domain agglomerates on the strain at break (ε_{rt}) in PUR: 1) without modifier and 2) with modifier

there can be observed some deviation from the straight line describing the dependence of this PUR feature on the size of hard domain agglomerates.

In the analyzed materials, an increase in the diameter of agglomerates is, among other reasons, the result of the increase in participation of the hard PUR segments. However, the relationships between the examined physico-mechanical properties and the participation of the hard segments are not linear functions.

The influence of the equivalent diameter of the hard domain agglomerates on the tensile strength (Fig. 12) can be described with a linear function but is different for each type of urea-urethane elastomer. In the case of PUR with and without a modifier, the lines describing this relationship are mutually parallel. PUR samples with a modifier added show higher strengths than those without the modifier. The changes in the strength of these PUR samples in function d_2 are similar to the changes in the phase separation degree (Fig. 7). This comparison makes possible to state that both the size of hard domains and the inter-molecular interaction level between the hard segments affect the tensile strength. The more hydrogen bonds are linking the hard segments together, the higher the tensile strength of the urea-urethane elastomers will be. The inversion of phases in PU5M unfavorably affected its abrasion wear resistance and permanent strain but favorably influenced the tensile strength.

It was stated that the introduction of a dispersing agent causes changes in the phase separation process and results in the formation of structures with different thermal characteristics. Within the framework of the study, the temperature changes of the maximum degradation speed of the rigid segments (T_{max1}) were analyzed as a function of the size of the hard domain agglomerates. The growth of the size of the hard domain agglomerates is connected with the fall of temperature T_{max1}. Increasing participation of flexible segments in the volume of the hard domain agglomerates, along with an increase in their diameter provide an explanation of this change.

CONCLUSIONS

Within the framework of this work and based on the analysis of AFM images of the domain structure of two groups of urea-nitrile urethanes with different macromolecule segments, the relationships were analyzed between the physico-mechanical properties, the thermal characteristics and the parameters describing the hard domain agglomerates of these materials. Many features of the two groups of urea-urethane elastomers changed in a linear way as the diameter of the hard domain agglomerates increased. Owing to the recognition of the nature of these relationships, for technical applications, it will be possible to select the desired type of polyurethane from the analyzed group. In the manufacture of products from urea-urethane elastomers, the recognized relationships can serve as a basis for the elaboration of technical control conditions.

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- *I. Steinborn-Rogulska, G. Rokicki* — Polikondensacja w stanie stałym — metoda otrzymywania polimerów o dużym ciężarze cząsteczkowym. Cz. I. Parametry wpływające na przebieg procesu (*j. ang.*)
- *K. Kelar, J. Olejniczak, K. Mencel* — Modyfikacja poliamidu 6 haloizytowymi nanorurkami
- *I. Legocka, E. Wierzbicka, T. M. J. AL-Zahari, O. Osawaru* — Wpływ modyfikowanego haloizytu na strukturę, właściwości cieplne i mechaniczne poliamidu 6
- *A. Karaszewska, J. Bucheńska* — Poliestrowe protezy naczyniowe — antybakteryjne i atrombogenne biomateriały. Cz. II. Wpływ dwuetapowej modyfikacji poliestrowych protez naczyniowych na wybrane właściwości fizykochemiczne, mechaniczne oraz mikrobiologiczne
- *B. Grabowska, M. Szucki, J. S. Suchy, S. Eichholz, K. Hodor* — Degradacja termiczna materiału na bazie celulozy stosowanego do budowy układów wlewowych do odlewów żeliwnych (*j. ang.*)
- *A. Iwan, L. Moroń* — Badanie przewodnictwa elektrycznego poliazometin o właściwościach ciekłokrystalicznych
- *W. Baranowski, K. Werner* — Analiza rozwoju pęknięć i lokalnego odkształcania rur z polietylenu