JANUSZ KOZAKIEWICZ[1), *)], GABRIEL ROKICKI[2)], JAROSŁAW PRZYBYLSKI[1)], PIOTR PAWŁOWSKI[2)]

Water-cured poly(urethane-urea)s containing soft segments originating from siloxane/carbonate macrodiols

Summary — Poly(urethane-urea)s (PUUs) containing oligosiloxane and oligocarbonate segments were obtained by moisture-curing of NCO-terminated prepolymers synthesized from isophoronediisocyanate (IPDI) and either oligocarbonate co-macrodiols containing oligosiloxane segments, which were made specifically for this purpose, or from a mixture of oligosiloxane diol and oligocarbonate diol. Starting macrodiols were characterized by FT-IR, 1H NMR, ^{13}C NMR and MALDI-TOF. For NCO-terminated prepolymers viscosity was tested. Molecular weight and NCO content was determined with size exclusion chromatography and titration, respectively. The progress of moisture curing was followed by FT-IR showing decrease in NCO band (*ca.* 2260 cm^{-1}) and was considered to be completed until that band disappeared. For resulting PUU elastomers obtained in the form of homogeneous films mechanical and thermal properties were tested. It was found that oligosiloxane-based PUUs containing sufficient amount of oligocarbonate segments, that can interact with the hard urethane and urea segments to increase the interfacial regions adhesion to a moderate level, exhibited exceptionally high mechanical strength. It can be anticipated that in this case oligocarbonate diols acted as good compatibilizers since only one glass transition temperature (T_g) was observed for these PUUs. Simple preliminary biocompatibility test (UV spectrum recorded for water extracts) indicated that all samples exhibited low absorbance from 0.019 at λ = 260.2 nm to 0.180 at λ = 228.2 nm.

Keywords: poly(urethane-urea), oligosiloxane diol, oligocarbonate diol, elastomer.

POLI(URETANO-MOCZNIKI) UTWARDZANE WODĄ ZAWIERAJĄCE GIĘTKIE SEGMENTY POCHODZĄCE OD MAKRODIOLI SILOKSANO/WĘGLANOWYCH

Streszczenie — W artykule przedstawiono wyniki badań nad otrzymywaniem i właściwościami elastomerycznych poliuretano-moczników (PUU) zawierających w łańcuchu segmenty oligosiloksanowe i oligowęglanowe. Polimery te otrzymano w wyniku utwardzania wodą (wilgocią z powietrza) prepolimerów uretanowych o łańcuchach zakończonych grupami NCO, syntezowanych z izoforonodiizocyjanianu (IPDI) i „ko-makrodioli" (z ang. *co-macrodiols*) oligowęglanowych otrzymywanych specjalnie w tym celu, lub z mieszaniny oligosiloksanodiolu i oligowęglanodiolu. Makrodiole używane w syntezie prepolimerów charakteryzowano za pomocą FT-IR, ^{1}H NMR, ^{13}C NMR i MALDI-TOF. W przypadku prepolimerów o łańcuchach zakończonych grupami NCO określano lepkość oraz oznaczano ciężar cząsteczkowy i zawartość NCO, odpowiednio, metodą chromatografii wykluczenia i poprzez miareczkowanie. Postęp utwardzania wilgocią śledzono metodą FT-IR pokazującą zanik pasma NCO (ok. 2260 cm^{-1}) i uznawano utwardzanie za zakończone po stwierdzeniu całkowitego zaniku tego pasma. Badano właściwości mechaniczne i termiczne uzyskanych w ten sposób elastomerów PUU mających postać jednorodnych folii. Stwierdzono, że PUU otrzymywane z udziałem oligosiloksanodioli zawierają ilość segmentów oligowęglanowych wystarczającą do skutecznego zwiększenia adhezji obszarów międzyfazowych poprzez oddziaływania z segmentami sztywnymi. Można sądzić, że w tym przypadku oligowęglanodiole pelniły rolę skutecznie działających kompatybilizatorów, gdyż dla tych polimerów zaobserwowano tylko jedną temperaturę zeszklenia. Prosty test sprawdzający wstępnie biozgodność (widmo UV wykonywane dla ekstraktów wodnych) wykazał, że absorbancja była niska dla wszystkich próbek i wynosiła od 0.019 przy λ = 260.2 nm do 0.180 przy λ = 228.2 nm.

Słowa kluczowe: poli(uretano-mocznik), oligosiloksanodiol, oligowęglanodiol, elastomer.

---

1) Industrial Chemistry Research Institute, ul. Rydygiera 8, 01-793 Warsaw, Poland.

2) Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warsaw, Poland.

*) Author for correspondence; e-mail: janusz.kozakiewicz@ichp.pl

Poly(dimethylsiloxane) (PDMS) and other related polysiloxanes are characterized by having low surface energy ($2.2—2.5 \cdot 10^{-6}$ J · cm^{-2}), oxidative and hydrolytic stability, good blood-contacting properties, low moisture permeability and high chain flexibility due to very low glass transition temperature (-120 °C), but have poor mechanical properties, especially abrasion, tear, and tensile strength. Polyurethanes (PUR) containing oligosiloxane segments in the polymer chain, called "poly(siloxane-urethane)s", have favorable blood contact properties compared to standard poly(ether-urethane)s [1], while poly(carbonate-urethane)s exhibit excellent mechanical properties and also oxidative as well as hydrolytic stability, but relatively poor blood contact properties. There is then an interest in combining the advantages of poly(siloxane-urethane)s and poly(carbonate-urethane)s in a PUR-type polymer containing both oligosiloxane and oligocarbonate segments. The major problem to overcome, associated with synthesizing poly(siloxane-urethane)s or any related polymers, is the incompatibility of the nonpolar oligosiloxane segments with polar urethane hard segments, which results in poor mechanical properties of such polymers. The low mechanical strength can be attributed to weak interfacial adhesion [2].

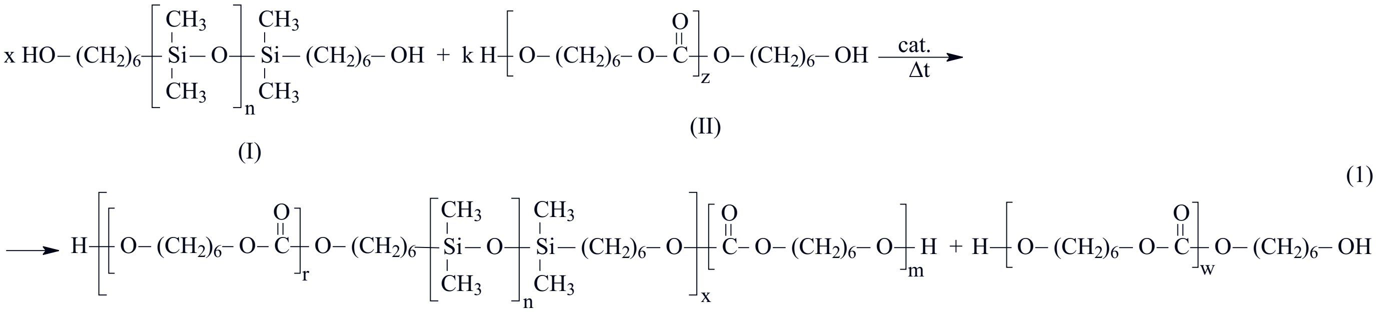
Attempts to produce a blend of PDMS with thermoplastic polyurethane were unsatisfactory due to deterioration of the PUR properties [3]. The blending of polysiloxane with poly(ether-urethane) showed a phase separation morphology [4]. However, selected works demonstrated that synthesis of siloxane-urethane or siloxane-urea segmented polymers (original works of Yilgor, Tyagi, McGrath and Wilkes as well as Wynne and Ho) allowed to overcome that incompatibility problem [5—9], but Chen *et al.* [10] later confirmed using ECSA (Electron Spectroscopy for Chemical Analysis) that oligosiloxane segments migrate to the polymer surface. More recently Gunatillake *et al.* [11] have demonstrated that when a relatively small amount of another macrodiol such as poly(hexamethylene oxide) was incorporated as a part of the soft segment along with α,ω-bis(6-hydroxyethoxypropyl)oligodimethylsiloxane the compatibility of the soft oligosiloxane and hard urethane segments could be significantly improved, which helped to strengthen the interfacial regions. It was also reported that improving interfacial adhesion can be achieved by introduction of polar groups to the PDMS backbone [12, 13] and the use of co-oligomers of oligosiloxanes and polar macrodiols such as oligoethers and oligoesters [14].

Incorporation of a high amount of oligosiloxane segments into the backbone of polyurethanes significantly improves their biostability. However, this way only small amount of oligosiloxane diols can be introduced into the polyurethane structure without decreasing its mechanical properties [2, 12—20]. Recently, Adhikari *et al.* [21] have investigated the effect of macrodiols structure on properties and morphology of poly(siloxane-urethane)s. The influence of different oligoetherdiols and oligocarbonatediols has been studied. The authors investigated also the effect of the siloxane chain extender 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) on polyurethane properties and morphology [22]. Segmented polyurethanes containing siloxane-carbonate soft segments and 4,4'-methylene diphenyl diisocyanate and 1,4-butanediol hard segments were also investigated recently by Choi *et al.* [23] with the aim to use them in biomedical applications. The authors found that the relevant polymers exhibited enhanced intersegment mixing and consequently lower mechanical modulus than those observed for segmented polyurethanes having predominantly PDMS soft segments. The use of poly(carbonate-siloxane) diol based polyurethanes in development of biomedical devices was also reported by another group of authors from the same research center [24].

Sakurai *et al.* [17] reported a hard-segment microdomain dissociation due to fatigue in thermoplastic polyurethane containing oligo(dimethyl siloxane) soft segments. The better fatigue resistance gained for a sample containing PDMS was attributed to lower crystallizability of the soft segment caused by PMDS, even if the soft segments were released during fatigue from constraint by hard-segment microdomains. The influence of soft segment molecular weight on the mechanical hysteresis and set behavior of poly(siloxane-urea)s with low hard segment contents was also studied recently by Yilgor *et al.* [18].

Poly(urethane-urea)s containing oligosiloxane soft segments, obtained by moisture curing of related NCO-terminated prepolymers had simplified structure and therefore very interesting mechanical and surface related properties and morphology [25, 26]. It was shown that surface layers of poly(urethane-urea)s obtained from oligosiloxane diols and oligo(tetramethyleneoxide) diols were enriched in oligosiloxane segments what confirmed earlier similar findings by Chen *et al.* [10] obtained for segmented poly(siloxane-urethane)s. Hydrophobization of polyurethane surface was also observed by Lim *et al.* [27] and by Król and Byczyński [28] for polyurethanes synthesized using oligosiloxane diol as the second diol. Polyurethanes containing oligosiloxane soft segments exhibit better biostability than typical polyurethanes and a surface of these polyurethanes has lower tendency to platelet and fibrinogen depositions during contact with blood [1, 29, 30].

The aim of this study was to investigate the effect of the macrodiols structure on properties of poly(urethane-urea)s containing oligosiloxane and oligocarbonate soft segments. Two kinds of co-oligomers obtained using transesterification and polymerization methods were used. The important reason for dealing with moisture cured poly(urethane-urea)s containing oligosiloxane/oligocarbonate segments was the expected better segment compatibility and hence better mechanical properties. The primary focus was increasing the interfacial adhesion between soft PDMS phase and hard segments.



$$x\,HO-(CH_2)_6-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_6-OH + k\,H\left[O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}\right]_z O-(CH_2)_6-OH \xrightarrow[\Delta t]{cat.}$$

(I) (II)

$$\longrightarrow H\left[\left[O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}\right]_r O-(CH_2)_6-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_6-O\right]_x\left[\overset{O}{\overset{\|}{C}}-O-(CH_2)_6-O\right]_m H + H\left[O-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}\right]_w O-(CH_2)_6-OH \tag{1}$$

(III)

$n \sim 10$; $m = 0, 1, 2, 3 ...$; $r = 0, 1, 2, 3 ...$; $x = 1, 2, 3 ...$; $kz = m + xr + w$

The current demand for polymeric biomaterials with improved biocompatibility and stability may benefit from development of oligosiloxane containing polyurethanes, especially those that are resistant to degradation when implanted for long periods of time.

EXPERIMENTAL

Materials

1,6-Hexanediol, 1,3-propanediol, dimethyl carbonate, ethylene carbonate and isophoronediisocyanate (IPDI), all delivered by Aldrich were used as received. α,ω-bis(6-hydroxyhexyl)poly(dimethylsiloxane) of structure given by formula (I) in eq. (1) was a commercial reagent with trade name Tegomer 2111 purchased from Goldschmidt AG. This oligosiloxane diol (MD1) containing two primary hydroxyl groups was characterized by molecular weight equal to 860, hydroxyl number of 130 mg KOH/g and viscosity at 25 °C 70 mPa · s.

Oligo(hexamethylene carbonate)diol [MD2, formula (II) in eq. (1)] was prepared from 1,6-hexanediol using a transesterification reaction with ethylene carbonate and NaCl as a catalyst, according to the method reported in [31, 32]. Molecular weight of the obtained product was 2100.

Trimethylene carbonate was prepared from 1,3-propanediol and dimethyl carbonate according to the procedure reported in [33, 34].

Synthesis of co-macrodiols

The first co-macrodiol [co-MD3, formula (III) in eq. (1)] was synthesized from MD1 (65.0 g, 0.0756 mol) and MD2 (140.0 g, 0.0667 mol) according equation (1).

The substrates were heated up to 170 °C in the presence of K_2CO_3 (0.5 g, 3.6 mmol) as a catalyst for 24 h until a homogeneous mixture was obtained and then for additional 24 h at the same temperature.

The second co-macrodiol [co-MD4, formula (IV) in eq. (2)] was synthesized by ring-opening polymerization of trimethylene carbonate (59.1 g, 0.58 mol) using MD1 (60 g, 0.0698 mol) as a starter according to equation (2).

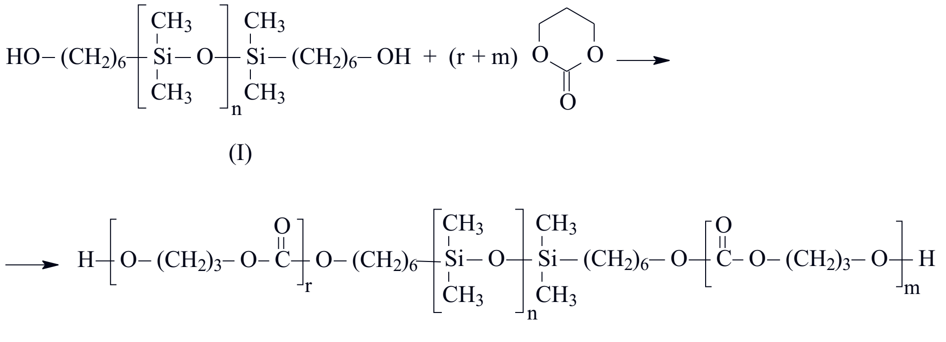
The reaction was carried out at 110 °C for 36 h without any catalyst until no absorption band (760 cm^{-1}) characteristic for six-membered cyclic carbonate was present in the IR spectrum of the sample.

All polyols were dried thoroughly by heating at 105 °C for 12 h under vacuum (0.1 Torr) prior to the reaction with isocyanate.

Synthesis of poly(urethane-urea) elastomers

Poly(urethane-urea) (PUU) elastomers were synthesized by a two-step bulk polyaddition method without using any catalyst. Synthesis of PUU from macrodiols MD1 and MD2 is presented below as an example.

A mixture of predried MD1 (30.4 g) and 2 (20.0 g) was degassed at 80 °C for 1 h under reduced pressure of



$$HO-(CH_2)_6-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_6-OH + (r+m) \longrightarrow$$

(I)

$$\longrightarrow H\left[O-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}\right]_r O-(CH_2)_6-\left[\overset{CH_3}{\underset{CH_3}{Si}}-O\right]_n-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_6-O\left[\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O\right]_m H \tag{2}$$

(IV)

$n = 10$; $m = 0, 1, 2, 3 ...$; $r = 0, 1, 2, 3 ...$

0.1 Torr. IPDI (31.4 g) was placed in a 500 cm^3 three-necked round-bottom flask fitted with a magnetic stirrer, nitrogen inlet and an addition funnel. The flask was then placed in an oil bath at 80 °C. IPDI was added to the macrodiol mixture dropwise through the addition funnel over a period of 30 min under a slow stream of dry nitrogen. After the addition was over, the reaction mixture was kept the same temperature for a period of 3 h with stirring. The reaction was carried out until no absorption band 3500 cm^{-1} corresponding to OH groups was present in the FT-IR spectrum of the prepolymer. To prepare films, the viscous prepolymer was poured onto glass plates and degassed under vacuum (0.1 Torr) for 30 min. The polymer quantity was calculated to achieve the cured film thickness of *ca.* 1 mm. The prepolymer curing was performed in a climatic chamber at constant temperature (50 °C) and humidity (50 %). The reaction with water (moisture) was carried out until no absorption band of NCO groups (2260 cm^{-1}) was present in the FT-IR spectrum of the polymer sample.

All poly(urethane-urea)s were prepared similarly, using the same NCO:OH molar ratio (3:1).

Methods of testing

The number-average molecular weights (M_n) of macrodiols were calculated based on hydroxyl numbers of macrodiols and ^1H NMR spectra. The intensity of proton signals of CH_2 groups adjacent to OH groups (3.6 ppm) was compared with the intensity of proton signals of CH_2 groups adjacent to carbonate groups (4.0 ppm) in the ^1H NMR spectrum of the macrodiol. The hydroxyl numbers of purified and dried macrodiols were determined by the phthalic anhydride reflux procedure in accordance with ASTM method D2849 [21].

IR spectra were recorded using KBr pellets on a Biorad FTIR spectrometer.

^1H NMR and ^{13}C NMR spectra were recorded on a Varian VXR 400 MHz spectrometer. Deuterated solvents were used and tetramethylsilane served as internal standard.

Macrodiols MALDI-TOF spectra were recorded on a Kratos Compact MALDI 4 V5.2.1 apparatus equipped with a 337 nm nitrogen laser with 3 ns pulse duration. The measurements were carried out in the linear mode of the instrument at the acceleration voltage of 20 kV. For each sample, spectra were averaged over 200 laser shots. The samples were dissolved in tetrahydrofuran (THF) to obtain concentration 5 mg/cm^3 and mixed with a solution of the MALDI-TOF matrix (2,5-dihydroxybenzoic acid, 0.2 M in THF). The laser power was moderated in the range 120—130 units characteristic for this apparatus in order to avoid distortion of the mass spectrum.

Dynamic viscosity of the urethane prepolymers was measured at 50 °C for share rate of 10 s^{-1} using viscometer Brookfield HBTDV II in the cone/plate system using cones No. CP52 and CP51.

Isocyanate group content in the prepolymers was established with titration method using butylamine in accordance with ASTM method D1638-74.

Gel permeation chromatography (GPC) was applied to determine weight-average molecular weight M_w and dispersity ($Đ$) of the urethane prepolymers. The system was equipped with Nucleogel columns 500-1 and 103-5, a refractive index detector, and was calibrated with narrow distribution polystyrene standards. Results are expressed therefore as polystyrene-equivalent molecular weights.

For testing mechanical properties the sheets *ca.* 1 mm thick were cut into dumbbell (type II) specimens in accordance with PN-EN ISO 527-1 and PN-EN ISO 527-2 standards. Tensile testing was carried out with an Instron Model 5566 Universal Testing machine. A 1 kN load cell was used and the crosshead speed was 500 mm/min. The results reported are mean values for five replicates. Hardness measurements were carried out using a Shore A Durometer.

Testing thermal properties was performed using differential scanning calorimetry (DSC). The samples were dried at 65 °C for 48 h under reduced pressure (0.1 Torr) to remove moisture prior to recording thermograms. DSC thermograms were recorded over the temperature range from -150 to 250 °C on a Perkin Elmer Pyris 1 DSC. The experiments were carried out at the heating rate of 20 °C/min under a nitrogen purge of 20 cm^3/min. Sample weights were 15—25 mg.

Preliminary test of PUU films biocompatibility was made by analysis of organic compounds impurities in water extracts. Extracts were prepared by heating the elastomer samples in water at 70 °C for 24 h. UV-light absorptions of the water extracts was measured at the wave length 190—300 nm.

RESULTS AND DISCUSSION

Characteristics of co-macrodiols

The MALDI-TOF spectrum of the synthesized co-MD3 is presented in Figure 1. Besides the series of peaks corresponding to pure oligo(hexamethylene carbonate)diol (the peaks denoted by letter "a" and characterized by a mass increment of 144 u and residual mass of 118 u) there are peak series which can be assigned to macromolecules being the combination of hexamethylene carbonate and dimethylsiloxane repeating units. These series of signals correspond to oligomers consisting of oligosiloxane and oligo(hexamethylene carbonate) fragments of different molecular weight. For example, the signal of 2054 corresponds to molecules containing 10 units of $Si(CH_3)_2O$ and 7 units of $OC(O)O(CH_2)_6$ terminated with 1,6-hexanediol and ionized with Na^+; the signal of 2136 corresponds to molecules containing 11 units of $Si(CH_3)_2O$ and 7 units of $OC(O)O(CH_2)_6$; the signal of 2198 — 10 units of $Si(CH_3)_2O$ and 8 units of $OC(O)O(CH_2)_6$ and so on.

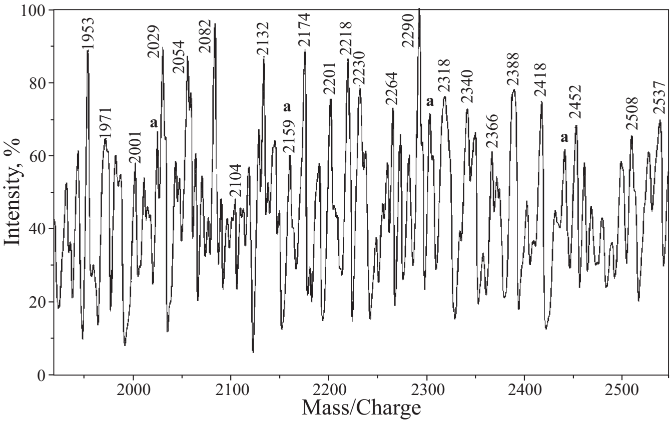


Fig. 1. A fragment of MALDI-TOF mass spectrum of co-MD3 [formula (III) in eq. (1)] obtained from MD1 and MD2 in the presence of K_2CO_3 at 170 °C with MD1:MD2 and molar ratio 1.13

Figure 2 shows the ^{13}C NMR spectrum of co-MD3. The presence of three signals of CH_2OH carbon atoms in the spectrum corresponding to the three different terminal groups: $Si(CH_2)_6OH$ (61.96 ppm), $Si(CH_2)_6OC(O)O(CH_2)_6OH$ (62.22 ppm) and $OC(O)O(CH_2)_6OC(O)O(CH_2)_6OH$ (62.53 ppm), confirms segmented structure of co-MD3 [formula (III) in eq. (1)].

co-MD4 [formula (IV) in eq. (2)] was synthesized by the ring-opening polymerization of trimethylene carbonate using MD1 [formula (I)] as a starter. In the MALDI-TOF spectrum of the product, similarly to the mass spectrum of co-MD3, besides of peak series corresponding to pure oligo(trimethylene carbonate)diol (the peaks characterized by a mass increment of 102 u and residual mass of 76 u) there are peak series which can be assigned to macromolecules being the combination of trimethylene carbonate and dimethylsiloxane repeating units. These series of signals correspond to oligosiloxane molecules terminated with oligo(trimethylene carbonate) fragments of different molecular weights.

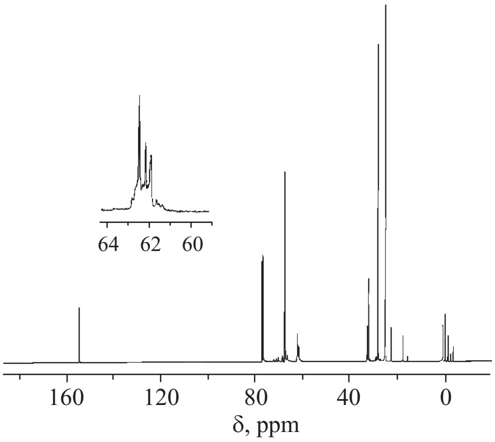


*Fig. 2. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of co-MD**3** obtained from MD1 and MD2 in the presence of K_2CO_3 at 170 °C with MD1:MD2 and molar ratio 1.13*

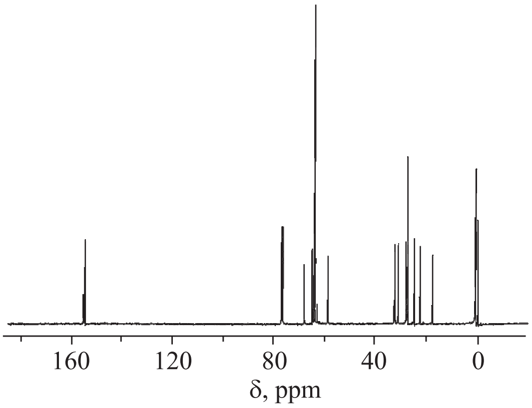


*Fig. 3. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of co-MD**4** obtained by ring-opening polymerization of trimethylene carbonate using MD**1** as a starter (molar ratio 8.3:1) carried out at 110 °C without any catalyst*

In the ^{13}C NMR spectrum of co-MD4, shown in Figure 3, there are three signals at the range 154.8—155.3 ppm which can be assigned to three different carbonyl groups: $(CH_2)_3OC(O)O(CH_2)_3$ of greater intensity (154.79 ppm) as well as $(CH_2)_6OC(O)O(CH_2)_3$ and $(CH_2)_3OC(O)O(CH_2)_3OH$ of smaller intensity (154.90 and 155.32 ppm), confirming the segmented structure of the macrodiols. Two signals of CH_2OH carbon atoms corresponding to different terminal groups: $Si(CH_2)_6OH$ of smaller intensity (62.30 ppm) and $OC(O)O(CH_2)_3OH$ of greater intensity (58.7 ppm) indicate that the part of macromolecules are terminated with oligosiloxane diol. It means that in the ring-opening polymerization of trimethylene carbonate not all OH groups of the oligosiloxane diol were used [eq. (2)].

Characteristics of poly(siloxane-urethane) prepolymers structure

Poly(siloxane-urethane) prepolymers were prepared from heterogeneous mixtures of MD1 and MD2 used in molar ratios 1:3 or 3:1, as well as from homogeneous co-MD3 and co-MD4. The molar excess of diisocyanate (3:1) used in the syntheses guaranteed that all prepolymer macromolecules were terminated with NCO groups. The resulting urethane prepolymers were colorless, transparent homogeneous liquids despite of oligomerols used.

In Table 1 characteristics of six prepared urethane prepolymers is presented. Due to different reactivity of IPDI isocyanate groups as well as high molar excess of IPDI used in the reaction with macrodiols, the prepolymers exhibited relatively low viscosity. The different reactivity of NCO groups diminishes probability of formation of prepolymers containing more than one macrodiol segment.

FT-IR spectra produced for all urethane prepolymers — similarly to the spectrum of prepolymer based on co-MD4 and IPDI shown in Figure 4 as an example — re-

T a b l e 1. Characteristics of urethane prepolymers obtained from IPDI and carbonate/siloxane macrodiols using NCO:OH molar ratio 3:1

Number of sample	Macrodiols (molar ratio)	Carbonate oligomer content mol. %	NCO content, %		$\overline{M}_n$	$\overline{M}_w$	Đ	Viscosity Pa · s
			calculated	found				
1	MD1	0	11.0	10.0	1910	2310	1.2	0.3
2	MD2	100	7.2	7.9	6970	15000	2.2	11.1
3	MD1/MD2 (3/1)	24.5	9.7	9.9	3520	9200	2.6	3.4
4	MD1/MD2 (1/3)	59.1	7.8	8.4	5740	12800	2.2	4.2
5	co-MD3	49.1	7.1	6.1	5030	11300	2.2	4.0
6	co-MD4	39.6	7.1	8.2	3960	5780	1.5	0.7

vealed signals assigned to C=O and NH in urethane groups (1745 and 3386 cm^{-1}, respectively) and to free NCO groups (2258 cm^{-1}). There were no signals from OH (around 3500 cm^{-1}) originating from starting macrodiols.

In the ^{13}C NMR spectrum of the prepolymer based on co-MD4 and IPDI, presented in Figure 5, there are four signals corresponding to NCO carbon atoms of the prepolymer (a — 122.61 ppm and b — 121.65 ppm) as well as unreacted IPDI (c — 122.70 ppm and d — 121.84 ppm). Higher intensity of the signal which can be assigned to the unreacted primary NCO group (121.84 ppm) indicates that the secondary isocyanate group of IPDI is more reactive in the reaction with OH groups as it was earlier observed by Kozakiewicz [25].

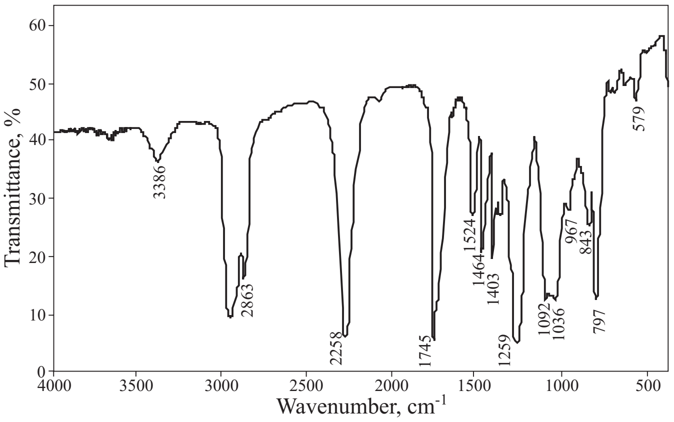


Fig. 4. FT-IR spectrum of the urethane prepolymer based on co-MD4 and IPDI (NCO:OH = 3:1)

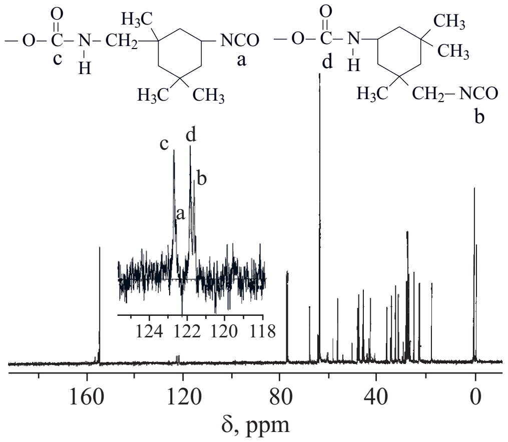


Fig. 5. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of the urethane prepolymer based on co-MD4 and IPDI (NCO:OH = 3:1)

From results listed in Table 1 it can be seen, that higher viscosity was observed for prepolymers containing larger amount of oligo(hexamethylene carbonate) segments. The prepolymer obtained from pure MD2 (sample 2) exhibited the highest viscosity. The lowest viscosity was observed for prepolymer obtained from MD1 (sample 1). The prepolymer containing oligo(trimethylene carbonate) segments (sample 6) exhibited much lower viscosity than that containing oligo(hexamethylene carbonate) segments for almost the same molecular weight and oligosiloxane content.

The presence of larger amount of carbonate segments in the urethane prepolymer increases a probability of good fitting of carbonyl groups to urethane protons and consequently stronger hydrogen bonds can be formed. Thus, higher viscosity was observed for the prepolymers with larger amount of carbonate segments.

Relatively low viscosity of the urethane prepolymer enables its good processability with coating or lamination methods without using any solvents. The urethane prepolymers were cured with air moisture and PUU elastomeric films were obtained. All PUU elastomers obtained in moisture curing process were transparent and colorless except the one containing 25 mol. % of MD2 and 75 mol. % MD1. In this case PUU films were nonhomogeneous, and phase separation was observed. These results were in contrast to those obtained for PUU containing 25 mol. % of oligo(tetramethylene oxide)diol and 75 mol. % of MD1 reported earlier by Kozakiewicz [25]. The relevant PUU films were clear and no phase separation was observed.

Mechanical properties of PUUs

The mechanical properties of PUUs are listed in Table 2. Oligosiloxane-based PUU (sample 1) showed the lowest ultimate strength and elongation at break of all homogenous samples and was the most stiff material (the stress at 100 % of elongation was the highest). However, the hardness of that PUU (sample 1) was moderate and comparable with hardness of the PUUs additionally containing oligocarbonate segments (samples 4, 5 and 6). In the series of the PUUs containing oligo(hexamethylene carbonate) segments (samples 4, 5 and 6), the mechanical properties showed a dependency on the carbonate/siloxane ratio of the macrodiol. The incorporation of MD2 made the PUUs more elastic (high elongation at break and low stress at 100 % of elongation) than the control sample 1. Elastomer based on pure MD2 (sample 2) exhibited the highest strength and hardness of all PUUs investigated. The tensile strength of PUU containing the mixture of MD1 and MD2 macrodiols (sample 4) was comparable to that of pure MD2-based PUU (sample 2). Shore hardness was, however, by almost 30 % lower. A hydrophobic oligomerol such as MD2 used in the proper amount appears to have the appropriate balance in interacting with both hard urethane and soft polysiloxane segments strongly binding those two phases, resulting in very significant improvements in mechanical properties. When lower amount of MD2 was used in a mixture with MD1, non-homogeneous elastomer films were obtained, in which distinct phase separation could be observed.

Table 2. Mechanical properties and glass transition temperature (T_g) of urethane prepolymers; sample numbers as in Table 1

Number of sample	Elongation at break %	Tensile strength MPa	Stress at 100 % elongation MPa	Shore hardness A	T_g, °C
1	160	25.4	21.0	53	-33.9
2	300	43.8	12.8	71	-28.8
3	25	9.4	–	53	-43.4a)
4	370	41.0	9.5	53	-45.3
5	470	26.8	6.4	53	-70.8
6	430	25.7	5.5	51	-26.6

a) Value measured for transparent phase containing PUU based on oligocarbonate soft segment.

It is characteristic that all elastomers containing oligosiloxane segments showed the same level of Shore hardness. Incorporation of carbonate macrodiols improved elasticity of PUUs in all cases, without changing Shore hardness. Moreover, PUUs containing two macrodiols (MD1 and MD2) or co-macrodiol exhibited improved elasticity in comparison to that of pure MD2-based PUU. The stress-strain curve shown in Figure 6 illustrated mechanical behavior of the elastomer based on co-MD3.

The observed differences in properties of PUUs can be attributed to the ability of co-macrodiol to interact with both urethane-urea hard segments and oligosiloxane soft segments. In the oligocarbonate series, co-MD3 was a good compatibilizing agent and the co-macrodiol-based PUU exhibited intermediate properties. In this case, the oligosiloxane and carbonate groups might enhance compatibility with soft and hard segments.

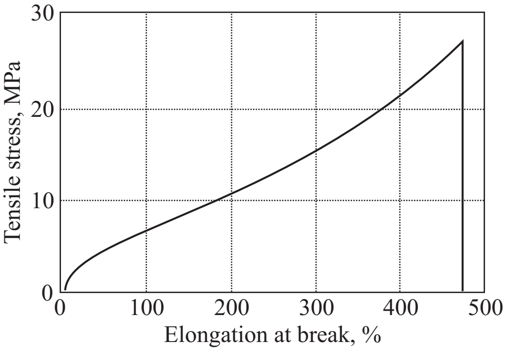


Fig. 6. Stress-strain curve of PUU elastomer based on co-MD3

There was no significant difference in PUUs properties observed for elastomers obtained from co-macrodiols containing co-MD3 and co-MD4 segments.

Poly(urethane-urea) thermal properties

DSC was used to investigate thermal properties of PUU and based on the results obtained, certain suggestions regarding the effect of co-macrodiol structure on PUU morphology could be formulated. Glass transition temperatures (T_g) of PUUs are collected in Table 2. The DSC thermogram of the PUU based on co-MD3 is shown in Figure 7.

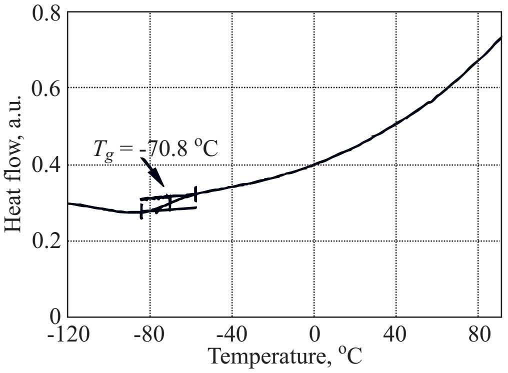


Fig. 7. The DSC thermogram of PUU based on co-MD3

Incorporation of oligo(hexamethylene carbonate) segments to oligosiloxane-based PUU led to lowering the glass transition temperature from -33.9 °C for MD1-based PUU (sample 1) to -45.3 °C for elastomer containing 59.1 mol. % of hexamethylene carbonate fragments in the macrodiol mixtures (sample 4). The T_g of sample 4 was also lower than that of MD2-based PUU (sample 2, T_g = -28.8 °C). However, the greatest decrease in T_g to -70.8 °C was observed for PUU obtained from co-MD3. The T_g of PUU based on co-MD4 was -26.6 °C.

In summary, the DSC results showed that incorporation of oligocarbonate segments into polymer chain increased binding of two phases of the PUUs.

Simple biocompatibility test

Preliminary study of PUUs biocompatibility was carried out by analysis of organic impurities in the water extract from PUU elastomers. These results are listed in Table 3. UV-absorption measurement at wave length in the range 190—300 nm indicated that all extracts exhibited low absorbance from 0.056 at λ = 260.2 nm to 0.123 at λ = 228.2 nm.

Table 3. Morphology and results of preliminary biocompatibility tests of urethane prepolymers; sample numbers as in Table 1

Number of sample	Film clarity	Phase separation	Absorbance		
			λ = 228.2 nm	λ = 248.9 nm	λ = 260.2 nm
1	+	no	0.099	0.080	0.060
2	+	no	0.120	0.090	0.061
3	–	yes	0.122	0.093	0.070
4	+	no	0.105	0.081	0.056
5	+	no	0.123	0.094	0.072
6	+	no	0.114	0.091	0.075

CONCLUSIONS

Modification of the moisture-cured siloxane-based poly(urethane-urea)s (PUUs) with oligocarbonate diols led to clear, homogeneous films of very good elasticity. Oligosiloxane-based PUUs containing sufficient amount of oligocarbonate segments that can interact with the hard urethane and urea segments to increase the interfacial regions adhesion to a moderate level exhibited exceptionally high mechanical strength. It can be anticipated, that oligocarbonate diols acted as good compatibilizers, since only one glass transition temperature was observed for these PUUs.

REFERENCES

1. Hergenrother R. W., Xue-Hai Y., Cooper S. L.: *Biomaterials* 1994, **15**, 635.
2. Speckhard T. A., Cooper S. L.: *Rubber Chem. Technol.* 1986, **59**, 405.
3. Akles B., Carreno C.: *Polym. Mater.Sci. Eng.* 1984, **50**, 440.
4. Shibata M., Kobayashi T., Yosomiya R., Seki M.: *Europ. Polym. J.* 2000, **36**, 485.
5. Yilgor I., Shahaban A., Steckle Jr. W. P., Tyagi D., Wilkes G. L., McGrath J. E.: *Polymer* 1984, **25**, 1800.
6. Tyagi D., Yilgor I., McGrath J. E., Wilkes G. L.: *Polymer* 1984, **25**, 1807.
7. Tyagi D., McGrath J. E., Wilkes G. L.: *Polym. Eng. Sci* 1986, **26**, 1371.
8. Ho T, Wynne K. J.: *Polym. Adv. Technol.* 1985, **6**, 25.
9. Cho G., Natanshon A., Ho T., Wynne K. J.: *Macromolecules* 1996, **29**, 2563.
10. Chen X. G., Gardella Jr. J. A., Ho T., Wynne K. J.: *Macromolecules* 1995, **28**, 1365.
11. Gunatillake P. A., Meijs G. F., McCarthy S. J., Adhikari R.: *J. Appl. Polym. Sci.* 2004, **76**, 2026.
12. Yu X., Nagarajan M. R., Gibson P. E., Cooper S. L.: *J. Polym. Sci., Polym. Phys. Ed.* 1986, **24**, 2681.
13. Yang C. Z., Li C., Cooper S. L.: *J. Polym. Sci., Polym. Phys. Ed.* 1991, **29**, 75.
14. Okkema A. Z., Fabrizius D. J., Grasel T. G., Cooper S. L., Zdrahala R. J.: *Biomaterials* 1989, **10**, 23.
15. Chun Y. C., Kim K. S., Shin J. S., Kim K. H.: *Polym. Int.* 1992, **26**, 177.
16. Phillips R. A., Stevenson J. S., Nagarajan M. R., Cooper S. L.: *J. Macromol. Sci. Phys.* 1988, **B27**, 245.
17. Sakurai S., Nokuwa S., Morimoto M., Shibayama M., Nomura S.: *Polymer* 1984, **35**, 532.
18. Yilgor I., Eynur T., Yilgor E. Y., Wilkes G. L., Dounis D. V., McLaughlin C.: *Polymer* 2011, **52**, 266.
19. Benrashid R., Nelson G. L., Linn J. H., Hanley K. H., Wade W. R.: *J. Appl. Polym. Sci.* 1993, **49**, 523.
20. Knaub P., Camberlin Y., Gerard J. F.: *Polymer* 1988, **29**, 1365.
21. Adhikari R., Gunatillake P. A., Mccarthy S. J., Meijs G. F.: *J. Appl. Polym. Sci.* 2000, **78**, 1071.
22. Adhikari R., Gunatillake P. A., McCarthy S. J., Meijs G. F.: *J. Appl. Polym. Sci.* 2002, **83**, 736.
23. Choi T., Masser K., Moore E., Weksler J., Padsalgikar A., Runt J.: *J. Polym. Sci. Part B: Polym. Phys.* 2011, **49**, 865.
24. Venkataramani S., Mehrabi M., Padsalgikar A.: *Proceedings of 32nd AustralAsian Polymer Symposium*, 13—16.02.2011, Coffs Harbour NSW (Australia).
25. Kozakiewicz J.: *Prog. Org. Coat.* 1996, **27**, 123.
26. Kozakiewicz J., Janik H., Kwiatkowski R., Włochowicz A.: *Polym. Adv. Technol.* 2000, **11**, 82.
27. Lim F., Yang C. Z., Cooper S. L.: *Biomaterials* 1994, **15**, 408.
28. Król P., Byczyński Ł.: *Polimery* 2008, **53**, 808.
29. Lemm W.: „Polyurethanes in Biomedical Engineering", Elsevier, Amsterdam 1984, p. 103.
30. Lewandowska-Szumieł M., Kozakiewicz J., Mrowka P., Jurkowska A., Sienkiewicz-Łatka E., Przybylski J., Okrój W., Walkowiak B.: *e-Polymers* 2007, **107**, 1.
31. Pawłowski P., Rokicki G.: *Polymer* 2004, **45**, 3125.
32. Tomczyk K. M., Parzuchowski P. G., Rokicki G.: *J. Appl. Polym. Sci.* 2011, **120**, 683.
33. Pawłowski P., Szymański A., Kozakiewicz J., Przybylski J., Rokicki G.: *Polymer J.* 2005, **37**, 742.
34. Polish Pat. 197 196 (2008).

Received 10 I 2012.