

Effect of different polyethers on surface and thermal properties of poly(urethane-siloxane) copolymers modified with side-chain siloxane

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Abstract Poly(urethane-dimethylsiloxane) (PU-PDMS) copolymers with 4,4'-methylenebis(cyclohexyl isocyanate), different polyethers i.e., poly(oxytetramethylene)diol, poly(ethylene glycol), poly(propylene glycol), and α,ω -dihydroxy terminated polydimethylsiloxane extended with 1,4-butanediol in two-step solution polymerization were obtained. The PU-PDMS were modified using 1.25 mol% of polydimethylsiloxane which was incorporated into main polyurethane backbone as a side chain. The structure of the synthesized PU-PDMS was confirmed by FTIR as well as ^1H and ^{13}C -NMR spectroscopy. The effect of different soft segments on free surface energy (FSE) components and thermal stability of poly(urethane-siloxane) copolymers was investigated. The activation energy of the thermal degradation of PU-PDMS using isoconversional methods (Ozawa–Flynn–Wall and Friedman) was calculated. It was concluded that molecular mass, thermal stability, and FSE of PU-PDMS copolymers depend on polyol used. The apparent activation energy at first step of degradation in nitrogen generally increases with the extent of conversion which may result from complex mechanism related to formation of decomposition products. Hydrophobic character of side-chain siloxane on surface properties of the PU-PDMS coatings was confirmed. The obtained coatings are generally soft with the relative hardness in the range of 0.120–0.027.

Keywords Polyurethane · Siloxane · Side chain · Surface free energy · Thermal stability · Kinetics

Introduction

Poly(urethane-siloxane) copolymers (PU-Si) are a class of hybrid polymers which are situated on a boundary between organic and inorganic materials. They consist of organic segments derived from polyurethane and inorganic siloxane structures. PU-Si materials combine advantages of both comonomers used, i.e., good tensile strength and abrasion resistance which are specific for polyurethane, with low free surface energy (FSE) and glass transition, great elasticity (especially at low temperature) as well as good thermal, chemical, and biological stability which are contributed to the system by polysiloxanes. Owing to their properties, PU-Si are widely used as protection coatings, medical implants, or even liquid bandage [1–5].

The modification of polyurethanes by siloxane is mostly achieved by introduction of usually linear polydimethylsiloxane into PU backbone as a part of soft segments [4, 6–8]. However, the investigations on polyurethanes with other polysiloxane structure have been recently developed [9–12].

Pergal et al. [9] performed studies on synthesis of novel polyurethane copolymers derived from 4,4-methylenediphenyl diisocyanate, 1,4-butanediol, and α,ω -dihydroxy-[poly(caprolactone)-poly(dimethylsiloxane)-poly(caprolactone)]. It was found from DSC and WAXS results that siloxane segments crystallized, and, additionally, SEM images confirmed the presence of a spherulitic morphology. The synthesis of moisture cured PU with the use of α,ω -bis(3-aminopropyl)diethoxysilane poly(trifluoropropylmethyl)siloxane (APFS) was performed by Shi and Wang [10]. They found that the extent of microphase separation of the samples would increase with the increase in APFS content, and result in the decrease in the tensile strength and the thermal stability. In other paper waterborne PU were synthesized

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with α,ω -bis(3-hydroxypropyl)-functionalized poly{dimethylsiloxane-comethyl [3-(2-acetylacetoxy)] propylsiloxane} [11]. This siloxane was used as self-cross-linking agent in reaction with dihydrazide for PU at ambient temperature. The cross-linked PU-Si revealed lowered water absorption. Wang et al. [13] synthesized PU-PDMS copolymers by modification of PU surface via grafting through the introduction of vinyl and Si-H groups onto the PU surface to improve the adhesion of PU to silicone rubber.

There are relatively little papers concerning studies on properties of PU-Si which are obtained with polysiloxane containing two reactive groups at one side of a chain. Owing to its structure, this siloxane was inbuilt as a pendant chain into main polyurethane backbone [14–17].

Li et al. [14] investigated the influence of siloxane length on the properties of PU-Si elastomers obtained both from main-chain as well as side-chain siloxanes. The molecular masses of the poly(urethane-siloxane) depended on the types of siloxanes used. Side-chain siloxanes yielded a higher molecular mass of PU copolymers than the main-chain siloxanes. The incorporation of main-chain siloxanes into polyurethane improved the elongation at break greatly, whereas side-chain siloxanes enhanced the ultimate tensile stress. The PU-Si anionomers containing pendant siloxane was studied as well. This kind of PU anionomers, which were cross-linked with N-methylmonoethanolamine, compared to main-chain siloxane PU films, showed larger advancing contact angles but lower gloss and poorer tensile strength at the same amount of PDMS and similar molecular mass [15]. Chen et al. [16] compared the properties of PU-Si anionomers in which polydimethylsiloxane was introduced into the PU chain either based on random distribution or through the block segment arrangement. The contact angle of the PU-Si film increased rapidly and reached a maximum at a siloxane amount of about 7%. Moreover, in the block poly(urethane-siloxane) anionomers, siloxanes moved to the surface much more easily than in the case of the random PU-Si, which as evidenced by the scanning electron microscope and energy dispersive spectroscopy (SEM-EDS) studies. However, there is still little known about thermal properties of this kind of PU-PDMS.

The aim of these investigations was to study the influence of different polyols (poly(oxytetramethylene)diol, poly(ethylene glycol), poly(propylene glycol), and α,ω -dihydroxy terminated polydimethylsiloxane) on surface and thermal properties of poly(urethane-siloxane) copolymers obtained with 4,4'-methylenebis(cyclohexyl isocyanate) and 1,4-butanediol which were modified with polydimethylsiloxane. This PDMS contained two hydroxyl groups located at one side of siloxane chain. Owing to its structure, the polydimethylsiloxane was introduced as side chain into main polyurethane backbone.

Experimental

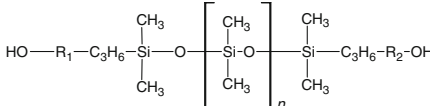
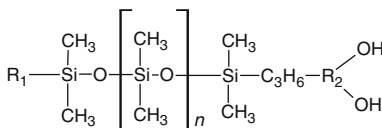
Materials

4,4'-Methylenebis(cyclohexyl isocyanate) (H_{12} MDI, 90% mixture of isomers) and dibutyltin dilaurate (DBTDL) from Aldrich were used without further purification. Poly(oxytetramethylene)diol (PTMO, $M_n = 1,000$ and 2,000), poly(ethylene glycol) (PEG $M_n = 1,000$), and poly(propylene glycol) (PPG, $M_n = 1,000$) were purchased from Aldrich. Two kinds of polysiloxanes α,ω -dihydroxy terminated polydimethylsiloxane (L-PDMS, $M_n \approx 1,000$) and side-chain siloxane (S-PDMS, $M_n \approx 2,736$) which structures are presented in Table 1 were kindly donated by Shin-Etsu (Japan). All the polyols were dried in a vacuum oven at 105 °C before use. 1,4-butanediol (BD, Aldrich) used as a chain extender was dried over 4 Å molecular sieves. 2-butanone (MEK, POCh, Poland) were distilled and dried over 4 Å molecular sieves as well.

Synthesis of polyurethane

The polyurethane (T1) was obtained in two-step solvent synthesis. At the 1st stage, H_{12} MDI was placed in 100-ml three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet and diluted in MEK. Then, PTMO ($M_n = 1,000$) diluted in MEK was added drop by drop to the flask. After that, DBTDL as catalyst was added. The reaction was allowed to proceed at 60 °C till content of unreacted isocyanate groups reached half of initial value (ca. 30 min). Then, at the 2nd step, BD was added and the temperature was raised to 60 °C. The mixture was maintained at this temperature for about 2 h till the -NCO content reached 0%. The conversion of -NCO at each step was determined by a standard dibutylamine back titration method [18]. The molar ratio of H_{12} MDI:PTMO:BD was 2:1:1.

Table 1 Structure of polydimethylsiloxane compounds

Symbol	Chemical structure	M_n
L-PDMS		~1,000
S-PDMS		~2,736

General procedure of synthesis of poly(urethane-siloxane) copolymers

All the poly(urethane-siloxane) copolymers contain 1.25 mol % of S-PDMS. The molar ratio of H₁₂MDI:polyol:S-PDMS:BD = 2:0.95:0.05:1. The PU-PDMS were obtained in similar procedure as described for polyurethane. At the 1st stage, H₁₂MDI was placed in 100-ml three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, and nitrogen inlet and diluted in MEK. Then, mixture of different polyether (PTMO, PEG, PPG or L-PDMS) and S-PDMS diluted in MEK were added drop by drop to the flask and DBTDL was added. The reaction was allowed to proceed at 60 °C till content of free isocyanate groups reached half of initial value (ca. 1 h). Then at the chain extension step BD was added, and the temperature was raised to 60 °C. The mixture was maintained at this temperature for about 2 h to reach total –NCO conversion.

Using above described procedures, 6 samples of copolymers were obtained with the solid content ca. 30 wt%. The structure of synthesized PU-PDMS was

presented in Fig. 1 and the detailed composition of PU-PDMS copolymers—in Table 2. The polymer coatings for further investigations were prepared by pouring the solution of the polymers on the apolar surface of poly(tetrafluoroethylene) (PTFE), followed by drying in a vacuum oven at 85 °C for 12 h. Then, the samples were conditioned at room temperature for 10 days before testing.

Characterization

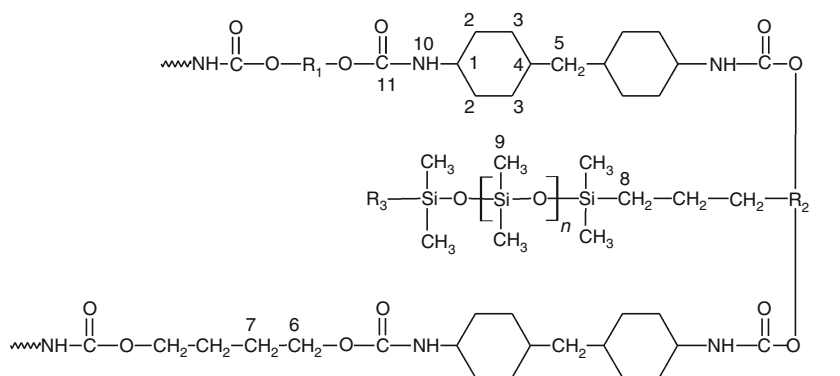
IR spectroscopy

IR spectra were recorded with the spectrophotometer Nicolet 6700 in air, within the range of 4,000–500 cm⁻¹, with the use of ATR technique. The obtained spectra were presented as the relation of transmittance (%) versus wave number $\bar{\nu}$ (cm⁻¹).

NMR spectroscopy

¹H NMR and ¹³C NMR spectra of the polymers were recorded with the use of the spectrometer FT NMR Bruker

Fig. 1 Structure of synthesized PU-PDMS copolymers



where R₁:

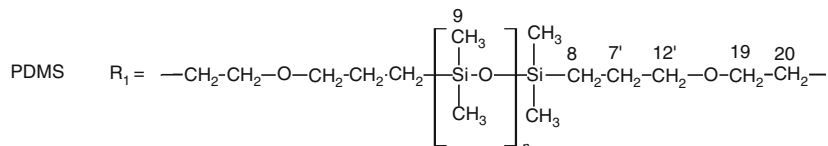
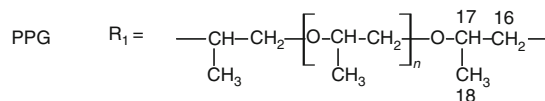
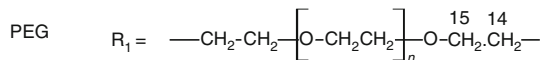
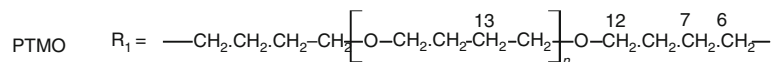


Table 2 Composition of PU-PDMS copolymers

Sample	Amount of monomers/mol								HS/wt% ^a	SS wt% ^b
	H ₁₂ MDI	PTMO 1000	PTMO 2000	PEG 1000	PPG 1000	L-PDMS 1000	S-PDMS	BD		
T1	2	1						1	38.1	61.9
T1S		0.95					0.05		44.2	55.8
T2S			0.95						28.3	71.7
E1S				0.95					44.2	55.8
P1S					0.95					
S1S						0.95				

^a Hard segment content (wt%) = (H12MDI + BD + S-PDMS) × 100 % / (H12MDI + BD + S-PDMS + polyol)

^b Soft segment content (wt%) = 100 % – hard segment content

Avance 500^H. The samples of PU-PDMS were dissolved in CDCl₃ and the solutions with the concentration of about 0.2 g dm⁻³ were prepared. TMS was used as a standard.

Gel permeation chromatography (GPC)

GPC chromatograms were performed using a Waters Alliance 2695 GPC system equipped with a Waters 2414 RI detector and a set of three serially connected 7.8 × 300 mm columns (Waters Styragel HR1, HR2 and HR4). The pore sizes of columns are as follows: 10, 100, and 1,000 Å. Molecular masses and polydispersity indices were calculated on the basis of point to point calibration curve of polystyrene Shodex standards in the range from 1.31 × 10³ to 3.64 × 10⁶ Da. THF was used as an eluent in a 0.6 mL min⁻¹ isocratic flow. Columns were maintained at 35 °C. All samples were prepared as ca. 10 wt% solutions in tetrahydrofuran.

Thermogravimetric analysis (TG)

Thermogravimetric analysis was performed using a Mettler Toledo TG/DSC1. The TG experiments have been carried out in nitrogen from 25 to 500 °C with varying heating rates 2.5; 5; 10; 20 °C min⁻¹ as well as in air gas flow from 25 to 600 °C with 10 °C min⁻¹ heating rate. The measurement conditions were as follows: sample mass ~5 mg, gas flow—50 cm³ min⁻¹, alumina pan. The degradation kinetics parameters in nitrogen were evaluated with the use of the Netzsch Thermokinetic Program.

Surface roughness measurements

The surface roughness of the coatings were investigated by means of profile method with the use a Mar Surf PS1 apparatus (Mahr GmbH, Germany), according to PN-EN ISO 12085:2009 standard. Measurements were performed at temperature 21 ± 0.1 °C, L_T = 5600 mm, and L_C = 0.800 × 5. The values of arithmetic mean deviation of the

assessed profile (R_a) and max. height of the profile within a sampling length (R_z) were used to characterize the coating roughness.

Contact angles measurement

The contact angles Θ were measured using the method suggested by Zisman [19] i.e., by means of optical goniometer (Cobrabid Optica—Warsaw) with a digital camera installed instead in axial extension of its lens. The standard liquid drops of water, formamide, or diiodomethane with the constant volume (5 μL) were applied on the surfaces of studied samples with the use of a special micropipette. The measurements were taken in temperature at 21 ± 2 °C. The values of contact angles were found from the geometric analysis of pictures taken for liquid drops, using the original software *Kropelka*. The result of contact angle for one standard liquid was average of 11 measurements after rejecting of extreme values.

Method for determination of the FSE components for solids

Physical parameters of the FSE for solids γ_S were found in the present study on the basis of the van Oss–Good (vOG) [20, 21] and Owens–Wendt (OW) [22] models.

The van Oss–Good model assumes that the FSE γ_S can be presented as a sum of two components [20, 21]:

$$\gamma_S = \gamma_S^{LW} + \gamma_S^{AB} \quad (1)$$

where γ_S^{LW}—FSE connected with long-range interactions (dispersion, polar and induction interactions), γ_S^{AB}—FSE connected with acid–base interactions as results from the Lewis theory which is composed of γ_S⁺—component related to Lewis acid and γ_S⁻—component related to Lewis base.

Taking into account the FSE components in the meaning as it was described above. van Oss and Good proposed an equation that establishes the relation between the FSE

parameters of the standard liquids (L) and of the investigated surface of solid (S):

$$\begin{aligned} & \left(\gamma_S^{LW} \gamma_{L,i}^{LW}\right)^{0.5} + \left(\gamma_S^+ + \gamma_{L,i}^- \right)^{0.5} + \left(\gamma_S^- + \gamma_{L,i}^+ \right)^{0.5} \\ & = \gamma_{L,i} \frac{(1 + \cos\Theta_i)}{2} \end{aligned} \tag{2}$$

where Θ —the experimentally found contact angle between a liquid drop and a solid surface under investigation, i —concerns the used standard liquid.

The Owens–Wendt model assumes that the FSE γ_S of the solid state may be presented as a sum of two components [22]:

$$\gamma_S = \gamma_S^d + \gamma_S^p \tag{3}$$

where γ_S^d —FSE connected with dispersion interactions (dispersion, polar, and induction interactions), γ_S^p —FSE connected with polar interactions.

Using the above described SFE components, Owens and Wendt proposed an equation that establishes the relation between the surface free energy parameters of the standard liquids (L) and of the investigated surface of solid (S):

$$\gamma_L \frac{1 + \cos\Theta}{2} = (\gamma_S^d \gamma_L^d)^{0.5} + (\gamma_S^p \gamma_L^p)^{0.5} \tag{4}$$

where Θ —the experimentally found contact angle between a liquid drop and a solid surface under investigation.

In order to find as well as to validate the values of SFE (γ_S) those two method ware applied. Moreover, in OW method two sets of standard liquids (water–formamide and diiodometane–formamide) for the PU-PDMS surface investigation were used. The values of SFE and its components for applied standard liquids were summarized in Table 3.

Persoz hardness

The Persoz hardness of the PU-Si coatings on stainless steel pieces (dimensions of 100 mm × 50 mm × 1 mm) was measured according to PN–EN ISO 1522:2001 standard in pendulum hardness tester (BYK-Gardner GmbH, Germany). The Persoz hardness was obtained as the time of

Table 3 Surface free energy values of the model standard liquids for OW and vOG models [23, 24]

Standard liquid	Free surface energy parameters/mJ m ⁻²							
	Owens–Wendt model			van Oss–Good model				
	γ_L	γ_L^d	γ_L^p	γ_L	γ_L^{LW}	γ_L^{AB}	γ_L^+	γ_L^-
Water	72.8	21.8	51	72.8	21.8	51.0	25.5	25.5
Formamide	58.0	39.0	19.0	58.0	39.0	19.0	2.28	39.6
Diiodomethane	50.8	48.5	2.3	50.8	50.8	0	0	0

oscillations decay of the pendulum on material surface to glass constant. The values obtained were the average of three replicates.

Results and discussion

Structural analysis of PU-PDMS copolymers

The chemical structures of the PU-PDMS copolymers were verified on the basis of both IR as well as ¹H and ¹³C NMR spectra.

Figure 2 shows the IR spectra of the PU-PDMS copolymers. An absence of NCO peak at 2,270 cm⁻¹ indicates that the isocyanate conversion was complete. The characteristic absorption peaks which confirm formation of polyurethane can be found at around 3,323 cm⁻¹ (–NH stretching), 1,700 cm⁻¹ (–C=O stretching, first amide band), 1,530 cm⁻¹ (–NH deformation, second amide band), and at 1,230 cm⁻¹ (C–N stretching, third amide band). The build-in of the PDMS segments into the anionomer chains was confirmed by the presence of the strong Si–CH₃ band at 800 cm⁻¹. Si–CH₃ deformation band at 1,257 cm⁻¹ can be found only in the S1S sample with large siloxane content because in the others PU-PDMS that signal is covered with amide III band at 1,230 cm⁻¹. Other characteristic IR bands present both in PU as well as PU-PDMS can be seen at around 1,035 and 1,097 cm⁻¹ (–Si–O–Si– and/or –C–O–C– bending) and 2,795–2,968 cm⁻¹ (C–H stretching).

Interpretation of ¹H and ¹³C NMR spectra of all poly(urethane-siloxane) copolymer is presented in Table 4, where the protons and carbons signals were assigned to the particular structural parts of the polyurethane chain [25]. The numbers of particular atoms were provided in Fig. 1. The recorded NMR spectra fully confirmed the structure of the copolymers.

The formation of polyurethane was confirmed by the presence of chemical shift at 8.00 ppm in ¹H NMR spectrum

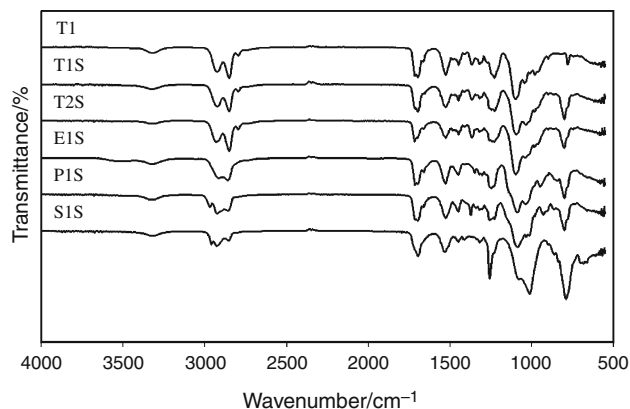


Fig. 2 FTIR spectra of poly(urethane-siloxane) copolymers

and 155 ppm in ^{13}C NMR spectrum which are attributed to proton 10 ($-\text{NHCOO}-$) and carbon 11 ($-\text{NHCOO}-$) in urethane bond respectively. There were no peaks at 124 ppm characteristic for the C atom in an isocyanate group which confirms that diisocyanate was completely reacted. The same conclusion resulted also from the IR analysis. Two signals at $\delta \approx 0.07$ ppm (^1H NMR) and $\delta \approx 1.03$ ppm (^{13}C NMR) assigned to corresponding atoms in methyl group in $(\text{CH}_3)_2\text{-SiO}$ which occur in all siloxane-modified samples confirm the build-in of PDMS into the polyurethane structure. In each synthesized polymer, there are structures derived from H_{12}MDI and BD which can be found in NMR spectra. In ^1H NMR spectra the signals from H_{12}MDI rings (**2**, **3**, **4**) were present in the 0.96–1.25 ppm range. Chemical shifts derived from BD occur at 1.56–1.68 ppm assigned to protons (**7**) in $-\text{CH}_2-$ and at 4.06–4.19 ppm assigned to protons (**6**) in $-\text{CH}_2\text{-OCONH}-$ group. The shifts for carbons in above-mentioned groups are also reflected in ^{13}C NMR spectra. Especially, the signals at $\delta = 25.72\text{--}28.06$ and $70.61\text{--}75.37$ ppm assigned to carbon (**7**) in $-\text{CH}_2-$ and (**6**) in $-\text{CH}_2\text{-OCONH}-$ groups, respectively, which are derived from BD. The chemical shifts of particular atoms in different polyols used are assigned in detail and summarized in Table 4.

Molecular mass distribution

The results of GPC analysis comprising number average molecular mass (M_n), mass average molecular mass (M_w), and polydispersity (M_w/M_n) were presented in Table 5. The largest molecular mass reveal unmodified PU sample T1. The polyurethane samples which were modified with side-chain siloxane resulted in lowering of this value (T1S). This may result from with poor segmental compatibility of nonpolar polydimethylsiloxane with hard segments and steric effect of side-chain siloxane [14, 26]. The mass average molecular mass depends on polyol used and decrease in order: T2S > P1S > T1S > S1S > E1S. The largest molecular mass for sample T2S may be related to longer polyol segment (PTMO 2000) as well as lower amount of side-chain siloxane in its composition.

Thermal properties of PU-PDMS copolymers

Thermal decomposition in nitrogen

TG and DTG profiles for the PU-PDMS were presented in Figs. 3 and 4 whereas Table 6 provides interpretation of both profiles. On the TG curves, two basic degradation

Table 4 Interpretation of ^1H NMR and ^{13}C NMR spectra

Type of H or C nucleus (Fig. 1)	Sample											
	T1		T1S		T2S		E1S		P1S		S1S	
	Chemical shift in NMR spectrum/ppm											
	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C	^1H	^{13}C
1	3.76	46.94	3.77	46.95	3.76	46.93	3.77	46.96	3.77	46.92	3.62	46.94
2	1.10	32.04	1.10	32.05	1.10	32.04	1.10	32.02	1.10	32.05	1.10	32.02
3	0.96	28.05	0.96	28.06	0.96	28.06	0.96	28.03	0.96	28.05	0.96	28.06
4	1.25	29.70	1.25	29.70	1.25	29.71	1.25	29.70	1.23	29.71	1.25	29.71
5	2.00	33.44	2.00	33.45	2.00	33.46	2.00	33.36	2.00	33.43	2.00	33.38
6	4.06	70.61	4.06	70.62	4.06	70.61	4.07	70.56	4.07	75.37	4.19	74.14
7	1.62	26.51	1.62	26.51	1.62	26.51	1.56	25.72	1.56	25.72	1.56	25.74
8	–	–	0.51	–	0.51	–	0.51	–	0.51	–	0.52	14.06
9	–	–	0.07	1.03	0.07	1.02	0.07	1.03	0.07	1.03	0.07	1.04
10	8.03	–	8.04	–	8.02	–	8.09	–	8.06	–	8.06	–
11	–	155.94	–	155.94	–	155.93	–	155.60	–	155.85	–	155.62
12	3.41	70.61	3.41	70.62	3.41	70.61	–	–	–	–	–	–
13	1.62	25.91	1.62	25.92	1.62	25.92	–	–	–	–	–	–
14	–	–	–	–	–	–	4.19	70.56	–	–	–	–
15	–	–	–	–	–	–	3.64	69.68	–	–	–	–
16	–	–	–	–	–	–	–	–	3.55	75.36	–	–
17	–	–	–	–	–	–	–	–	3.40	73.36	–	–
18	–	–	–	–	–	–	–	–	3.14	17.32	–	–
19	–	–	–	–	–	–	–	–	–	–	3.62	69.04
20	–	–	–	–	–	–	–	–	–	–	4.19	74.14

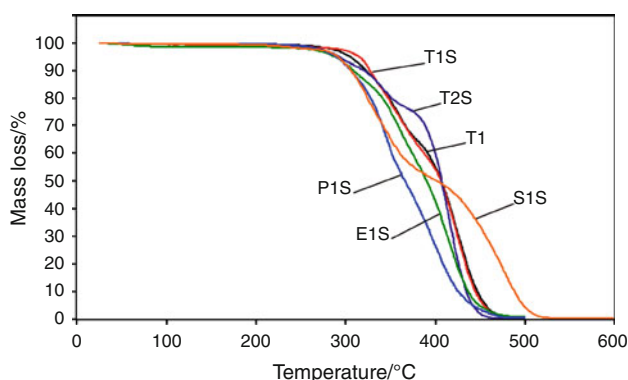
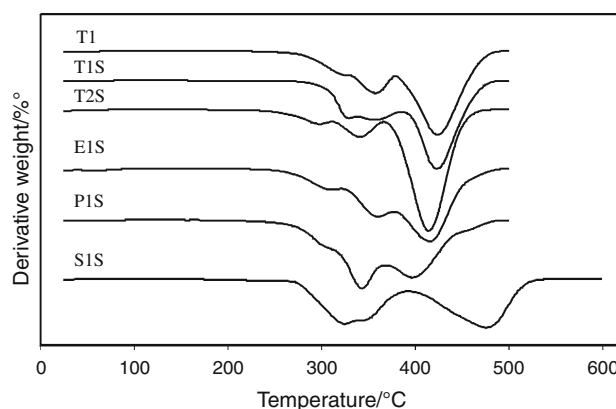
Table 5 Molecular masses of PU-PDMS copolymers

Sample	$M_n/\text{g mol}^{-1}$	$M_w/\text{g mol}^{-1}$	M_w/M_n
T1	29,076	214,433	7.37
T1S	12,098	21,788	1.80
T2S	20,465	35,753	1.75
E1S	8,300	12,024	1.45
P1S	14,024	25,332	1.81
S1S	8,682	15,296	1.76

stages can be distinguished. However, the DTG profiles reveal basically two main peaks but also additionally shoulder peak at the beginning of decomposition. That may suggest that the first degradation stage may comprise a few processes (parallel reaction, subsequent reactions or “overlapping” reactions, and possibly evaporation of remaining solvent which has been occluded) [27].

Decomposition of PU-PDMS, in terms of 5 % mass loss (T_5 %), takes place in the narrow temperature range of 284–288 °C for samples modified with S-PDMS containing PTMG 2000, PEG, PPG, or even S-PDMS soft segments. The beginning of the decomposition starts in the least thermal stable link which in polyurethanes is definitely urethane bond. Thus, the kind of soft segment does not strong influence T_5 %. However, there is visible effect of S-PDMS modification on the increase in 5 % mass loss temperature for the sample T1S in comparison to unmodified polyurethane (T1).

The mass loss at the first stage of degradation amounts to 23–52 wt% that corresponds to disintegration of rigid segments derived from H_{12} MDI, BD, and S-PDMS. Temperature of maximum degradation rate at stage I ($T_{\max 1}$) amounts to 322–357 °C. Among the samples synthesized with PTMO, the largest $T_{\max 1}$ revealed the unmodified polyurethane T1. Introduction of 1.25 mol % of S-PDMS to T1 sample resulted in slightly lowering of this value from 354.79 to 352.55 °C. The siloxane-modified sample T2S composed of PTMO 2000 soft segments show lowest

**Fig. 3** TG curves of poly(urethane-siloxane), recorded in nitrogen**Fig. 4** DTG curves of poly(urethane-siloxane), recorded in nitrogen

$T_{\max 1}$ than the corresponding sample synthesized with PTMO 1000. This phenomenon can result from lower siloxane amount in the former sample. Among all the synthesized PU-PDMS the lowest $T_{\max 1}$ amounts to 322 °C revealed S1S sample indeed, but one should know that this peak is spited, which may influence on accuracy of this value. The mass loss at the second stage of degradation amounts to 47–76 wt% that corresponds to disintegration of soft segments derived from polyols [28, 29]. The maximal mass loss at this stage is observed for the T2S sample, where to soft segment content is the largest. Temperature of maximum degradation rate at stage II ($T_{\max 2}$) amounts to 394–472 °C. The largest $T_{\max 2}$ revealed S1S sample, where polydimethylsiloxane segments predominate.

Thermolytic decomposition ends at the temperature which is above 450 °C but for S1S sample which contain polydimethylsiloxane soft segments that temperature exceeds 530 °C. The copolymers underwent nearly 100 % decomposition. No solid residue found after degradation may confirm formation of volatile cyclic siloxane compounds.

Thermal decomposition in air

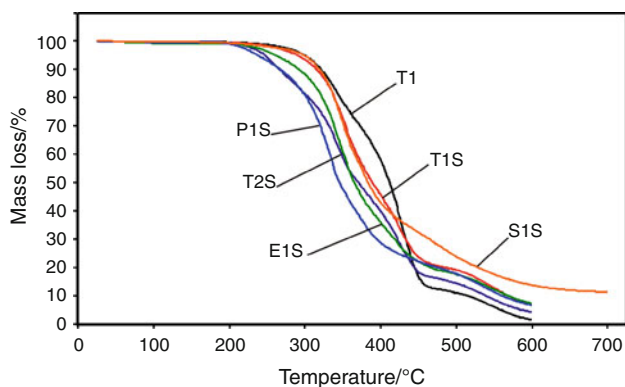
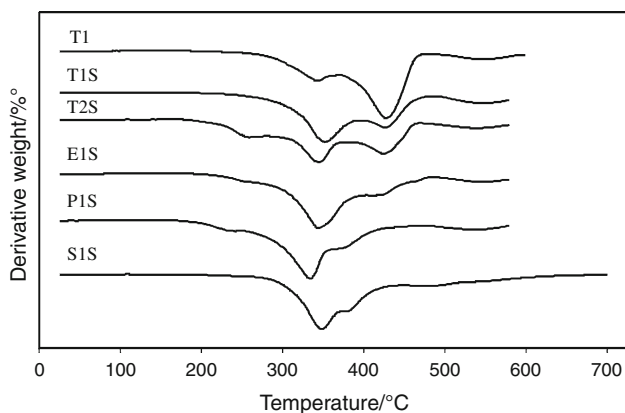
Thermal decomposition of PU-PDMS copolymers in air follows a more complex pattern. Figures 5 and 6 present TG and DTG curves, which were recorded for PU-PDMS at the heating rate of 10 °C min⁻¹, while Table 7 provides interpretation of TG and DTG profiles.

The 5 % mass loss appears at 235–296 °C for all copolymers modified with S-PDMS and depends on soft segment used. For all samples, this temperature is generally lower in air than in nitrogen except for S1S. Moreover, the largest T_5 % from all PU-PDMS revealed S1S sample which comprise large amount of siloxane structures. The temperature of 5 % mass loss in side-chain siloxane-modified polyurethanes decreases in order: S1S > T1S > E1S > T2S > P1S. In contrast to nitrogen atmosphere, the modification of polyurethane with S-PDMS resulted in lowering T_5 % in air.

Table 6 Decomposition temperature of PU-PDMS at 10 °C min⁻¹ in nitrogen

Sample	T_5 %/°C	T_{50} %/°C	T_{max1} /°C	Mass loss at stage I of degradation/%	T_{max2} /°C	Mass loss at stage II of degradation/%	Residue at 500 °C/%
T1	301.04	403.57	354.79	35.5	421.09	64.1	0.4
T1S	311.10	402.48	352.55	41.4	419.72	58.4	0.1
T2S	288.87	403.82	338.14	23.8	411.53	76.1	0.1
E1S	284.40	387.44	357.74	42.9	412.52	56.3	0.8
P1S	286.13	363.43	340.72	52.2	394.42	47.5	0.3
S1S	287.58	399.26	322.00	48.7	472.61	51.1	0.3*

* For S1S residue at 600 °C

**Fig. 5** TG curves of poly(urethane-siloxane), recorded in air**Fig. 6** DTG curves of poly(urethane-siloxane), recorded in air

The DTG profiles of the tested samples, for decomposition in air, demonstrate basically three maximum peaks for samples contained PTMO, which may suggest that the degradation process is composed of three stages. However, for the remaining samples only two main peaks can be distinguish because of the presence of shoulder peaks, which may additionally suggest more complex mechanism of degradation. Temperature of maximum degradation rate at stage I amounts to 332–350 °C. The modification of polyurethane

with S-PDMS resulted in increase T_{max1} . Among the PU-PDMS, the lowest T_{max1} amounts to 332.64 °C revealed P1S sample containing poly(propylene glycol) soft segments.

The end of degradation temperature in air for the PU-PDMS studied is larger than in nitrogen and exceeds 550 °C. The amount of solid residue after degradation for all modified samples at 600 °C was larger than for unmodified PU and exceeded 6.5 %. However, for the sample T2S where amount of siloxane was lower, this value amounts to 4.1 %. On the other hand, the largest residue (11.1 % even at 700 °C) was observed for S1S sample. Those findings seem to make the evidence for the formation of complex silicon-based structures in the pyrolysis process. The structures are formed on the surface and probably create the insulating layer which slows down further decomposition of the polymer, as it was observed for polyurethane-siloxane copolymers [30].

Kinetic analysis of the decomposition process

In order to study thermal degradation of PU-PDMS copolymers in detail, kinetic analysis of the observed thermal decomposition processes of those polymers in nitrogen was performed.

The general expression for the kinetic description of degradation of solids is [31]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (5)$$

where α is the conversion degree defined as the ratio of the actual mass loss to the total mass loss, $k(T)$ is the reaction rate constant, and $f(\alpha)$ is the kinetic model function. After substitution of the Arrhenius equation [32] and in non-isothermal conditions, when an expression responsible for the heating rate $\beta = \frac{dT}{dt}$ is added to (5), one arrives at:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E_a}{RT}\right) d\alpha \quad (6)$$

where A —frequency factor, E_a —activation energy, R —universal gas constant, T —absolute temperature.

Table 7 Decomposition temperature of PU-PDMS at 10 °C min⁻¹ in air

Sample	T_5 %/°C	T_{50} %/°C	T_{max1} /°C	Mass loss at stage I of degradation/%	T_{max2} /°C	Mass loss at stage II of degradation/%	T_{max3} /°C	Mass loss at stage III of degradation/%	Residue at 600 °C/%
T1	297.22	411.13	341.24	29.5	427.00	58.4	547.18	10.7	1.4
T1S	287.56	388.35	350.93	52.8	424.14	27.5	543.86	13.2	6.6
T2S	244.85	368.79	342.62	51.7	422.57	31.8	533.80	12.3	4.1
E1S	258.46	364.26	342.79	81.5	543.48	11.4	–	–	7.2
P1S	235.29	344.52	332.64	78.8	533.24	14.6	–	–	6.5
S1S	296.09	382.78	346.36	66.6	474.84	22.3	–	–	11.1*

* For S1S residue at 700 °C

Two isoconversional methods by Ozawa–Flynn–Wall (OFW) [33, 34] and Friedman [35] were employed to evaluate of kinetic parameters in thermal decomposition of polymers under dynamic conditions in nitrogen. These methods may be used to determine and to monitor changes in the activation energy during the degradation process, without assumption of reaction model. Kinetic studies of solids with the use of isoconversional methods are extensively discussed in the literature [36–38]. The O–F–W method is based on the Doyle approximation [39], and it resolves itself to the use of the following equation:

$$\ln \beta = \ln \left(\frac{A E_a}{R} \right) - \ln g(\alpha) - 5.3305 + 1.052 \frac{E_a}{RT} \quad (7)$$

In order to find the activation energy value E_a for a given degree of conversion α , one should take a series of measurements for different heating rates β . Then, for a fixed degree of conversion ($\alpha = \text{const}$), straight lines are obtained in the diagram $\ln \beta = f(1/T)$ for which the slope is defined as $m = 1.052 \frac{E_a}{R}$.

The Friedman isoconversional method [35] is based the following equation:

$$\ln \frac{d\alpha}{dt} = \ln A + \ln f(\alpha) - \frac{E_a}{RT} \quad (8)$$

In order to find the activation energy value E_a for a given degree of conversion α , one should take a series of measurements for different heating rates β . Then, for a fixed degree of conversion ($\alpha = \text{const}$), straight lines are obtained in the diagram $\ln \left(\frac{d\alpha}{dt} \right) = f(1/T)$ for which the slope is defined as $n = -\frac{E_a}{R}$.

Figures 7 and 8 illustrate the relationship between the activation energies (E_a) of the PU-PDMS and the degree of conversion by O–F–W and Friedman, respectively. The results obtained by both methods are similar. The presence of minimum at about $\alpha = 0.25$ which may suggest that degradation that takes place in two steps is observed. For the T2S sample, this minimum is shifted toward lower α values, which results from lower hard segments content. This is because the hard

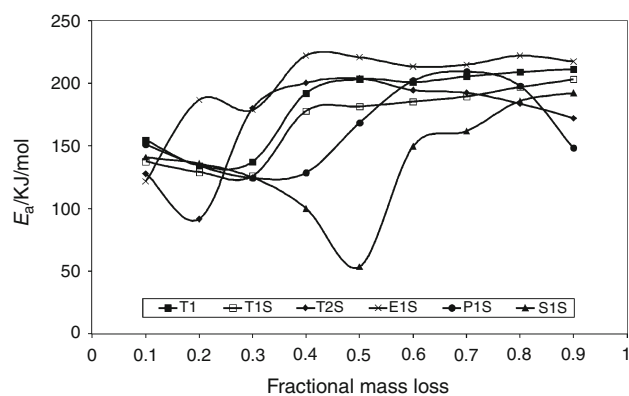


Fig. 7 Activation energy values calculated from the Friedman analysis of the degradation process of PU-PDMS copolymers

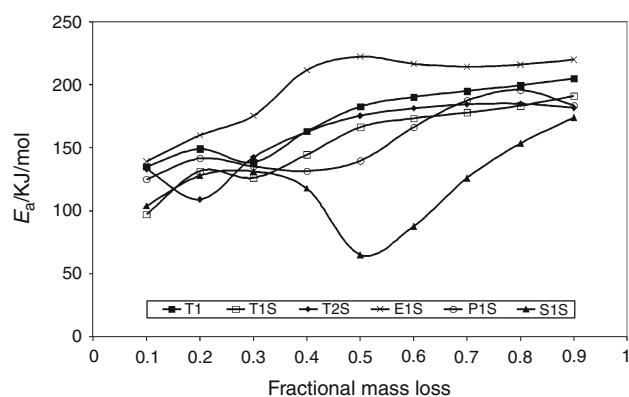


Fig. 8 Activation energy values calculated from the Ozawa–Flynn–Wall analysis of the degradation process of PU-PDMS copolymers

segments degrade at first step. The apparent activation energy at this step generally increases with the extent of conversion, which may result from complex mechanism of degradation at this stage related to formation of decomposition products and their diffusion through the solid sample. At the second stage of degradation, activation energy remains almost unaffected, which may be related to liquid polyol decomposition, where diffusion of volatile decomposition products is facilitated. The second stage of thermal degradation of S1S sample with PDMS

Table 8 Roughness and Persoz hardness of PU-PDMS coatings

Sample	$R_a/\mu\text{m}$	$R_z/\mu\text{m}$	Persoz hardness
T1	0.844	4.0	0.120
T1S	0.384	2.05	0.041
T2S	0.215	0.81	0.077
E1S	0.531	3.60	0.044
P1S	0.222	1.09	0.039
S1S	0.125	0.58	0.027

soft segments is shifted to larger degree of conversion. Moreover, the apparent activation energy at this step increases with extent of degradation and is the lowest among all the copolymers. At this step, hydroxyl terminated PDMS is produced which then depolymerize, starting from chain ends, and forms volatile cyclic oligomers. This siloxane rearrangement via kinetically favored path requires much less activation energy as compared to the high siloxane Si–O bond energy of $460.5 \text{ kJ mol}^{-1}$ [40]. At higher temperature, radical mechanism of PDMS degradation occurs through homolytic Si–CH₃ bonds scission leading to cross-linking, which results in increase of activation energy [41].

Surface properties of the coatings obtained from PU-PDMS copolymers

Roughness

The surface of PU-PDMS films are smooth since the R_a and R_z values are very low as resulted from roughness data presented in Table 8. The largest $R_a = 0.844 \mu\text{m}$ and $R_z = 4.0 \mu\text{m}$ reveals unmodified sample T1. For the coatings containing siloxane both parameters are lower which may results from the migration of siloxane chains toward the film surface as described in [16]. This production of smoother surface may be additionally confirmed by the lowest R_a and R_z for S1S copolymer with the largest siloxane amount.

Contact angle and FSE

The contact angles for the coatings and the FSE components were presented in Table 9.

The least contact angles Θ were observed for the virgin polyurethane coating T1. The contact angles increase with the increasing polarity of the model liquids in order: diiodomethane, formamide, and water. The contact angles Θ for every model liquid in the poly(urethane-siloxane) case were larger than in the virgin polyurethane and were not affected by the kind of polyol used. This can be attributed to migration of pendant siloxane chain to the surface of coatings.

Similar trend is observed for the FSE results. The PU-PDMS coatings are generally slightly polar materials with the FSE in the range $14.7\text{--}21.1 \text{ mJ m}^{-2}$. On the total, FSE mainly influence γ_S^{LW} compound related to long-range interactions in van Oss–Good method. In case of method by Owens–Wendt, the contribution of γ_S^{d} compound related to dispersion interactions is significant. The maximal value of FSE (28.9 mJ m^{-2}) reveals the virgin polyurethane sample. Introduction of 1.25 mol% of S-PDMS results in lowering this value to 17.6 mJ m^{-2} (T1S), which additionally confirms hydrophobic character of siloxane used. The amount of S-PDMS in the coating made from T2S is lower (5.2 wt%) than in corresponding T1S (8.0 wt%) which results in larger FSE (18.7 mJ m^{-2}) for the former. For comparison, the FSE found in previous study of polyurethane synthesized with MDI, PTMO 1000, and BD but with about 5.5 wt% of linear L-PDMS modification was larger and amounted to 28.3 mJ m^{-2} [42]. The FSE of PU-PDMS depends on polyol used. The lowest value of FSE as expected revealed S1S sample, where additional siloxane structures were derived from soft segments participate in lowering of FSE due to migration to polymer surface. Among side-chain polysiloxane-modified PU-PDMS the largest FSE reveals E1S sample, which results from contribution of polar PEG.

Table 9 Experimental values of the contact angles and the FSE parameters calculated by van Oss–Good and Owens–Wendt methods

Sample	Contact angle measurements Θ/deg			Parameters of the FSE/ mJ m^{-2}										
				van Oss–Good method					Owens–Wendt method					
	Diiodomethane	Formamide	H ₂ O	γ_S^{LW}	$\gamma_S^{\text{+}}$	$\gamma_S^{\text{-}}$	γ_S^{AB}	γ_S	γ_S^{d}	γ_S^{p}	γ_S	γ_S^{d}	γ_S^{p}	γ_S
T1	60.8 ± 1.9	74.0 ± 1.3	88.0 ± 1.0	28.1	0	6.5	0	28.1	24.9	4.0	28.9	27.0	1.1	28.1
T1S	80.0 ± 1.5	90.4 ± 2.3	104.7 ± 2.1	17.5	0	2.0	0	17.5	16.2	1.4	17.6	17.0	0.5	17.5
T2S	77.9 ± 2.1	88.7 ± 1.7	103.7 ± 0.6	18.6	0	2.0	0	18.6	17.3	1.4	18.7	18.2	0.5	18.7
E1S	73.3 ± 2.3	82.4 ± 1.9	95.5 ± 2.4	21.1	0	4.5	0	21.1	18.6	3.2	21.8	19.7	1.4	21.1
P1S	75.6 ± 1.7	88.6 ± 2.2	104.7 ± 1.7	19.8	0	1.6	0	19.8	18.9	0.9	19.8	19.9	0.2	20.1
S1S	85.5 ± 1.7	94.7 ± 2.4	105.5 ± 2.2	14.7	0	3.0	0	14.7	13.2	1.8	15.0	14.3	0.5	14.8

Persoz hardness

The Persoz hardness of the polyurethane coatings on stainless steel is presented in Table 8. The obtained coatings are generally soft with the relative hardness in the range of 0.120–0.027. The largest Persoz hardness reveals unmodified PU sample, which may result from higher cohesive forces in urethane segments leading to relatively denser physical cross-linking. The drop in hardness for all the coatings which were obtained from siloxane-modified samples was observed. The siloxane-modified sample T2S composed of PTMO 2000 soft segments show largest hardness than the corresponding sample synthesized with PTMO 1000 which may result from lower siloxane amount in T2S sample. The Persoz hardness values for the obtained PU-PDMS coatings are generally lower than for poly(urethane-siloxane) anionomers modified with side-chain siloxane for which this value amounts to ca. 0.245 [43].

Conclusions

A series of PU-PDMS containing different soft segment structures was successfully synthesized. It was concluded that molecular mass of PU-PDMS copolymers depend on polyol used. Thermal degradation of PU-PDMS in nitrogen is basically a two stage process, but, in air, it is more complex. The temperature of 5 % mass loss in air for side-chain siloxane-modified polyurethanes decreases in order: S1S > T1S > E1S > T2S > P1S. In contrast to nitrogen atmosphere, the modification of polyurethane with S-PDMS resulted in lowering $T_5\%$ in air. The apparent activation energy at first step of degradation in nitrogen generally increases with the extent of conversion which may result from complex mechanism related to formation of decomposition products. At the second stage, E_a remains almost unaffected except S1S sample with PDMS soft segments. The PU-PDMS coatings are generally slightly polar materials with the FSE in the range 14.7–21.1 mJ m⁻². Hydrophobic character of side-chain siloxane on surface properties of the PU-PDMS coatings was confirmed. Moreover, the FSE of the PU-PDMS depends on polyol used. The obtained coatings are generally soft with the relative hardness in the range of 0.120–0.027. The largest Persoz hardness reveals unmodified PU sample, which may result from higher cohesive forces in urethane segments leading to relatively denser physical cross-linking than in siloxane-modified samples.

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