Poly(urethane–siloxane)s based on hyperbranched polyester as crosslinking agent: synthesis and characterization

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Abstract: A series of novel polyurethane crosslinked structures (PUs) was prepared from α,ω-dihydroxy-(ethylene oxide–poly(dimethylsiloxane)–ethylene oxide) (EO–PDMS–EO), 4,4'-methylenediphenyl diisocyanate and Boltorn® hyperbranched polyester of the third pseudo generation. The hydroxy-functional hyperbranched aliphatic polyester with 26 end groups was used as a crosslinking agent. In order to improve the compatibility of all the reactants during the synthesis, the PU samples were prepared by two-stage, step-growth polymerization in solution. The content of the soft EO–PDMS–EO segments was varied in the range from 15 to 40 wt. %. The influence of the EO–PDMS–EO content on the swelling behavior, crosslink density, hardness, and the thermal and surface properties of the synthesized PUs was investigated. The structure of the synthesized polyurethanes was confirmed by the presence of specific bands in the Fourier transform infrared spectra. Swelling studies were performed to determine the crosslink density and polyurethane networks with lower EO–PDMS–EO contents had higher crosslink densities. The glass transition temperature of the synthesized PUs, determined by differential scanning calorimetry, slightly increased from 50 to 58 °C on decreasing the EO–PDMS–EO content because of the higher crosslink density of the samples. Increasing the EO–PDMS–EO content led to better thermal stability, as was evidenced by the onset temperature of weight loss. The surface of the polyurethane networks became more hydrophobic with increasing EO–PDMS–EO content. The surface morphology of synthesized polyurethanes was analyzed by scanning electron microscopy.

Keywords: polyurethane networks; hyperbranched polyester; poly(dimethylsiloxane); crosslink density; thermal properties; surface properties.

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INTRODUCTION

Polyurethanes (PUs) based on hyperbranched polyesters (HBPs) have attracted great attention due to their excellent mechanical properties and good biocompatibility. Additionally, the presence of a large number of end functional groups in HBPs, good compatibility with different materials, the presence of nanoscale cavities within the structure of HBPs contribute to the unique physical and chemical properties of polyurethane networks.[1,2] Potential applications of polyurethanes based on HBPs in the fields of coatings, drug delivery, membranes and nanomaterials have been reported.[1–4] Generally, PU networks are prepared using urethane prepolymers combined with crosslinkers having a functionality of three or more.[5] The HBPs which have a large number of end hydroxyl groups can react with the isocyanate groups of the urethane prepolymer and form networks.[6] In addition, they contain a large number of ester groups, which could create H-bonds with the carbonyl and amine groups of adjacent chains in the polyurethane networks. The properties of PU networks depend especially on the composition and chemical structure of all components, on the molecular weight of the soft segments and particularly on the nature of the employed crosslinking agent.[7]

The introduction of poly(dimethylsiloxane) (PDMS) into the polymer chains has the advantage of imparting some of the attractive properties of PDMS to polyurethanes, such as high flexibility, biocompatibility, excellent thermal, oxidative and hydrolytic stability, and low surface energy.[8–11] Combinations of polyurethanes and poly(dimethylsiloxane)s has attracted special attention due to the good thermal stability and high flexibility at low temperatures given by the PDMS part and the enhanced mechanical strength and abrasion characteristics conveyed by the polyurethane. However, PDMS has a low surface energy and a low value of the solubility parameter, which result in incompatibility of PDMS with other polymers. In order to overcome this, a mixture of macrodiols or a special type of macrodiols was used in order to increase the compatibility of the reactants and, therefore, to achieve better mechanical properties.[12–17]

Recently some papers dealing with the use of hyperbranched polymers for the synthesis of PU crosslinked structures have been published. Czech *et al.* and Okrasa *et al.*[18,19] synthesized polyurethane networks using Boltorn® HBP of the fourth pseudo generation polyethers or polyesters and 4,4'-methylenediphenyl diisocyanate (MDI) or 4,4'-methylenedicyclohexyl diisocyanate. Cao and Liu[20] prepared a series of novel hyperbranched polyurethanes using a second pseudo generation hyperbranched polyester as the crosslinker and investigated the phase transition behavior and the morphology of the products. Maji and Bhowmick[21] used Boltorn® HBPs of the second, third and fourth pseudo generations for the preparation of PUs. Moreover, the results of a study[22] are available on poly(urethane–siloxane) networks based on isophorone diisocyanate, *α,ω*-dihydroxybu-

tyl-poly(dimethylsiloxane) and a hybrid diol containing hydrolysable Si–OC$_2$H$_5$ groups besides OH groups in which crosslinked structure was formed by silica domains. However, to the best of our knowledge, PDMS macrodiols have not been used for the preparation of poly(urethane–siloxane) crosslinked structures based on Boltorn® HBP of the third pseudo generation. Polyurethane networks prepared from this specific combination of reactants enables the exploitation of their good features and simultaneously introduces good thermal and surface properties, swelling ability, rubber elasticity and other properties which are important for different applications, especially for coatings.

In the work presented herein, a series of novel polyurethane crosslinked structures based on ethylene oxide–poly(dimethylsiloxane)–ethylene oxide (EO––PDMS–EO) as soft segments and 4,4'-methylenediphenyl diisocyanate and hyperbranched polyester of the third pseudo generation (BH-30) as components of the hard segments was prepared. In the synthesis of PU networks, the ethylene oxide blocks served as compatibilizers between the non-polar PDMS prepolymer and the polar MDI and BH-30. In addition, in order to improve the compatibility of all reactants during the synthesis, PU samples were prepared by two-step, step-growth polymerization in solution. The EO–PDMS–EO content was varied in the range from 15 to 40 wt. %. The influence of the EO–PDMS–EO content on the swelling behavior, hardness, and the thermal and surface properties of the synthesized PU samples were investigated.

EXPERIMENTAL

Materials

α,ω-Dihydroxy-(ethylene oxide–poly(dimethylsiloxane)–ethylene oxide) (α,ω-dihydroxy-(EO–PDMS–EO)), supplied by ABCR, (M_n = 1000 g mol^{-1}) was dried over molecular sieves (0.4 nm) before use. The number-average molecular weight (M_n) determined by ^{1}H--NMR spectroscopy,[23] was 1200 g mol^{-1} and this value was used in the calculations of the compositions of the reaction mixtures for the synthesis of the polyurethanes. The molecular weight of the central PDMS-block was 1090 g mol^{-1}, whereas the terminal ethylene oxide sequences consisted of one unit. 4,4'-Methylenediphenyl diisocyanate (MDI) (supplied by Aldrich) with an isocyanate content of 33.6 wt. %, was used as received. Commercially available Boltorn® hydroxy-functional aliphatic hyperbranched polyester of the third pseudo generation (BH-30) was kindly supplied by Perstorp Specialty Chemicals AB (Sweden) and dried at 50 °C under vacuum for 48 h prior to use. The aliphatic hyperbranched polyester is based on 2,2-bis(hydroxymethyl)propionic acid as the monomer and tetrafunctional ethoxylated pentaerythrytol as the core.[24] For the exact calculation of the amounts of all components necessary for the synthesis of polyurethanes, the value of the molecular weight determined by vapor pressure osmometry (M_n= 3080 g mol^{-1}) and hydroxyl number of BH-30 determined by the titration method (HN = 474.1 mg KOH g^{-1}) were used.[25] Consequently, the exact functionality, f_n, of the used BH-30 was calculated (f_n = 26). The solvent N-methylpyrrolidone (NMP), supplied by Across, was dried over calcium hydride and distilled before use. Tetrahydrofuran (THF), supplied by J. T. Baker, was refluxed with lithium aluminum hydride and distilled before use. Toluene (from Lach-Ner) was used as received. The catalyst was stannous octanoate (Sn(Oct)$_2$), supplied by Aldrich.

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Synthesis of the polyurethanes

A series of polyurethanes was synthesized by two-stage, catalyzed step-growth polymerization in solution using α,ω-dihydroxy-(ethylene oxide–poly(dimethylsiloxane)–ethylene oxide) macrodiol, 4,4'-methylenediphenyl diisocyanate and a hyperbranched aliphatic polyester as the crosslinking agent. This series consisted of four samples (PU3-40, PU3-30, PU3--20 and PU3-15) of different EO–PDMS–EO contents. The last two numbers in the designation of the synthesized samples represent the weight percent of EO–PDMS–EO in the reactants. The mixture of solvents NMP/THF was used as the reaction medium. This solvent mixture and the used ratio (NMP/THF, 7/1 v/v) were found to be the best choice for the synthesis of the investigated PUs. The molar ratio of the reactive –NCO and –OH groups (from HBP and α,ω-dihydroxy-(EO–PDMS–EO)) for all samples was kept at a constant value of 1.05.[16] The amount of the catalyst was 0.15 mol % Sn(Oct)$_2$, based on α,ω-dihydroxy-(EO–PDMS––EO).[16] The composition of the synthesized PUs and weight of the reactants used for the synthesis of the PUs are presented in Table I. As an example, the synthesis of a PU network based on BH-30 with 40 wt. % soft EO–PDMS–EO segments (PU3-40 sample, Table I) is described.

TABLE I. Composition of the synthesized PUs and weight of reactants used for their preparation

Sample	Content of soft EO–PDMS–EO segment wt. %[a]	EO–PDMS–EO g	BH-30 g	MDI g
PU3-40	40	5.000	3.040	4.463
PU3-30	30	4.000	4.013	5.321
PU3-20	20	3.000	5.382	6.619
PU3-15	15	2.500	6.461	7.707

[a]Soft segment content = $[m(\text{EO–PDMS–EO})/(m(\text{MDI}) + m(\text{BH-30}) + m(\text{EO–PDMS–EO}))] \times 100$

A four necked round-bottom flask equipped with a mechanical stirrer, an inlet for dry argon, a reflux condenser and a dropping funnel was charged with 5.000 g (4.167 mmol) of α,ω-dihydroxy-(EO–PDMS–EO), 4.463 g (17.85 mmol) of 4,4'-methylenediphenyl diisocyanate, 35 mL of NMP and 5 mL of THF. The flask was heated to 40 °C in a silicone oil bath and the reaction started by the introduction of 0.41 mL of a solution of stannous octanoate in NMP. The reaction mixture was stirred for 30 min at 40 °C to prepare the NCO-terminated prepolymer, which was considered to be obtained when the theoretical –NCO content (4.94 wt. %) was attained.[16] The content of –NCO groups during the reaction was determined using the dibutylamine back titration method.[26] In the second stage of reaction, 3.040 g (0.9870 mmol) of hyperbranched polyester was dissolved in 26 mL NMP and added drop-wise into the NCO-terminated prepolymer solution, and the reaction was continued at 40 °C for 1 h. The obtained mixture was then cast into glass dish, previously lubricated with a very small amount of silicone oil. The crosslinking reaction was continued in a force-draft oven at 50 °C for 50 h and 1 h at 110 °C and finally 10 h at 50 °C in a vacuum oven at 0.5 mm Hg. The polyurethane samples were obtained as yellow films (thickness of about 2 mm). The films were kept in a desiccator. Samples were maintained at room temperature for about two weeks before characterization.

Characterization of the polyurethanes

The FTIR spectra of the PUs were recorded on an ATR NICOLET 380 spectrometer. The scanning range was from 400 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and 64 scans were collected for each sample.

Swelling measurements were performed on rectangular-shaped specimens, with dimension of 1.2×2.1×0.20 cm^3 (weighing approximately 0.20 g), by immersion of the samples in toluene for 48 h and in THF for 24 h at room temperature. The applied duration of the swelling measurements in both solvents was chosen because this was sufficient to achieve equilibrium swelling of the examined PUs, which was previously confirmed by separate periodical measurements of the weight of swollen samples until a constant mass was obtained. After swelling, the swollen samples were dried in vacuum oven at 0.5 mm Hg and 50 °C to remove the absorbed solvent and the weight of the deswollen specimens was measured. Data from three different specimens of each PU sample were averaged. Values of the equilibrium degree of swelling, q_e, were calculated using conventional gravimetric method and the following equation:

$$q_e = \frac{w - w_0}{w_0} \tag{1}$$

where, w_0 and w are the sample weights before and after swelling, respectively.

The crosslink density, v, of the PUs was calculated according to the Flory–Rehner Equation: [27]

$$v = -\frac{\ln\left(1 - V_{PU}\right) + V_{PU} + \chi V_{PU}^2}{V_s\left(V_{PU}^{1/3} - \dfrac{V_{PU}}{2}\right)} \tag{2}$$

where, χ is the interaction parameter between the solvent (THF) and polymer, which is equal to 0.34,[28] V_s is the molar volume of THF (81.7 cm^3 mol^{-1})[28] and V_{PU} is the volume fraction of the crosslinked polymer in the swollen specimen, which was calculated from the density of the PUs (ρ_{PU} from 1.065 g cm^{-3} for PU3-15 to 1.149 g cm^{-3} for PU3-40), the density of THF ($\rho_s = 0.889$ g cm^{-3}),[29] and the weights of the swollen and deswollen PU samples.[27]

Differential scanning calorimetry (DSC) measurements were realized using a DSC Q1000V9.0 Build 275 thermal analyzer. The samples were analyzed under a nitrogen atmosphere from –90 to 230 °C, at a heating and cooling rate of 10 °C min^{-1}. The glass transition temperatures (T_g) of the PU networks were determined from the second heating run as an average of three measurements.

Thermogravimetric analysis (TGA) was performed using a TGA Q500 V6.3 Build 189 instrument under dynamic nitrogen, in the temperature range from 25 to 700 °C. The gas flow rate was 50 cm^3 min^{-1} and the heating rate was 10 °C min^{-1}. The weight of the samples was approximately 10 mg.

Wide angle X-ray scattering (WAXS) was performed using a PW1710 diffractometer with CuK_α radiation employing a copper anode (tube: 40 kV, 30 mA, $\lambda = 0.154178$ nm). The diffraction patterns were obtained in the Bragg angle range of 5–50°. The scan speed was 0.02 s per step in all measurements.

The hardness measurements were performed using a Shore A apparatus (Hildebrand, Germany) on polymer films. The results of the measurements were registered one second after penetration of the needle into the sample. The average of at least five measurements was used.

The surface morphology of the PU samples was analyzed by field emission scanning electron microscopy (SEM). The samples were adhered to aluminum sample holders and sputter coated with Au layer. The microphotographs of the PUs were obtained using a JEOL JSM--6610 instrument at a working distance of *ca*. 14 mm and an accelerating voltage of 20 or 30 kV.

Water contact angle measurements of the PU samples were performed on a Krüss DSA100 instrument using the sessile drop method. Single 20-µL drops of distilled water were deposited on the surface of the polymer films and the contact angles were measured after 30 s, at a temperature of 26 °C. In all cases, at least five measurements were made, and the average contact angle was then calculated.

RESULTS AND DISCUSSION

A series of novel polyurethanes with crosslinked structure based on α,ω-di-hydroxy-(ethylene oxide–poly(dimethylsiloxane)–ethylene oxide), 4,4'-methyl-enediphenyl diisocyanate and Boltorn® hyperbranched polyester of the third pseudo generation was synthesized by two-stage, step-growth polymerization in solution. During the synthesis of all samples, the total molar ratio of –NCO and –OH groups (from HBP and α,ω-dihydroxy-(EO–PDMS–EO)) was kept constant. The chemical structures of α,ω-dihydroxy-(EO–PDMS–EO), MDI and the hyperbranched polyester of the third pseudo generation (BH-30) are shown in Fig. 1. The results obtained in a previous work showed that polymerization in the melt and incompatibility of the non-polar EO–PDMS–EO with polar reactants, *i.e.*, hyperbranched polyester of the second pseudo generation and MDI, led to the formation of heterogeneous PU networks.[30] Therefore, in this work a two-step, step-growth polymerization in solution was applied to improve the compatibility between reactants during the synthesis of the PU networks, using the mixture NMP/THF as the reaction medium. In the first stage of reaction, the NCO-terminated prepolymer was synthesized in an argon atmosphere by reacting hydroxy-terminated EO–PDMS–EO prepolymer with MDI until the theoretical –NCO content of 4.94 wt. % was attained. In the second stage of the reaction, the NCO–terminated prepolymer was reacted with multifunctional BH-30 as crosslinker to form the PU network. The EO–PDMS–EO content was varied in the range from 15 to 40 wt. % (Table I). Thus, a different degree of chemical crosslinking was in a controlled manner brought into the structure of the synthesized PUs through the hard segments (BH-30 and MDI).

FTIR Spectroscopy of the synthesized polyurethane networks

The structure of the synthesized polyurethanes was verified by FTIR spectroscopy. Typical infrared spectra of the hyperbranched polyester BH-30 and the polyurethane samples are presented in Fig. 2. In FTIR spectrum of the hyperbranched polyester, hydroxyl groups as a broad absorption band at 3300 cm^{-1} can be observed, while the characteristic peak at 1723 cm^{-1} was ascribed to the carbonyl ester groups. The IR absorption bands characteristic for the ether groups (1010–1120 cm^{-1}), C–O linkage of ester groups (1040–1210 cm^{-1}) and –CH$_2$–

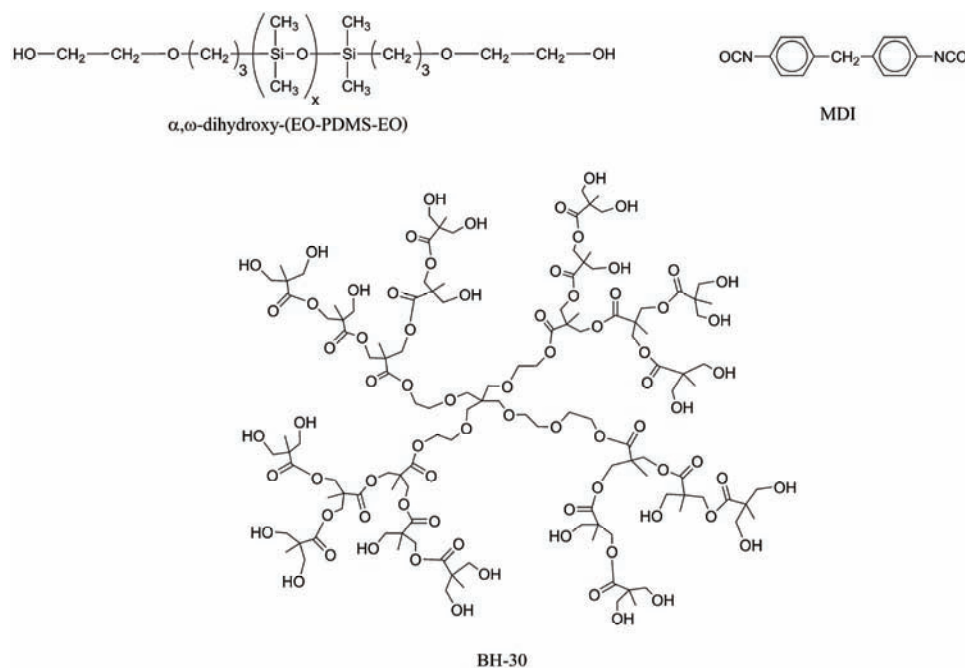and –CH$_3$ groups (2900–3000 cm^{-1}) can also be observed in the FTIR spectrum of BH-30.

Fig. 1. Chemical structures of α,ω-dihydroxy-(EO–PDMS–EO), MDI and the hyperbranched polyester of the third pseudo generation (BH-30).
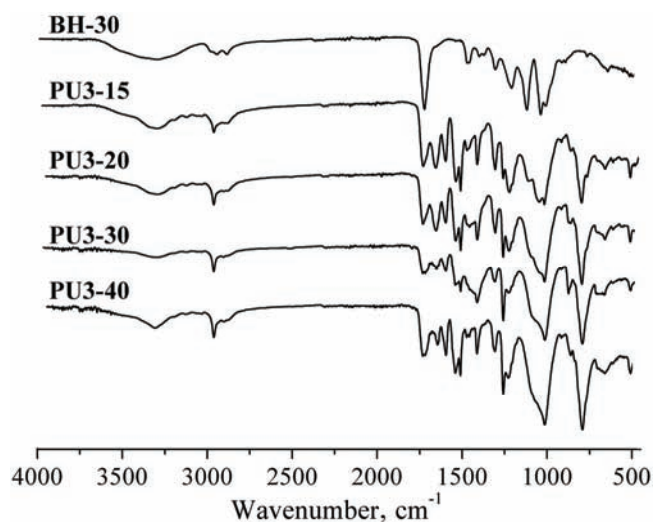

Fig. 2. FTIR Spectra of the hyperbranched polyester BH-30 and the synthesized polyurethanes.

In FTIR spectra of the synthesized polyurethane samples, the bands around 3310 cm^{-1} (H-bonded urethane N–H stretch) and 1710 cm^{-1} (H-bonded urethane C=O) were assigned to the urethane linkage. The amide II and amide III bands for polyurethanes appeared at 1537 and 1258 cm^{-1}, respectively. The carbonyl ester groups show a characteristic band at 1725 cm^{-1}. The intensive bands at 1016 and 1080 cm^{-1} correspond to the Si–O–Si and C–O–C groups. The absorption band at around 790 cm^{-1} was ascribed to the Si–CH$_3$ linkage. The rest of the bands at 2961, 2903 and 2875 cm^{-1} were assigned to the presence of symmetric and asymmetric –CH$_2$– and –CH$_3$ groups, while the bands at 1597 and 1413 cm^{-1} were assigned to the aromatic C=C. As shown in Fig. 2, none of the samples exhibited an apparent band at 2270 cm^{-1}, which means that all the –NCO groups were consumed during the reaction.

Swelling measurements and hardness of the synthesized polyurethane networks

The swelling behavior of the synthesized PU samples was investigated in THF and toluene. The values of equilibrium degree of swelling of the PUs determined in toluene and in THF are summarized in Table II. The equilibrium swelling degree of samples increased from 0.783 to 1.889 (in THF) and from 0.003 to 0.188 (in toluene) as the EO–PDMS–EO content increased from 15 to 40 wt. %. Therefore, the equilibrium degree of swelling was found with increasing soft EO–PDMS–EO content (Fig. 3). The solvent uptake was much higher after immersion of synthesized PUs in THF (Table II). Although the solubility parameters of THF and toluene are similar,[28] the results obtained in this work indicate that better solvatation of the PU samples was achieved in THF. The reason for this behavior is the difference in polarity between THF and toluene; hence, the polar THF can easily diffuse into the PU networks leading to better solvatation of the PU samples in THF.

TABLE II. The equilibrium swelling degree, q_e, crosslink density, v, glass transition temperature, T_g, and water contact angle of the synthesized PUs

Sample	q_e		$v \times 10^4$ / mol cm^{-3}	T_g^a / °C	Water contact angle, °
	THF	Toluene	THF		
PU3-40	1.8897±0.0050	0.1876±0.0031	3.76	52.1±0.1	93.9±0.9
PU3-30	1.5884±0.0044	0.1774±0.0020	5.92	57.0±0.2	87.3±1.1
PU3-20	0.8701±0.0040	0.1414±0.0031	17.95	58.2±0.1	86.6±0.8
PU3-15	0.7828±0.0035	0.0031±0.0007	23.11	50.4±0.1	87.0±1.1

[a]Determined by DSC analysis from the second heating run

Calculation of crosslink density of the synthesized PUs was performed using the results obtained from equilibrium swelling in THF according to the Flory––Rehner Equation.[27] These results are shown in Table II. It can be observed that the crosslink density of the PU samples increased with decreasing EO–PDMS––EO content. Additional crosslinking could have occurred through the formation

of allophanates, which also would decrease the swelling ability of the PUs in THF. Thus, for the series of synthesized PUs, the polymers with a higher cross-link density values are less flexible and hence have a lower solvent uptake.
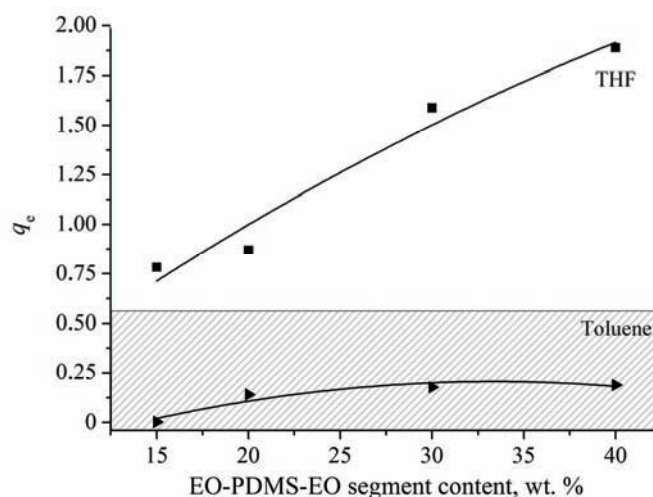

Fig. 3. Equilibrium degree of swelling, q_e, of the synthesized PUs determined in toluene and in THF *vs*. the content of EO–PDMS–EO.

The results of hardness measurements show that the hardness of the synthesized polyurethanes increased with decreasing EO–PDMS–EO content, from 83 Shore A to 88 Shore A. The PU samples with lower EO–PDMS–EO content showed slightly higher hardness because of the higher crosslink density of the samples.

Thermal properties of the synthesized polyurethane networks

Determination of the glass transition temperature (T_g) of the synthesized samples was performed using DSC at a heating rate of 10 ° min^{-1}, under a nitrogen atmosphere. The DSC curves of the synthesized PU samples obtained during the first and second heating runs are shown in Fig. 4. The broad endothermic peak around 150 °C, observed in the DSC curves during the first heating run, corresponds to H-bond interactions in PU samples.[2] This peak was absent in the curve obtained during the second heating run, indicating that the samples were completely cured. As a result, the T_g values of the polyurethane samples determined in the second run were higher in comparison with those obtained in the first run. According to the literature,[13] the EO–PDMS–EO prepolymer exhibits two T_gs, at –105 and –8 °C, while the T_g of BH-30 is 31 °C.[31] The T_g values of the PUs synthesized in this work, determined during the second heating run, were in the range from 50 to 58 °C (Table II). The obtained results show that the T_g values of these PU samples depended on the hard segment (MDI and BH-30)

content. As the content of hard segments increased, the values of the T_g also increased, except for the last sample in PU series (sample PU3-15). The increase of T_g is due to the higher crosslink density of PUs. Crystallization or melt peaks were not observed for any of the samples.
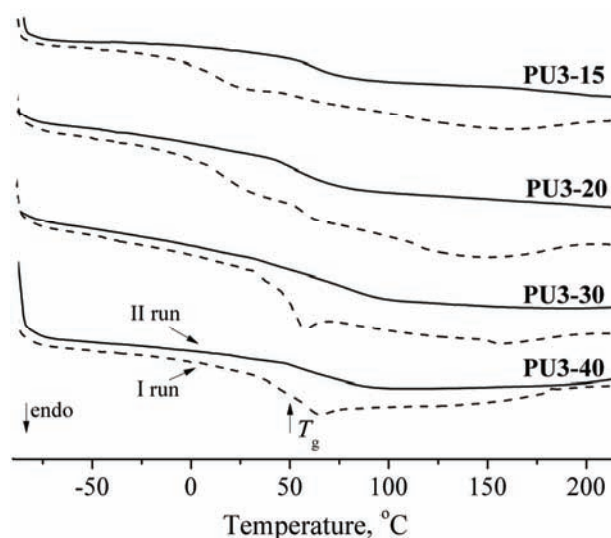

Fig. 4. DSC Thermograms of the synthesized polyurethane samples obtained during the first and second heating run.

The thermal stability of the synthesized PU samples was investigated by thermogravimetric (TG) analysis at heating rate of 10 °C min^{-1} under a dynamic nitrogen atmosphere. The recorded TG curves and the differential TG (DTG) curves for selected PU networks presented in Fig. 5, while some characteristic temperatures of thermal degradation and the temperatures corresponding to the DTG peaks are listed in Table III. From the presented results, it can be seen that weight loss of these PU networks started between 266 and 298 °C, as observed from the temperature of 15 % mass loss, and the temperature increased with increasing content of EO–PDMS–EO in the PU networks (except for the sample PU3-40). From Fig. 5 it is not possible to observe any specific trend in the thermal stability of the synthesized PU network between the temperatures corresponding to 15 and 50 % of weight loss. In the very short temperature range, between temperatures, which correspond to the 50 and 70 % of weight loss, thermal stability of PU samples increases with increasing crosslink density, which is in accordance with results given in the literature.[20,21] However, at higher temperatures, thermal stability increased with increasing soft segment content. From the obtained results, it can be concluded that mechanism of the thermal degradation of the synthesized PU samples is very complex and influenced by the soft EO–PDMS–EO content, *i.e.*, the crosslink density.
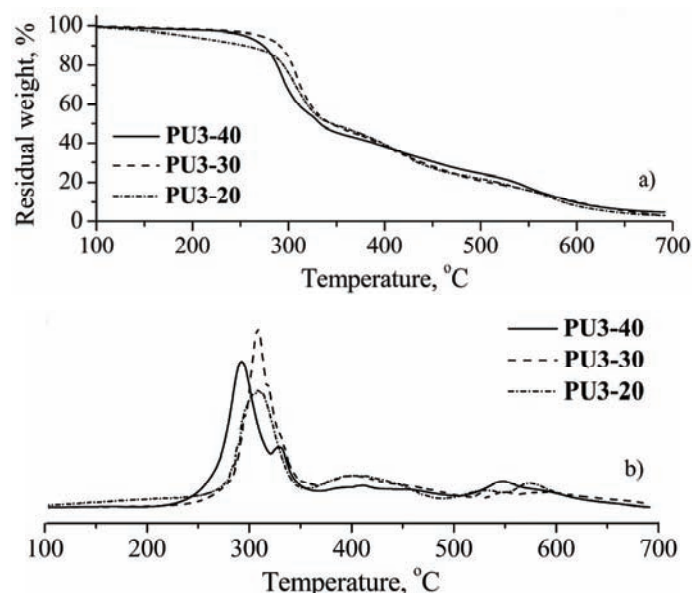
Fig. 5. TG and DTG Curves of the synthesized PU samples, determined at
a heating rate of 10 °C min^{-1}, under a nitrogen atmosphere.

TABLE III. Characteristic temperatures of thermal degradation and temperatures of DTG peaks

Sample	$T_{15\%}$ / °C	$T_{50\%}$ / °C	$T_{70\%}$ / °C	$T_{95\%}$ / °C	T_{max} / °C
PU3-40	283	333	453	673	292/329/412/548
PU3-30	298	344	439	654	308/318/403/565
PU3-20	285	345	434	635	305/309/404/550
PU3-15	266	337	425	640	305/318/401/561

From the DTG curves presented in Fig. 5 and results listed in Table III, it could be concluded that thermal degradation of the synthesized PU networks is a four-step process in nitrogen. During the first step of the thermal degradation, urethane bonds, which are thermally the weakest links in the PU samples, decomposed, resulting in the dissociation to the original macrodiol and isocyanate, the formation of a primary or secondary amine, an alkene and carbon dioxide.[32] During the second step of the thermal degradation, the ester components decomposed, while PDMS degraded in the third step. Aromatic compounds decomposed in the temperature region 500–600 °C (Table III).

WAXS Analysis of the synthesized polyurethane networks

The X-ray diffractograms of the synthesized PU samples are given in Fig. 6. All diffractograms contain two amorphous halos at $2\theta = 12°$, arising from the phase-separated PDMS segments, and at $2\theta = 20°$, arising from the non PDMS-containing segments, *i.e.*, MDI and BH-30.[33] This behavior demonstrates that the

PDMS formed a completely separated phase in the polyurethanes at room temperature. There was no evidence of any crystallinity from WAXS analysis, which is consistent with the data obtained by DSC.
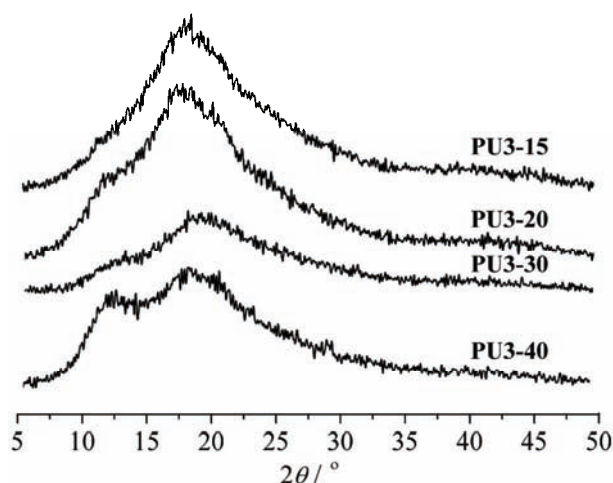

Fig. 6. X-Ray diffractograms of the synthesized polyurethane samples.

Investigation of morphology of the synthesized polyurethane networks

The surface morphology of PU films was investigated by scanning electron microscopy (SEM) and the obtained microphotographs of the PU samples are shown in Fig. 7. It is well known that polyurethanes based on PDMS show the presence of microphase-separated structures because of the large differences between solubility parameters of PDMS and the urethane components.[33] From the obtained results, it could be concluded that the surface morphology of the PU samples based on EO–PDMS–EO and the hyperbranched polyester is quite complex and significantly affected by the content of EO–PDMS–EO and the crosslink density. The SEM microphotographs showed that the hard domains had some physical associations/connectivity (hydrogen bonding) with each other, an effect that is thought to become more pronounced on the surface of the sample PU3-40. Furthermore, the SEM results of the samples PU3-30 and PU3-15 indicated increased homogeneity of the samples and improved compatibility of all components (Fig. 7). Therefore, the general view of the surface revealed a homogeneous structure, characteristic of the synthesized crosslinked polymers. The SEM results of the samples indicated increased phase mixing with increasing crosslink density of PUs.

The EDX analysis, performed to identify the type of the atoms present in the polyurethane samples at a depth of 100–1000 nm from the surface,[22] confirmed the presence of all expected elements (C, O, Si and N). The results obtained from

EDX analysis are displayed in Fig. 8 and tabulated in Table IV. It could be noticed that the N-percentage determined by EDX analysis on the surface of samples decreased with increasing EO–PDMS–EO content, *i.e.*, with decreasing urethane content. On the other hand, Si-percentage on the surface of samples increased with increasing of EO–PDMS–EO content. This suggests that there is increased content of PDMS on the surface of the PU samples, which confirms the tendency of PDMS to migrate to the surface of PU networks. Additional confirmation of this conclusion was obtained from theoretically calculated Si wt. % in the synthesized samples (from 4.54 for PU3-15 to 12.15 wt. % for PU3-40), which were smaller than the values experimentally determined by EDX surface analysis. These results are in agreement with data obtained by water contact angle measurements of the PU samples.
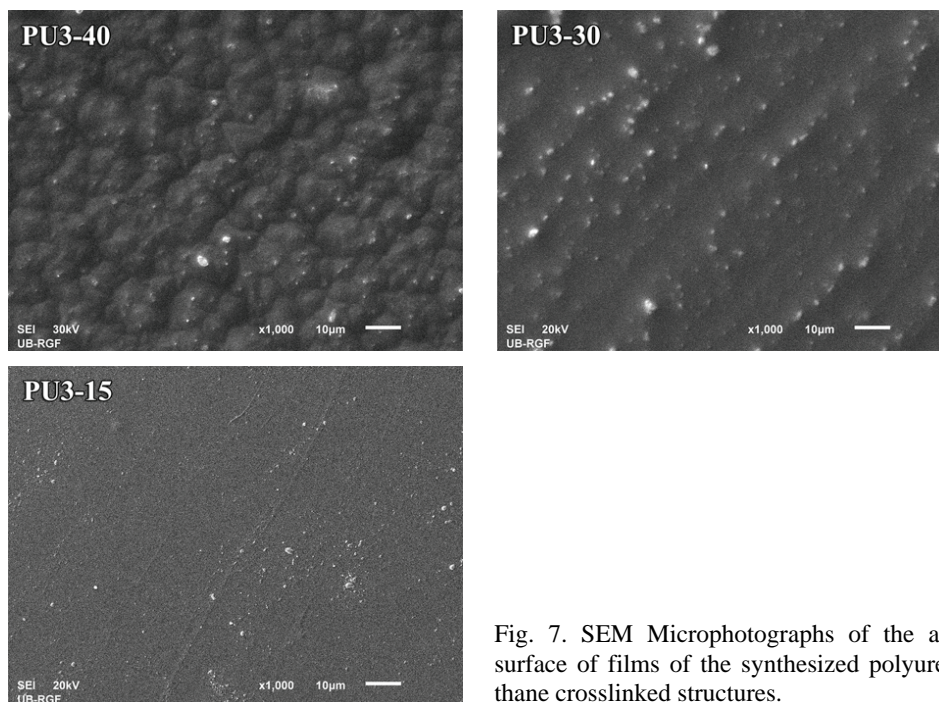

Fig. 7. SEM Microphotographs of the air surface of films of the synthesized polyurethane crosslinked structures.

Water contact angle of the synthesized polyurethane networks

The wettability and hydrophobicity of the surface of the synthesized PU samples were investigated by static water contact angle measurements and the obtained results are reported in Table II. Samples that have a water contact angle greater than 90° are considered hydrophobic. The value of the water contact angle for the PU networks increased from 86.6 to 93.9° with increasing content of EO–PDMS–EO in the polymers. This behavior may be ascribed to a tendency

of the PDMS segments to migrate to the surface caused by the very low surface energy of PDMS, which hence covered most of the surface of the Pus, which resulted in a reduction of the surface tension. As expected, the wettability of the polyurethane networks decreased, *i.e.*, the hydrophobicity increased, with increasing weight fraction of EO–PDMS–EO.
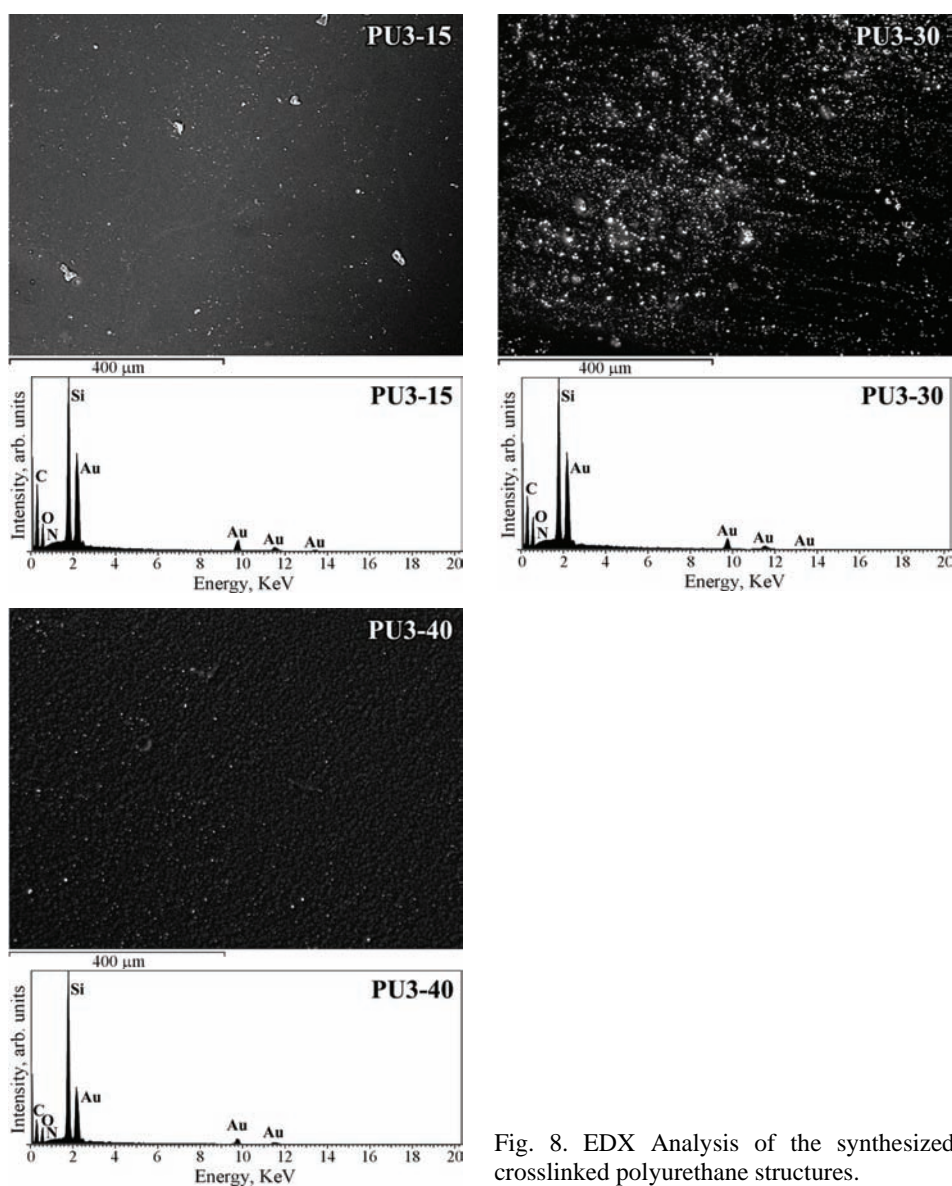

Fig. 8. EDX Analysis of the synthesized crosslinked polyurethane structures.

In comparison with the PUs based on BH-30 prepared by other authors, the PU networks synthesized in this study had a similar crosslink density.[21] In addition, the thermal stability of the synthesized PU networks was similar to the thermal stability of other PU networks based on PDMS[34] and slightly higher than the thermal stability of some PUs based on HBP.[35] In addition, a good waterproof performance of the synthesized PUs was obtained, which could be improved by increasing the EO–PDMS–EO content.

TABLE IV. Results of EDX analysis of the synthesized PUs

Element	PU3-15		PU3-30		PU3-40	
	wt. %	at. %	wt. %	at. %	wt. %	at. %
C K	60.34	69.72	54.56	60.77	52.63	63.64
N K	6.89	6.97	5.03	5.24	4.63	4.81
O K	23.36	18.69	27.25	27.46	24.19	21.96
Si K	9.41	4.62	13.28	6.53	18.55	9.59

CONCLUSIONS

Two-stage, step-growth polymerization in solution was used to prepare novel poly(urethane–siloxane) crosslinked structures based on a hyperbranched polyester of the third pseudo generation. In the first stage, 4,4'-methylenediphenyl diisocyanate was reacted with α,ω-dihydroxy-(ethylene oxide–poly(dimethylsiloxane)–ethylene oxide), which was followed by reaction of the obtained NCO-terminated prepolymer with a hydroxy-functional hyperbranched polyester in the second stage. In this manner, polyurethane crosslinked structures of different soft EO–PDMS–EO segment contents (15–40 wt. %) were synthesized. The formation of the expected structures was verified by FTIR spectroscopy. The influence of the EO–PDMS–EO content on some properties of the obtained polyurethane networks was investigated by DSC, WAXS, TGA, SEM, swelling measurements, as well as hardness and water contact angle measurements. The swelling behavior showed that the crosslink density of the polyurethane samples was enhanced by decreasing the EO–PDMS–EO content. The equilibrium degree of swelling of the synthesized PUs determined in toluene and in THF increased with increasing content of EO–PDMS–EO. The surface morphology of the synthesized polyurethanes, investigated by SEM analysis, revealed that phase mixing increased with the increase crosslink density of the PUs. The observed glass transition temperature of the PUs increased with decreasing EO–PDMS–EO content. Thermal stability of the synthesized PUs increased with increasing EO––PDMS–EO content at the beginning of thermal degradation. The surface of the polyurethane networks became more hydrophobic with increasing weight fraction of PDMS. Finally, it could be concluded that inclusion of the PDMS prepolymer with ethylene oxide sequences in the PUs based on hyperbranched polyester resulted in networks with good swelling behavior, thermal and surface pro-

perties in comparison to some similar PU networks presented in the literature and prepared from other types of macrodiols, which makes the synthesized PU networks good candidates for coatings, matrices for drugs encapsulation and composites.

И З В О Д

ПОЛИ(УРЕТАН-СИЛОКСАНИ) НА БАЗИ ХИПЕРРАЗГРАНАТОГ ПОЛИЕСТРА КАО УМРЕЖИВАЧА: СИНТЕЗА И КАРАКТЕРИЗАЦИЈА

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У овом раду приказана је синтеза, структура и нека својства нових умрежених полиуретана припремљених полазећи од *α,ω*-дихидрокси-(етиленоксид–поли(диметилсилоксан)––етиленоксид) претполимера (ЕО–PDMS–ЕО), 4,4'-метилендифенилдиизоцијаната и Boltorn® хиперразгранатог полиестра треће псеудо-генерације. Хиперразгранати хидрокси функционални алифатски полиестар са 26 крајњих група служио је као умрежавајући агенс при синтези полиуретана. У циљу побољшања компатибилности реактаната током синтезе, полиуретани су синтисани двостепеном полимеризацијом у раствору. Садржај меког ЕО–PDMS–ЕО сегмента вариран је у опсегу од 15 до 40 мас. %. Испитан је утицај ЕО–PDMS–ЕО садржаја на понашање при бубрењу, густину умрежавања, тврдоћу, термичка и површинска својства синтисаних полиуретана. Структура синтисаних полиуретана потврђена је FTIR спектроскопијом. Понашање при бубрењу је испитивано како би се одредила густина умрежавања и показано је да полиуретанске мреже са нижим ЕО–PDMS–ЕО садржајем имају већу густину умрежавања. Резултати диференцијалне скенирајуће калориметрије показали су повећање температуре остакљивања полиуретана од 50 до 58 °C са смањењем ЕО–PDMS–ЕО садржаја као последицу веће густине умрежености узорака. Синтисани полиуретани са већим садржајем ЕО–PDMS–ЕО сегмената показују бољу термичку стабилност, што је потврђено порастом почетне температуре деградације, одређене TG анализом. Хидрофобност површине полиуретана је расла са повећањем садржаја ЕО–PDMS–ЕО у одговарајућем узорку. Површинска морфологија синтисаних полиуретана је анализирана скенирајућом електронском микроскопијом.

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