Phase Structure and Thermal Stability of Crosslinked Polyurethane Elastomers based on Well-Defined Prepolymers

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ABSTRACT: Taking advantage of the DSC method, general procedures were presented for qualitative and quantitative evaluation of the phase separation degree and the crystalline phase content in polyurethane elastomers with well-defined structures. Those elastomers were obtained not only in a typical one-step method but also in the prepolymer method with the use of urethane oligomers with controlled molecular weight distribution (MWD). Prepolymers with well defined chain structures and narrow distributions of their molecular weights (MWD) $\overline{M}_w/\overline{M}_n = 1.1$–1.3 were produced in a multistage method, i.e., in step-by-step polyaddition of 2,4- and 2,6-TDI with polyoxyethylenediols or with polycaprolactonediols of varied molecular weights. Isocyanate oligomers obtained at individual stages were then crosslinked with triethanolamine, whereas hydroxyl-terminated oligomers were crosslinked with 4,4′,4″-triphenylmethane triisocyanate (Desmodur RE). The obtained polyurethane elastomers were found to be char-

acterized by the presence of five phases: soft phase consisted of flexible polyol-type segments, crystalline phase made of soft segments, crystalline and amorphous hard phase made of hard segments, and intermediate phase, which was a composition of the soft and hard segments. The polyurethanes obtained out of prepolymers with defined MWD were characterized by better phase separation of the soft segments and increased structural order inside the hard phase as well as by better thermal stability than polyurethanes obtained from the typical one-step method. The structural effects were also discussed on the thermal properties of the synthesized elastomers as analyzed by the TG and DTA methods. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1464–1474, 2007

Key words: TDI; polyurethanes; evaluation methods for phase separation degree; differential scanning calorimetry; thermogravimetric analysis

INTRODUCTION

On the background of numerous polyurethane plastics (PU) and their numerous applications, segmented PU elastomers stand out as high-quality engineering plastics and coating materials. Supermolecular structures of those polymers define their mechanical and thermal properties which are critical for their applications in the automotive industry (machine elements), in civil engineering (anticorrosive coatings), and in medicine (endoprostheses).

It is well-known from the state of art that most elastomers, i.e., also polyurethane elastomers, have their basic chains organized in hard and soft segments. Hard segments are made of urethane or urea compounds, derived from isocyanates and low-molecular-weight chain extenders like water, glycols, and diamines. Flexible segments, on the other hand, are made of ether or ester groups, which have been derived from polyol feedstocks.[1,2] The hard segments, which are

polar and high-melting, interact strongly with each other by numerous hydrogen bonds between urethane and urea groups. Those segments will not mix at the temperature below 120°C with less polar and fusible flexible segments. Considerable diversification in polarity is responsible for the fact that hard segments separate from flexible segments and form the so-called hard domains. Hence, the polymer becomes a polyphase system in the microscale. The urethane groups, which link the hard segments and the flexible segments together by means of both covalent bonds and hydrogen bonds, are usually arranged at the border line between domains. However, the microphase separation is not complete and hence some hard segments can be found dispersed within the domains of soft segments to form the intermediate phase.[3]

Phase separation degree within a PU material is dependent on many factors: types of diisocyanate and polyol employed to produce prepolymers,[4,5] type of chain extending compound,[6] type of polyfunctional compound used in the crosslinking process,[7,8] sizes of hard and soft segments, method of synthesis, and at the final stage of the crosslinking process—on temperature and mechanical method adopted to mold the final product.

The hard and soft phase of PU have the crystalline structures in most cases. Their amorphous parts make the amorphous phases and intermediate phase.[2,9–12]

Thermal stability of PUs is also defined by their supermolecular structures. Some heat needs to be provided initially to melt the crystalline phase and only further heating the polymer up above 120°C will result in changes in its chemical structures—cleavage of bonds and degradation of structural segments.[13–17] Thermal stability of a PU elastomer is also affected by type of raw materials,[18] soft and hard segments contents,[19] density of crosslinking,[13,20] type of crosslinking bonds, type of chain extension, and method utilized for the production of that elastomer.[1]

It should be stated, in general, that the segmented structure of PU creates favorable conditions for phase separation and thus it exerts the advantageous influence on thermal and physical–mechanical properties of elastomers. There is still a problem of finding relations between the structural features and the properties. This task is very hard since the chemical structures of PUs are strongly diversified, and the relations sought should cover the chemical structures as well as strongly diversified size of macromolecules and the supermolecular structures of phases which are partly miscible only.

Having considered the above-mentioned aspects, we suggested relatively simple procedures in this study—based solely on DSC measurements—for qualitative and quantitative morphological evaluation of supermolecular structures which can be found in polyurethane elastomers. Special attention was paid to the applicability of those procedures when evaluating the impacts of the molecular weights and molecular weight distribution in the synthesized polyurethane prepolymers on the phase structures of elastomer items molded therefrom. For our research, we used polyurethanes with well-defined chemical structures, which had been synthesized earlier in our originally developed method.[21–23] The more regular structure can be obtained by the prepolymer chain growth control. To achieve this, polyurethane prepolymers should be synthesized in the excess of one of the monomers. Isocyanate prepolymers or urethane-hydroxyl prepolymers were reacted correspondingly with selected polyols or with 2,4-TDI and 2,6-TDI. The excess of the used monomer (diisocyanate or diol, respectively) have to be removed from the reaction system. The prepolymers synthesized in our experiments had well-defined structures and narrow MWDs. Finally, such long structures of urethane oligomers were subjected to crosslinking by means of a trifunctional reacting substance, triethanolamine or 4,4′,4″-triphenylmethane triisocyanate, which made it possible to produce new elastomers.

Irrespective of the problems presented earlier, improved thermal stability and mechanical performance could be expected as the positive consequence of the regular structures of the so synthesized elastomers. We think it is advisable to verify that hypothesis and hence, within this work and on the basis of obtained structural data, the findings from the thermal tests carried out with the use of TG and DTA methods were also presented. On the other hand, the structural effects in the synthesized elastomers on their mechanical properties turned out so complex that they need to be dealt with separately.
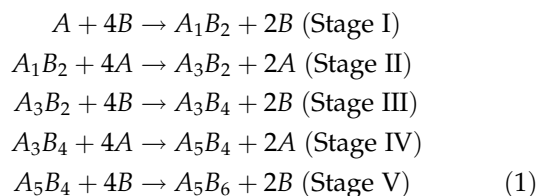
EXPERIMENTAL

Raw materials and reagents

- 2,4- and 2,6-tolylene diisocyanate (TDI): a commercial product (Aldrich) was used in the study. It was a mixture of 2,4-TDI and 2,6-TDI isomers at the ratio of 80 and 20%, respectively.
- Polyoxyethylene glycols (POG) with $\overline{M}_n = 200$, 300, 400, 600, and 1000 g/mol, from Aldrich. The glycols were dried under vacuum in N_2, at 110°C, during 2 h.
- Polycaprolactone diols (PCD) with $\overline{M}_n = 530$ and 1250, from Aldrich.
- Triethanolamine (TEA) (pure), from POCh-Gliwice, Poland.
- Desmodur RE (D-RE) (4,4′,4″-triphenylmethane triisocyanate), from Bayer A.G., Germany.

Synthesis of urethane oligomers with controlled MWD

The method for the production of urethane oligomers with controlled distribution of molecular weights has already been presented in our earlier reports.[21–23] Those oligomers were obtained in a step-growth polyaddition process, which was composed of a few stages and in which excessive amounts of one or the other monomers were used at individual stages. The process followed the scheme as below:

$$A + 4B \rightarrow A_1B_2 + 2B \text{ (Stage I)}$$
$$A_1B_2 + 4A \rightarrow A_3B_2 + 2A \text{ (Stage II)}$$
$$A_3B_2 + 4B \rightarrow A_3B_4 + 2B \text{ (Stage III)}$$
$$A_3B_4 + 4A \rightarrow A_5B_4 + 2A \text{ (Stage IV)}$$
$$A_5B_4 + 4B \rightarrow A_5B_6 + 2B \text{ (Stage V)} \quad (1)$$

where A is the polyol component and B is the isocyanate component.

The objective of using a considerable excess of one of monomers was to restrict the molecular weight and to obtain possibly a monodisperse polymer. Unconverted excess monomers are undesirable because of their disadvantageous effects on the properties of products. Hence, monomers A or B were removed from the reaction mixture after every step by means of extraction.

And such purified intermediates were then employed in further polyaddition steps.

Synthesis of polyurethane

Prepolymer method

To produce cast elastomers, the synthesized urethane oligomers with —NCO terminal groups were cured with the use of TEA, while hydroxyurethane oligomers—with the use of Desmodur RE. All the crosslinking reactions were carried out at the equimolar ratio of —NCO and —OH groups. After thorough mixing of components and deaeration under reduced pressure (about 270 h Pa), the gelating mixture was introduced to closed PTFE molds provided with silicone separators. The molds were then kept at 25°C over 24 h. The test pieces were pulled out of molds and were subjected to seasoning at ambient temperature over 14 days at minimum. The obtained PUs were marked with symbols, e.g. PU-I-200 (2), where the Roman numeral indicated the stage in which the prepolymer material utilized for the production of polyurethane had been synthesized, the Arabic numeral indicated the molecular weight of polyol taken for the synthesis, and the numeral in brackets, i.e. (2), denoted the prepolymer-based method for the synthesis of PU (Table I). The sample codification adopted in that study corresponds to that presented in our earlier paper.[23] The only difference is that the letter "b" is omitted since only those prepolymers were subjected to chain extension from which the unconverted monomers A or B had earlier been extracted.

One-step method

PUs were synthesized starting from the same ratio of raw materials as employed for the prepolymer method. All components were mixed thoroughly, then the composition was degassed and poured into prepared PTFE molds with silicone separator plates, which gave adequate shapes to the test pieces. The hardening process was realized at room temperature. The obtained PUs were marked with analogous symbols, e.g. PU-I-200 (1), where the numeral in brackets, i.e. (1), referred the sample to the one-step method (Table I).

For example, the polyurethane PU-II-400 (2) derived from the oligomer A_3B_2, e.g., II-400, and Desmodur RE in the prepolymer method, has the corresponding polyurethane PU-II-400 (1) that has been synthesized in the reaction of 3 mol of component A, 2 mol of component B (TDI), and 2/3 mol of Desmodur RE.

The measured amounts of raw materials, i.e., TDI, selected polyol and crosslinking agent, were charged to a glass vessel provided with a vacuum connection. After thorough mixing, the composition was deaerated and then test pieces were formed.

DSC method

A Mettler Toledo type 822[e] differential calorimeter (DSC) with Star[e] System software was employed to analyze thermal properties of cured PUs. The instrument was calibrated with the use of Zn and In standards.

The samples (0.0010 g) were placed in aluminum crucibles. These were weighed to the nearest 0.00001 g and placed in the measuring chamber. Initially, the

TABLE I
Specifications for the Obtained Polyurethanes

| Type of polyol (A) and its M_n | Prepolymer method | One-step method | | |
	Symbol of polyurethane sample	Molar ratio of raw materials $A : B$	Symbol of polyurethane sample	Type of chain extender
POG 200	PU-I-200 (2)	1 : 2	PU-I-200 (1)	TEA
	PU-II-200 (2)	3 : 2	PU-II-200 (1)	D–RE
POG 300	PU-II-300 (2)	3 : 2	PU-II-300 (1)	D–RE
	PU-IV-300 (2)	5 : 4	PU-IV-300 (1)	D–RE
POG 400	PU-II-400 (2)	–	–	D–RE
	PU-IV-400 (2)			D–RE
POG 600	PU-II-600 (2)	–	–	D–RE
	PU-IV-600 (2)			D–RE
POG 1000	PU-I-1000 (2)	–	–	TEA
	PU-II-1000 (2)			D–RE
	PU-III-1000 (2)			TEA
	PU-IV-1000 (2)			D–RE
PCD 530	PU-I-530 (2)	1 : 2	PU-I-530 (1)	TEA
	PU-III-530 (2)	3 : 4	PU-III-530 (1)	TEA
	PU-V-530 (2)	5 : 6	PU-V-530 (1)	TEA
PCD 1250	PU-I-1250 (2)	–	–	TEA
	PU-II-1250 (2)			D–RE
	PU-III-1250 (2)			TEA
	PU-IV-1250 (2)			D–RE

samples were heated up to 250°C at the rate of 10°/min to eliminate stresses, which possibly could be left after the molding process, and then they were cooled down to −80°C. After another 10 min, their progressive heating was initiated at the rate of 10°/min. The measurements were taken within the temperature range of from −80 to 250°C, in the environment of nitrogen, which was passed at the rate of 30 cm^3/min.

Temperatures for phase transitions (T_m, T_g) and the values for enthalpy of fusion ΔH_m were found by means of a generally known method. In Table II, the values were also provided for: initial temperature (T_{onset}), maximum temperature (T_{max}), and final temperature (T_{end}) for individual transitions, as had been read out from thermograms. Heats of fusion for hard phase and for soft phase were referred to 1 g of that phase in the sample under investigation.

Degrees of crystallinity for hard and soft phases were calculated from the equations:

$$W_{c,h} = \frac{\Delta H_{m,h}}{\Delta H_{m,100\%}} \times 100\% \qquad (2)$$

$$W_{c,s} = \frac{\Delta H_{m,s}}{\Delta H_{m,100\%}} \times 100\% \qquad (3)$$

where $W_{c,h}$ is the degree of crystallinity for hard phase (%), $W_{c,s}$ the degree of crystallinity for soft phase (%), $\Delta H_{m,h}$ the enthalpy of melting for hard phase (J/g), $\Delta H_{m,s}$ the enthalpy of melting for soft phase (J/g), $\Delta H_{m,100\%}$ the enthalpy of melting for a completely crystallized homopolymer within a given block (J/g).

For hard segments from triethanoloamine and TDI $\Delta H_{m,100\%} = 146.1$ J/g.[24]

For hard segments derived from Desmodur RE and from TDI $\Delta H_{m,100\%} = 163.6$ J/g. This value was determined according to the method described by Pyda et al.[25] For polyols PCD and POG, these values equal to: $\Delta H_{m,PCD, 100\%} = 135$ J/g[26] and $\Delta H_{m,POG,100\%} = 182.5$ J/g,[27] respectively.

The heat capacity changes during glass transition T_g were calculated according to the following equation:[28]

$$\Delta C_p = \frac{Q_k - Q_p}{m\beta} \times w \qquad (4)$$

where ΔC_p is the heat capacity changes for a given segment in T_g, (J/g deg), Q_k the heat flow at the end of transition, (mW), Q_p the heat flow at the beginning of transition (mW), m the mass of sample (mg), β the heating rate (deg/s), w the mass fraction of a given block in the polymer, as calculated for PUs obtained from the prepolymer method on the basis of GPC findings, and for PUs obtained from the one-step method on the basis of material balance (%).

Phase separation degrees of soft blocks were calculated from the formula (3), while the soft phase quan-

TABLE II
Specifications of Phase Transition Temperatures for the Obtained Polyurethanes

| Symbol of PU sample (as per Table 1)	$T_{g,s}$ (°C)	$T_{m,s}$ (°C)				$T_{g,ip}$ (°C)	$T_{g,h}$ (°C)	$T_{m,h}$ (°C)			
		T_{onset}	$T_{max.}$	T_{end}	$\Delta T_{m,s}$			T_p	T_{max}	T_{end}	$\Delta T_{m,h}$
PEG	−66.38	–	–	–	–	–	–	–	–	–	–
PU-I-200 (2)	−48.23	–	–	–	–	–	62.22	206.39	209.39	216.04	9.65
PU-II-200 (2)	−48.95	–	–	–	–	28.65	–	188.70	191.17	208.28	19.58
PU-II-300 (1)	−51.45	–	–	–	–	8.86	–	172.72	178.19	201.62	28.90
PU-IV-300 (1)	−54.31	–	–	–	–	5.65	–	198.58	207.37	219.43	20.85
PU-II-300 (2)	−55.88	–	–	–	–	15.05	–	176.12	179.57	195.19	19.07
PU-IV-300 (2)	−58.86	–	–	–	–	15.97	–	191.37	195.60	214.57	23.20
PU-II-400 (2)	−61.22	–	–	–	–	−9.24	21.25	202.36	207.14	222.43	20.07
PU-IV-400 (2)	−63.97	–	–	–	–	−4.14	81.85	182.29	192.44	216.51	34.22
PU-II-600 (2)	−62.55	–	–	–	–	−31.26	–	182.29	187.42	215.61	33.32
PU-IV-600 (2)	−62.62	–	–	–	–	−13.67	61.28	–	–	–	–
PU-II-1000 (2)	−63.78	20.89	23.49	27.43	6.54	−40.92	–	–	–	–	–
PU-IV-1000 (2)	−64.24	–	–	–	–	−35.94	56.66	–	–	–	–
PCD	−65.11	–	–	–	–	–	–	–	–	–	–
PU-I-530 (1)	−61.98	–	–	–	–	9.84	–	205.42	208.47	227.32	21.90
PU-III-530 (1)	−63.67	–	–	–	–	−7.53	–	I 197.82	214.61	226.18	28.36
								II 226.18	229.03	247.25	21.07
PU-V-530 (1)	−62.13	–	–	–	–	−5.49	–	I 207.10	214.93	224.12	17.02
								II 224.12	226.65	241.38	17.26
PU-I-530 (2)	−62.65	–	–	–	–	12.41	–	214.76	219.75	238.46	23.70
PU-III-530 (2)	−63.88	–	–	–	–	5.83	–	220.13	221.27	225.54	5.41
PU-V-530 (2)	−63.88	–	–	–	–	1.87	–	196.23	214.30	223.49	27.26
PU-II-1250 (2)	−60.16	–	–	–	–	−36.97	–	–	–	–	–
PU-IV-1250 (2)	−64.71	31.96	38.61	43.21	11.25	−40.54	–	–	–	–	–
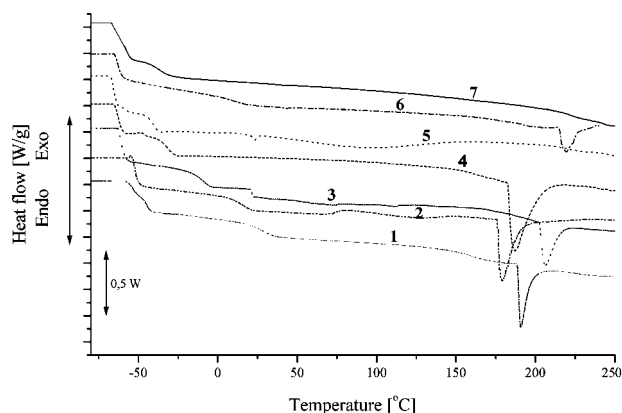
Figure 1 DSC thermograms of PU elastomers based on well-defined prepolymers obtained at the second stage with the use of different glycols (as per Table I). 1 – PU-II-200 (2); 2 – PU-II-300 (2); 3 – PU-II-400 (2); 4 – PU-II-600 (2); 5 – PU-II-1000 (2); 6 – PU-II-530 (2); 7 –PU-II-1250 (2).

tity outside the soft phase was calculated from the eq. (4):[27,29]

$$SR_s = \frac{\Delta C_{p,s}}{\Delta C_{p,a}} \times 100\% + W_{c,s} \quad (5)$$

$$SR_h = \frac{\Delta C_{p,h}}{\Delta C_{p,a}} \times 100\% + W_{c,h} \quad (6)$$

where SR_s is the phase separation degree of soft segments (%), SR_h the phase separation degree of hard segments (%), $\Delta C_{p,s}$ the heat capacity changes of soft segment during glass transition (J/g deg), $\Delta C_{p,a}$ the heat capacity changes during glass transition T_g for a completely amorphous homopolymer within a given block (J/g deg).

The values of $\Delta C_{p,a}$ of the hard segments were determined by extrapolation of $\Delta C_p = f(\Delta H_m)$ according to the method described by Pyda et al.[25] $\Delta C_{p,a,\text{TDI/TEA}}$ = 0.114 J/g deg, $\Delta C_{p,a,\text{TDI/D-RE}}$ = 0.139 J/g deg. The values of $\Delta C_{p,a}$ for POG and for PCD they amount to $\Delta C_{p,a,\text{POG}}$ = 0.129 J/g deg and $\Delta C_{p,a,\text{PCD}}$ = 0.450 J/g deg,[27] respectively.

The weight percentages for a given block in the intermediate phase as well as in the hard and soft phases were calculated according to the following equations:[30]

$$w_{\text{ip},h} = w_{p,h} - \frac{SR_h \, w_{p,h}}{100\%} \quad (7)$$

$$w_{\text{ip},s} = w_{p,s} - \frac{SR_s \, w_{p,s}}{100\%} \quad (8)$$

$$w_{s,s} = \frac{SR_s \, w_{p,s}}{100\%} \quad (9)$$

$$w_{h,h} = \frac{SR_h \, w_{p,h}}{100\%} \quad (10)$$

where $w_{\text{ip},h}$ is the weight percentage of hard segments in intermediate phase (%), $w_{\text{ip},s}$ the weight percentage of soft segments in intermediate phase (%), $w_{s,s}$ the weight percentage of soft segments in soft phase (%), $w_{h,h}$ the weight percentage of hard segments in hard phase (%), $w_{p,h}$ the weight percentage of hard segments in polymer (%), and $w_{p,s}$ is the weight percentage of soft segments in polymer (%).

The total of shares for hard blocks and soft blocks in the intermediate phase makes the share of the intermediate phase ($w_{p,\text{ip}}$) in the polymer:

$$w_{p,\text{ip}} = w_{\text{ip},h} + w_{\text{ip},s} \quad (11)$$

Method for thermal stability measurements

Thermal performance of PUs was investigated with the use of a F. Paulik, J. Paulik, L. Erdey derivatograph (Hungary).

The samples of about 200 mg were used in our tests. One determination took 100 min to complete and the temperature was gradually increased from 20 to 800°C. The DTA, TG, and DTG curves were recorded. The DTA method was sensitive to 1/10°. The measurements were taken in the environment of air.

RESULTS AND DISCUSSION

Phase structure of polyurethane elastomers

The examples of DSC thermograms for studied PUs are presented in Figures 1–3. Thermal characteristics were provided in Table II for the studied samples, while changes in heat capacity ($\Delta C_{p,s}$, $\Delta C_{p,h}$) at T_g, enthalpies of melting ($\Delta H_{m,s}$, $\Delta H_{m,h}$), phase separation degrees (SR_s, SR_h) as well as degrees of crystallinity ($W_{c,h}$, $W_{c,s}$) were calculated from the relations (2–6)
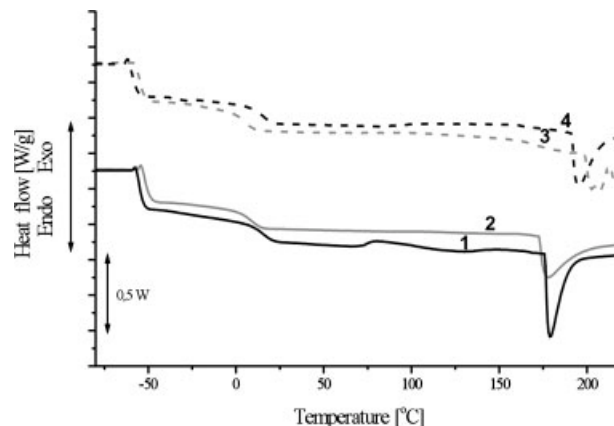

Figure 2 DSC thermograms of PU based on well-defined prepolymers and obtained in a one-step method with the use polyoxyethylene glycol (Table I). 1 – PU-II-300 (2); 2 – PU-II-300 (1); 3 – PU-IV-300 (1); 4 – PU-IV-300 (2).
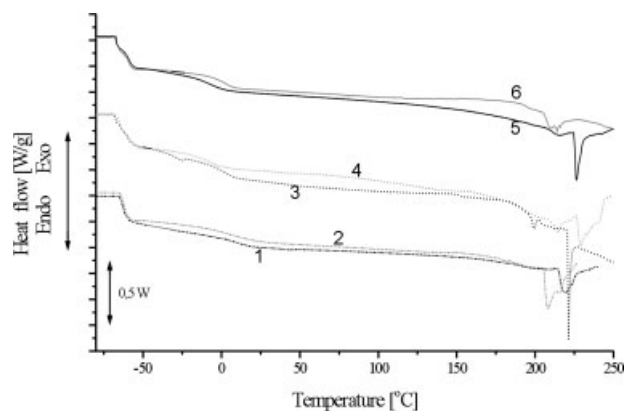
Figure 3 DSC thermograms of PU based on well-defined prepolymers and obtained in a one-step method with the use polycaprolactone diol (Table I). 1 – PU-I-530 (2); 2 – PU-I-530 (1); 3 – PU-III-530 (2); 4 – PU-III-530 (1); 5 – PU-V-530 (2); 6 – PU-V-530 (1).

and collected in Table III. Based on known values of SR_s and SR_h as well as weight percentages for individual blocks within the polymer ($w_{p,s}$, $w_{p,h}$), the eqs. (7–11) were then utilized to calculate weight percentages for individual blocks in soft phase ($w_{s,s}$), in intermediate phase ($w_{ip,s}$, $w_{ip,h}$) and in crystalline phase ($w_{h,h}$), and finally the share of intermediate phase in the polymer ($w_{p,ip}$). The results from those calculations were shown in Table IV, and additionally they were pre-

sented graphically for elastomer PU-IV-400 (2) in the form of diagram (Fig. 4).

(2) or (3) clearly outlined glass transition areas can be observed in the low-temperature range of DSC thermograms. The glass transition of soft segments ($T_{g,s}$) is visible in the temperature region of from −65°C to −48°C, which moves toward lower temperatures when $\overline{M}_n$ of polyol increases (Fig. 1, Table II). The values of T_g for POG and PCD ($T_{g,POG} = -67$°C, $T_{g,PCD} = -64$°C) can be found in reports.[27] The T_g values of the pure POG and PCD soft segments were determined by means of DSC ($T_{g,POG} = -66.38$°C, $T_{g,PCD} = -65.11$°C). $T_{g,s}$ was usually lower for higher values of $\overline{M}_n$ what can be explained by stiffening of polyol chain ends in a soft segment by chemical bonds with hard urethane blocks.

Our investigations suggest that $T_{g,s}$ usually declines with the increase in the length of a urethane segment within a series of PUs produced from prepolymers. That can make a prove for higher purity of soft phase.

Another glass transition area ($T_{g,ip}$) can be observed within the temperatures of from −41°C to 35°C and that probably corresponds to relaxation of mixed amorphous intermediate phase (soft and hard segments). This transition is usually accompanied by a small endothermic peak related to relaxation of enthalpy in the crystalline part of those segments.[31]

A third glass transition region can be seen in the elastomer samples denoted as PU-I-200, (2) PU-II-400, (2)

TABLE III
Specifications for Values of Heat Capacity Changes for Hard, Soft Segments, and Intermediate Phase ($\Delta C_{p,h}$, $\Delta C_{p,s}$, $\Delta C_{p,ip}$) during Glass Transition (T_g), Enthalpy of Melting for Hard and Soft Phases ($\Delta H_{m,h}$, $\Delta H_{m,s}$), Degrees of Crystallinity for Hard and Soft Segments ($W_{c,h}$, $W_{c,s}$) as well as Phase Separation Degrees for Hard and Soft Segments (SR_h, SR_s)

Symbol of PU sample (as per Table 1)	$\Delta C_{p,s}$ (J/g K)	$\Delta H_{m,s}$ of soft phase (J/g)	$W_{c,s}$ of soft phase (%)	SR_s	$\Delta C_{p,ip}$ (J/g K)	$\Delta C_{p,h}$ (J/g K)	$\Delta H_{m,h}$ of hard phase (J/g)	$W_{c,h}$ of hard phase (%)	SR_h
PU-I-200 (2)	0.096	–	–	74.42	–	0.068	5.43	3.72	63.37
PU-II-200 (2)	0.057	–	–	44.19	0.029	–	35.45	21.67	21.67
PU-II-300 (1)	0.055	–	–	42.64	0.040	–	67.67	41.36	41.36
PU-IV-300 (1)	0.057	–	–	44.19	0.044	–	22.02	13.46	13.46
PU-II-300 (2)	0.063	–	–	48.83	0.036	0.014	63.55	38.84	38.84
PU-IV-300 (2)	0.057	–	–	44.19	0.042	–	52.64	32.18	32.18
PU-II-400 (2)	0.062	–	–	48.06	0.024	0.031	51.60	31.54	53.84
PU-IV-400 (2)	0.043	–	–	33.33	0.051	0.026	51.42	31.43	50.14
PU-II-600 (2)	0.054	–	–	41.86	0.080	–	111.36	68.07	68.07
PU-IV-600 (2)	0.048	–	–	37.21	0.075	0.039	–	–	28.06
PU-II-1000 (2)	0.053	3.90	2.14	43.23	0.122	–	–	–	–
PU-IV-1000 (2)	0.043	–	–	33.33	0.151	0.074	–	–	53.24
PU-I-530 (1)	0.059	–	–	13.11	0.024	–	42.90	29.36	29.36
PU-III-530 (1)	0.060	–	–	13.33	0.039	–	90.41	61.88	61.88
PU-V-530 (1)	0.056	–	–	12.44	0.039	–	32.09	21.96	21.96
PU-I-530 (2)	0.060	–	–	13.33	0.014	–	24.08	16.48	16.48
PU-III-530 (2)	0.058	–	–	12.89	0.034	–	21.60	14.78	14.78
PU-V-530 (2)	0.060	–	–	13.33	0.041	–	32.95	22.55	22.55
PU-II-1250 (2)	0.052	–	–	11.55	0.094	–	–	–	–
PU-IV-1250 (2)	0.043	0.42	0.31	9.87	0.104	–	–	–	–

TABLE IV
Specifications for Weight Percentages of the Individual Segments in PU ($w_{p,s}$, $w_{p,h}$), in Soft ($w_{s,s}$), Intermediate ($w_{ip,s}$, $w_{ip,h}$) and Hard Phases ($w_{h,h}$) as well as Weight Percentage of the Intermediate Phase in Polymer ($w_{p,ip}$)

Symbol of PU (as per Table 1)	$w_{p,\,s}$ (%)	$w_{s,\,s}$ (%)	$w_{ip,\,s}$ (%)	$w_{p,\,h}$ (%)	$w_{h,\,h}$ (%)	$w_{ip,\,h}$ (%)	$w_{p,\,ip}$ (%)
PU-I-200 (2)	28.56	21.25	7.31	71.44	45.27	26.17	33.48
PU-II-200 (2)	51.12	22.59	28.53	48.88	10.59	38.29	66.82
PU-II-300 (1)	59.88	25.53	34.35	40.12	16.59	23.53	57.88
PU-IV-300 (1)	61.43	27.15	34.28	38.56	5.19	33.37	67.65
PU-II-300 (2)	61.15	29.86	31.29	38.85	15.09	23.76	55.05
PU-IV-300 (2)	61.53	27.19	34.34	38.47	12.38	26.09	60.43
PU-II-400 (2)	67.60	32.49	35.11	32.40	17.44	14.96	50.07
PU-IV-400 (2)	68.00	22.66	45.34	32.00	16.04	15.96	61.30
PU-II-600 (2)	75.59	31.64	43.95	24.41	16.62	7.79	51.74
PU-IV-600 (2)	76.34	28.41	47.93	23.66	6.64	17.02	64.95
PU-II-1000 (2)	83.59	36.14	47.45	16.41	–	16.41	63.86
PU-IV-1000 (2)	84.28	28.09	56.19	15.72	8.37	7.35	63.54
PU-I-530 (1)	54.01	7.08	46.93	45.99	13.50	32.49	79.42
PU-III-530 (1)	66.84	8.91	57.93	33.16	20.52	12.64	70.57
PU-V-530 (1)	70.02	8.71	61.31	29.98	6.58	23.40	84.71
PU-I-530 (2)	53.74	7.17	46.57	46.26	7.62	38.64	85.21
PU-III-530 (2)	67.92	8.75	59.17	32.08	4.74	27.34	86.54
PU-V-530 (2)	69.83	9.31	60.52	30.17	6.80	23.37	90.69
PU-II-1250 (2)	86.12	9.95	76.17	13.88	–	13.88	90.05
PU-IV-1250 (2)	86.92	8.58	78.34	13.08	–	13.08	61.42

PU-IV-400, (2) PU-IV-600 (2) and PU-IV-1000 (2) within 21–82°C (Table II), that is connected with glass transition of hard segments ($T_{g,h}$).

Rather no crystallization in the soft phase within the PUs studied—DSC thermograms generally do not present any sharply outlined endothermic melting lines for soft segments. However, a small thermal effect can be seen within 21–44°C in thermograms of samples denoted as PU-II-1000 (2) and PU-IV-1250 (2) (Table III). The melting points for neat polyols POG and PCD are close to each other ($T_{m,POG,PCD}$ = 69°C).[27] All PUs covered by our study presented lower melting points in relation to neat components. The observed temperature depression can result from the effect(s) of share and structure of hard blocks as well as of extent of defects in the crystalline structure. The tendency to crystallize is revealed by the soft phase when its purity is high. It is growing with the increasing $\overline{M}_n$ of polyol and hence with the increasing content of soft segments in the polymer.

An endothermic peak is visible within 170–250°C, which results from melting of hard segments (Figs. 1–3, Table II). Endothermic lines for PUs obtained from the classical one-step method have wider bases ($\Delta T_{m,h}$ = 13–34) deg. In case of equivalent PUs obtained by the prepolymer method, the differences $\Delta T_{m,h}$ are much smaller and their values amount to 5–27°. This makes the evidence for a more defective crystalline structure of polyurethanes obtained from the one-step method.

Two endothermic regions typical for melting can be observed in thermograms for the samples PU-III-530 (1) and PU-V-530 (1) (Fig. 3, Table II). This suggests that different types of crystalline structures can form within hard blocks.

Generally, higher melting points have been observed for longer linear urethane segments what can be accounted for by improved order within supramolecular structures. The above-mentioned depression of temperature can also be observed when hard segments undergo melting, what most probably results from disorder in the crystalline structure due to amorphous components present in the mixture.

PUs synthesized from POG usually offer higher degrees of crystallinity (Table III) and lower values of $\Delta T_{m,h}$ (Table II) in relation to PUs obtained from PCD. No endothermic region of melting for the latter can sometimes be observed, or it is so small, that it is hard to determine $T_{m,h}$.
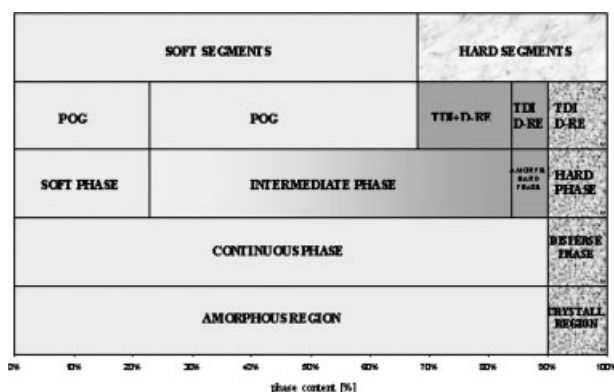

Figure 4 Phase diagram of PU-IV-400. (2).

In general, crosslinked PUs obtained from the one-step method are characterized by a lower degree of crystallinity than their counterparts produced in prepolymer-based processes, and segments derived from Desmodur RE undergo crystallization more readily than the structures formed by TEA and TDI.

Microseparation for POG-derived segments is much more distinct than that for PCD-derived ones (Fig. 4, Tables III and IV). In this case, the reason for such a high content of intermediate phase can be the ability of PCD to form additional hydrogen bonds with carbonyl groups, what improves miscibility of hard blocks and soft blocks in polyester-urethanes.[28,31]

The increasing value of $\overline{M}_n$ of polyol has been observed to reduce the degree of separation for soft phase and to increase its propensity for crystallization. No clear effect has been noticed from $\overline{M}_n$ of polyol on the order within the hard phase.

The data reported earlier suggest also that SR_s for most PUs studied is reduced with the increasing length of the linear polymer chain. However, no effect can be observed from the chain length on changes in degree of crystallinity and SR_h within hard segments. As results from our earlier investigations,[21–23] when $\overline{M}_n$ of oligomers which form linear segments in crosslinked PUs increases, their polydispersity increases, too. This situation must have adverse effects on orderly arranged structures by creating steric hindrances for molecules and thus weakening the intermolecular forces.

Lower separation of soft segments and higher share of those segments in the intermediate phase have been found for PUs obtained from the one-step method. More orderly structures within the hard phase have been clearly outlined in polymers produced by extending the prepolymer chains a few times.

In general, one can state that morphology of the produced polyurethane elastomers is affected by the conditions adopted for the polyaddition and crosslinking processes. Irrespective of that, some additional process disturbances and hard-to-control changes in test piece molding conditions could be responsible for differences in the structure of phases and for the presence of various type defects in the supermolecular structures.

Thermal stability of polyurethane elastomers

Figures 5 and 6 presents a few selected DTA, TG, and DTG thermograms, which are specific for most PUs studied, and Table V provides a more detailed interpretation for them.

As can be seen from the reported data, the thermal degradation process of the synthesized elastomers is complicated and it incorporates a few stages. The initial sample mass decrement of 1–3%, which takes place at 60–70°C, results probably from physical desorption of volatile organic components out of the sample. At a
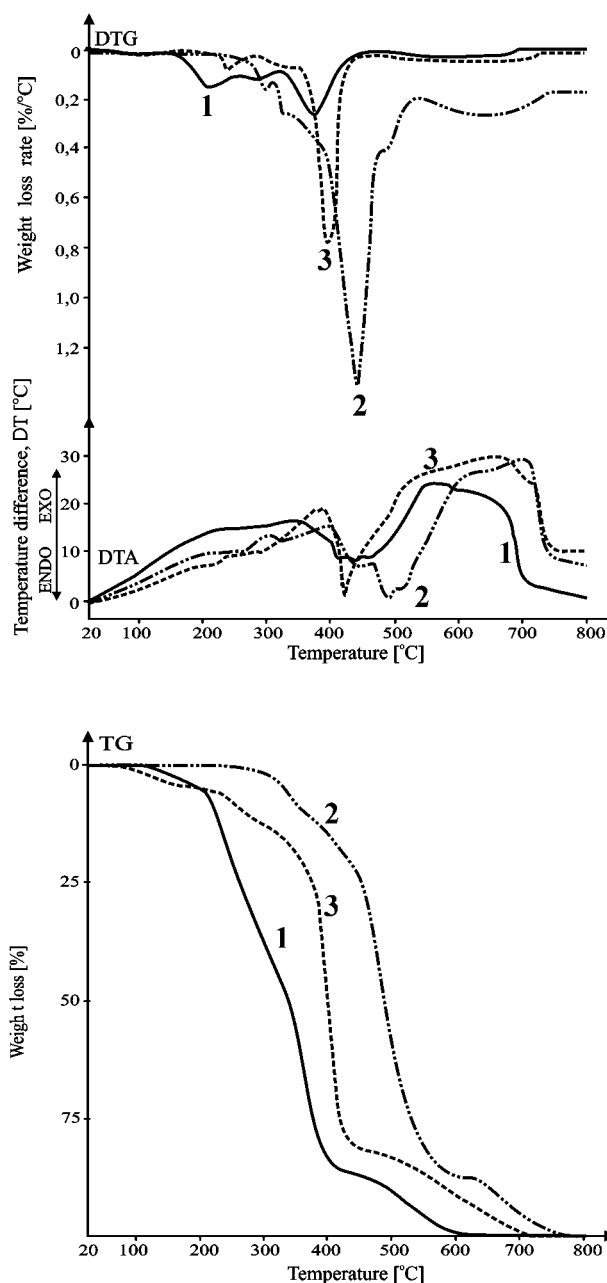

Figure 5 DTA, TG, and DTG thermograms of PU elastomers based on well-defined prepolymers obtained at the first stage with the use of different glycols (as per Table I). 1 – PU-I-200 (2); 2 – PU-I-1250 (2); 3 – PU-I-1000 (2).

somewhat higher temperature, evaporation of water can be observed.

The mass loss as seen at 180–350°C is caused by oxidative degradation; that is accompanied by a small exothermic effect in the DTA curve. In case of some PUs, TG measurements reveal even some gain in weight over that temperature range what most probably results from oxygen addition.[18]

The degradation process takes up speed at the temperature above 300°C, and the profiles of thermograms (i.e., presence of a few overlapping peaks) disclose that
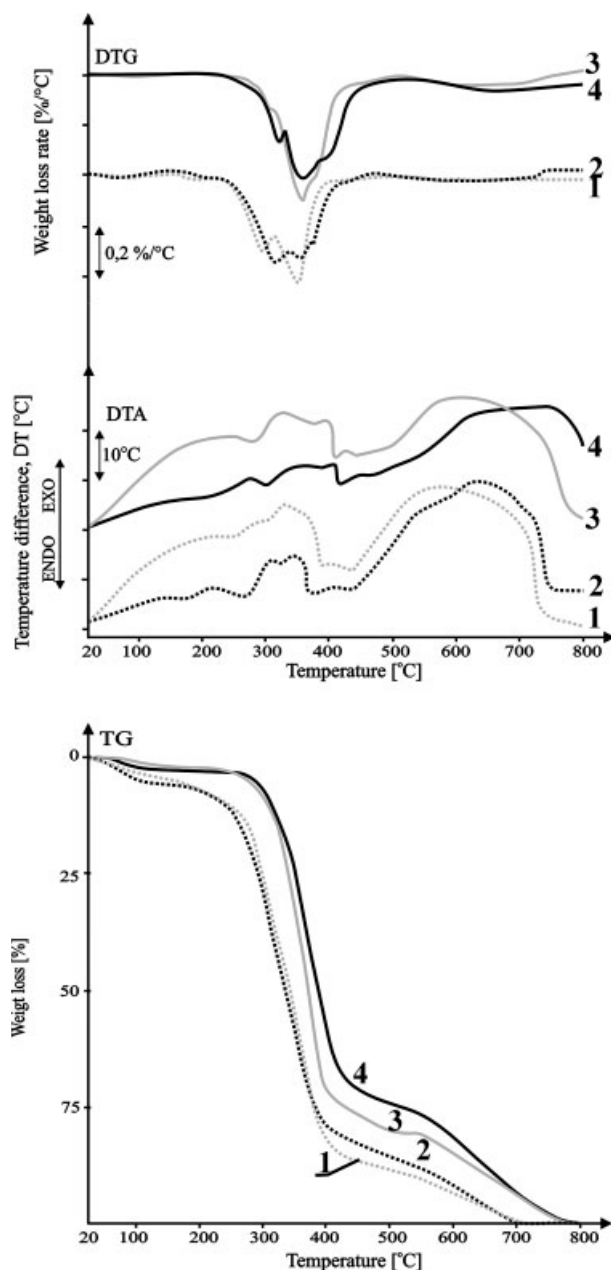
Figure 6 DTA, TG, and DTG thermograms of PU based on well-defined prepolymers and obtained in a one-step method with the use polyoxyethylene glycol (Table I). 1 – PU-V-300 (1); 2 – PU-V-300 (2); 3 – PU-II-300 (1); 4 – PU-II-300 (2).

it is not a single chemical reaction that we have observed but a few reactions have occurred which form the thermal decomposition process. Two peaks can be seen in the DTG curve (Table V, Figs. 5 and 6): within 260–420°C (I) and within 360–440°C (II). DTA thermograms show that both the considered reactions are endothermic in their nature. The maximum temperature for the reaction (I) can be caused by the urethane group destruction. While in the reaction (II) it is probably caused by the destruction of ether bonds in

polyetherurethanes and ether bonds in polyester-urethanes, respectively.

With the increase of the polyol chain length, the heat effect of endothermic processes within 260–420°C becomes lower and lower, while the effect at 360–440°C becomes more important. This can be correlated with the increasing share of ether-type bonds or ester-type bonds with simultaneous reduction in the number of urethane groups.

A peak appears in the DTA curve above the temperature of 450°C, which represents exothermic process. TG and DTG thermograms reveal a small gain in mass in that place. This suggests the oxidation reaction of low-molecular-weight solid products. The degradation process is in practice completed above 700°C, and the sample mass is reduced nearly to zero then.

It can be seen from the analysis of the findings that the generally improved thermal stability of ether-type and ester-type bonds is connected with the increased chain length of polyol. Long and flexible polyol chains—as presented in the previous chapter—form soft domains and their size increases with the increasing length of polyol chains. Thermal stability of ether-type bonds is apparently affected advantageously by bigger soft domains. Heat resistance of urethane groups usually improves for longer oligodiol chains despite the fact that no clear effect from the polyol chain length on the structure of hard phase has been observed earlier.

The thermal decomposition temperature decreases slightly with the increase of the length of linear urethane segment. As has been found in our study, the longer the linear urethane segment is, the higher the content of soft segments in a polymer, but at the same time, the lower the degree of phase separation is, what reduces the volume of soft phase. No relation of that type can be seen, however, in case of polyester-urethanes.

The above-mentioned effects are additionally overlapped by a decrease in thermal stability of urethane-type bonds caused by the increasing length of the urethane segment, what is observed in many samples, and what probably results from inferior order of supermolecular structures within hard segments.

Generally, PUs obtained by the one-step method undergo degradation at lower temperatures than their counterpart compounds obtained by the prepolymer method (Fig. 6).

In many cases, PUs that have been crosslinked with Desmodur RE have superior thermal stability than their analogues that have been crosslinked with TEA. However, three-cyclic Desmodur RE offers better stabilization of urethane groups and better structural stiffening of hard segments than the TDI isomers in combination with TEA. The findings confirm the general rule according to which polyesterurethanes are more stable thermally than polyetherurethanes; ester bonds undergo

TABLE V
Specification for Thermal Stability of PU

Symbol of PU (as per Table 1)	$T_{5\%}$ (°C)	$T_{10\%}$ (°C)	$DTG_{max}.I$ (°C)	$DTG_{max}.II$ (°C)	Residue in temp. 700°C (%)
PU-I-200 (1)	165	200	270	380	3
PU-II-200 (1)	250	290	330	370	9
PU-I-200 (2)	160	190	260	370	0
PU-II-200 (2)	230	280	330	370	3
PU-II-300 (1)	270	300	360	380	6
PU-IV-300 (1)	260	290	340	360	0.5
PU-II-300 (2)	270	305	360	390	7
PU-IV-300 (2)	240	285	340	390	2
PU-II-400 (2)	240	290	–	380	0
PU-IV-400 (2)	250	290	325	380	0.5
PU-II-600 (2)	290	330	–	400	4
PU-IV-600 (2)	285	330	–	390	0.1
PU-I-1000 (2)	200	230	–	400	2.5
PU-II-1000 (2)	310	350	–	400	4.5
PU-III-1000 (2)	230	300	–	395	0
PU-I-530 (1)	210	240	350	–	0
PU-III-530 (1)	240	290	350	390	0
PU-V-530 (1)	260	300	370	405	0
PU-I-530 (2)	220	230	350	420	1
PU-III-530 (2)	230	260	350	390	0
PU-V-530 (2)	270	300	370	410	1.5
PU-I-1250 (2)	290	320	–	430	1.5
PU-II-1250 (2)	330	360	420	440	1
PU-III-1250 (2)	270	310	390	–	0

"–" means no peak in thermogram.
$T_{5\%}$, $T_{10\%}$ – mean weight loss 5% and 10%.

decomposition within 390–440°C while ether bonds decompose as early as at 360–400°C.

CONCLUSIONS

The presented DSC, DTA, and TG methods made it possible to provide reasonably easily morphological evaluations of phase structures of polyurethane elastomers and to find correlations between the obtained data and thermal stability of those materials. Careful interpretation of DSC thermograms enabled a quantitative insight into the phase structures of polyurethane elastomers synthesized in various methods from a common pool of raw materials. Five phases could be distinguished within PUs studied: hard crystalline phase, hard amorphous phase, composed of hard TDI segments and a crosslinking agent, intermediate phase being a mixture of hard and soft blocks, soft amorphous phase composed of polyol-derived soft segments; and in some samples also the crystalline soft phase. The crystalline phase in all cases makes the disperse phase in the continuous phase. It was stated that the PU phase structure depends on $\overline{M}_n$ polyole, the length of the urethane linear chain and on the polyurethane synthesis method.

This approach made it also possible to evaluate the effects from chemical structures present in the studied PUs, i.e., ether and ester groups as well as the cross-

linking compounds: Desmodur RE and TEA on elastomers phase structure.

On the basis of measured values for heat of fusion and specific heat at glass transition temperatures, T_g and T_m, respectively, it was possible to plot phase diagrams for those polyurethanes what creates a general picture of the supermolecular structures. It should be stressed here that the presented procedure is so general that it is applicable also for the analysis of phase structures of other polymer materials.

Based on the findings from TG and DTA measurements within positive temperatures, thermal stability of produced PU elastomers was assessed. Exactly as expected, this was found to be affected not only by the type(s) of raw material(s) but also by supermolecular structures, by average molecular weight of polyol molecules built-in into polyurethane chains, by density of covalent crosslinking within a PU elastomer, and by the method employed to produce that PU. Our next research report will present the attempt to find the explanation(s) for effect(s) of the known phase structures of the studied elastomers on their mechanical properties. It will be advisable to investigate into correlations between the arrangement order in the elastomeric structures (phase separation degrees SR_h and SR_s as well as crystallinity degrees $W_{c,h}$, $W_{c,s}$) and their mechanical properties. The thermal properties as described in this study, when supplemented by the mechanical strength data, will make it possible to sug-

gest some spectrum of potential outlets for the developed materials.

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