Siloxane-Based Segmented Poly(Urethane-Urea) Elastomer: Synthesis and Characterization

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ABSTRACT: A series of segmented poly(urethane-urea) block copolymers were synthesized with varying proportions of polydimethylsiloxane diols in combination with polytetramethylene ether glycol (PTMG) using 4,4'-methylenediphenyl diisocyanate followed by chain extension with a (50:50 mol %) mixture of 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (M-CDEA) and 1,4-butanediol (BD). The molecular structures of polydimethylsiloxane urethane-ureas were characterized by ATR-FTIR and ^{1}H-NMR spectroscopic techniques. Distribution of siloxane domain and its influence on surface roughness were investigated by scanning electron microscopy (SEM) and atomic forced microscopy (AFM), respectively. The mechanical and thermal properties of the elastomers were studied by thermogravimetric analysis, dynamical mechanical thermal analysis, and tensile measurement. The results showed that by incorporation of polydimethylsiloxane diol and M-CDEA chain extender in polyurethane formulation, some improvements in thermal stability, fire resistance and surface hydrophilicity were achieved. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

INTRODUCTION

Segmented polyurethanes are multi-block copolymers which possess suitable flexibility and microphase-separated structure. These polymers exhibit very interesting mechanical and thermal properties due to both their chemical structure and certain extent of phase separation between their hard and soft blocks.[1,2] However, these polymers also suffer from some disadvantages such as yellowing, poor weathering and low heat and fire resistance.[3–5] Polyurethanes have been widely used as elastic fibers, coating materials, bonding agents, and artificial leather.[6,7]

Polydimethylsiloxane (PDMS) offers the advantages of low surface tension, unique flexibility, and a wide range of service temperature due to its low glass transition temperature ($-123°C$), small elasticity change versus temperature, oxidative and hydrolytic stability, good gas permeability and biocompatibility, low moisture permeability, high thermal stability, chemical inertness, dielectric stability, shear stability, resistance to ultraviolet radiation and high compressibility.[8–10] However, PDMS exhibits rather poor properties such as low abrasion, tear, and tensile strength which can be modified by combination with other polymers including polyurethanes.[11,12]

Incorporation of a non-polar macrodiol such as PDMS diol into the polyurethane backbone is generally difficult because of its poor compatibility with conventional compounds employed in polyurethane synthesis.[13,14] The poor compatibility is attributed to weak interfacial adhesion.

The introduction of polar functionality into PDMS backbone will improve interfacial adhesion and it has also been found that when a relatively small amount of a second macrodiol (co-macrodiol) is incorporated as part of the soft segment along with polydimethylsiloxane (PDMS) diol, the compatibility of the siloxane and urethane could be significantly improved, which helps to strengthen the interfacial regions.[15]

Diamine chain-extended polyurethanes [poly(urethane-urea)s] are usually phase-separated into high T_g (sometimes crystalline) hard domains and relatively low T_g soft domains. The degree to which the hard and soft segments microphase separate from each other and the resulting morphology have a profound effect on the ultimate properties of the copolymer.[2,16]

The chemical structure of raw materials such as polyols, diisocyanate and chain extenders, used in polyurethane-urea synthesis, should significantly influence its properties and morphology.[1]

We have previously reported the effect of a series of new diamine chain extenders on polyurethane-urea properties and morphology.[17] It was concluded that M-CDEA among the other diamines yields to a polyurethane-urea with higher thermal stability. It was also hypothesized that another way to improve the

Table I. Components and Their Quantities in the Synthesis of Polyurethane-Ureas Samples

Sample	MDI (g)	Hard segment (%)	Polyol (g)		Chain extender (g)	
			PDMS	PTMG	M-CEDA	BD
PUS	5.01	22.73	25.00	–	1.89	0.45
PUS20	5.01	25.94	5.00	16.00	1.89	0.45
PUS50	5.01	24.64	12.50	10.00	1.89	0.45
PUS80	5.01	23.45	20.00	4.00	1.89	0.45
PUR	5.01	26.88	–	20.00	1.89	0.45

fire resistance of polyurethane-ureas without significantly sacrificing the mechanical properties was to introduce PDMS as a reactive macodiol.[18]

Although there are several reported research works on PDMS chain-extended polyurethane in literature, to the best of our knowledge, no work has been published on PDMS polyol-based polyurethane-urea along with 4,4'-methylene-bis(3-chloro-2,6-diethylaniline) (M-CDEA) chain extender.

The aim of this study was to investigate the effect of PDMS content on the properties and morphology of M-CDEA chain extended polyurethane-urea. PDMS macrodiols with molecular weights of 2500 were selected for this study. The soft segments were composed of various contents of PDMS and PTMG and the hard segments were based on 4,4-methylenediphenyl diisocyanate (MDI), while chain extenders were a mixture of (50:50 mol %) BD and M-CDEA. M-CDEA has superior properties to other amine chain extenders and it is known as an excellent chain extender to prepare high-quality polyurethane (PU) elastomers.[17]

Molecular structure characterizations, thermal, morphological, surface, and mechanical properties of the products were studied. A burn test investigation of fire resistance is also reported.

EXPERIMENTAL

Materials

Hydroxyl-terminated PDMS (with number average molecular weight of 2500 g/mol) was obtained from Evonik, Germany and methylenediphenyl diisocyanate (MDI) of Merck, Germany was used as received. Polytetramethylene ether glycol (PTMG with number average molecular weight of 2000 g/mol) and 1,4-butanediol (BD) were obtained from Merck, Germany. All the diols were dried thoroughly under vacuum for at least 12 h prior to synthesis. 4,4'-Methylene-bis(3 chloro-2,6-diethylaniline) (M-CDEA) was purchased from Lonza group, Switzerland and used as received. Tetrahydrofuran (THF) and toluene were dried over sodium and dimethylformamide (DMF) was dried over CaH_2.

Synthesis of Polyurethane-Urea Elastomers

The polyurethane-urea elastomers (PUUs) were synthesized by a two-step solution polymerization method. Molar ratios of polyols; isocyanate; chain extenders were kept constant at 1: 2: 1. The weights of MDI, BD and MCDEA were kept constant at

5.01, 0.45, and 1.89 g, in the order given, for all samples. A typical two-step solution polymerization procedure was performed as follows:

Molten MDI was placed in a three-necked round flask equipped with a stirrer, nitrogen inlet, and additional funnel and placed in an oil bath at 68°C. The macrodiols, PDMS, 5 g (0.2 mol) and PTMG, 16 g (0.8 mol), were dissolved in mixture (50:50 v/v) of dried THF and toluene and added into the flask. The successful synthesis of such PDMS based polyurethane-urea can be quite dependent on proper solvent selection. This is mainly due to the large difference in solubility parameter of highly polar urethane-urea and nonpolar polydimethylsiloxane segments. This phenomenon can result in undesirable macroscopic phase separation during the polymerization.[12]

After mixing for 2 h, 1,4-butanediol, 0.45 g (0.5 mol) was added into the reactor and after 10 min; the solution of M-CDEA, 1.89 g (0.5 mol) in dried DMF was added into the reactor. Mixture of 1,4-butanediol and M-CDEA was selected for easier fabrication of final product. Viscous polymer was then cast onto a Teflon mold and cured for 24 h in an oven at 100°C. PDMS/PTMG component ratio in the prepared polyurethane samples are presented in Table I as 100 mol % PDMS to 100 mol % PTMG with PDMS/PTMG ratios at 20/80, 50/50, 60/40, and 80/20 mol %. The chemical structures are given in Scheme 1.

Polymer Characterization

Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis was performed on a Bruker Equinox FTIR spectrometer (Germany) equipped with a Golden Gate single reflection ATR-FTIR attachment (attenuated total reflection) accessory. The resolution for all infrared spectra was 4 cm^{-1}, and there were 16 scans for each spectrum. The test specimens were in the form of polymeric sheets.

Nuclear Magnetic Resonance Spectroscopy (NMR). ^{1}H-NMR spectra were recorded using deuterated dimethyl sulfoxide (DMSO) as a solvent on a Bruker, 500 MHZ.

Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry was performed under nitrogen atmosphere on a Netzsch DSC 200 F (Netzsch, Bavaria, Germany) fitted with an air cooling compressor at a constant rate of 10°C/min starting from −130 up to 250°C, 250 to −130°C and finally from −130 to 300°C to eliminate thermal history.

Thermogarvimetric Analysis (TGA). The thermal stability of polyurethane-urea was investigated using a TGA /PL 1500/ polymer laboratory instrument (UK). The heating rate was 10°C/min and applied up to 550°C under nitrogen gas and then from 550 to 700°C in oxygen atmosphere. The weight of the sample was around 10 mg.

UL 94. UL 94 measures plastics flammability. Modified UL-94 burn test was performed according to the testing procedure of FMVSS (Federal Motor Vehicle Safety Standard) 302/ ZSO 3975 [19]. Tests were conducted on a (12.7 cm × 1.27 cm × 0.127 cm) bar specimen.

Dynamic Mechanical Thermal Analysis (DMTA). DMTA was performed on a Triton, Model Tritec 2000 DMA (UK) using
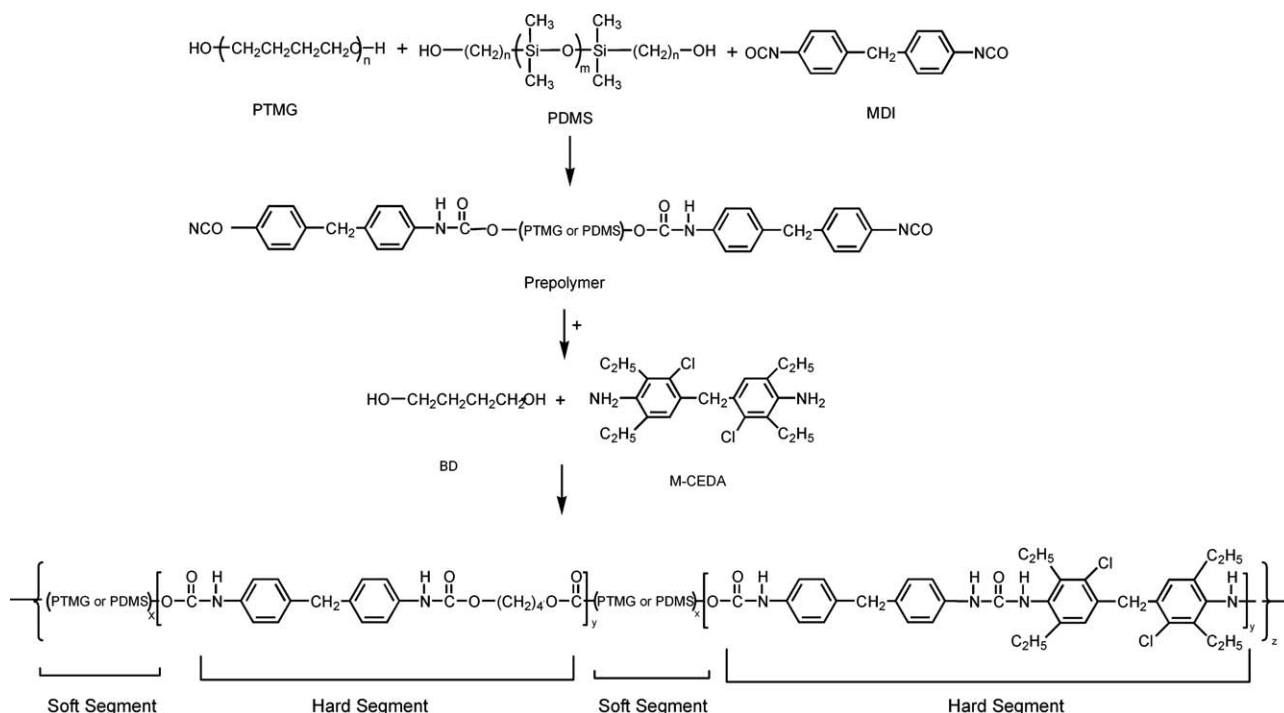
Scheme 1. Chemical structures of the components used in the preparation of polyurethane-urea.

rectangular test specimens(0.1mm × 20mm × 50mm), in the tension mode and 0.3% strain. The analysis was carried out in the temperature range of -150 to +150°C at a heating rate of 5°C/min at a frequency of 1 Hz, and liquid nitrogen was used for cooling.

Atomic Force Microscopy (AFM). A Dual Scope non-contact mode atomic force microscope (Denmark), 25-200E model: DS with 10 nm radius silicon probe was used to study the surface of PUUs films. The roughness was calculated by SPM-DME software.

Scanning Electron Microscopy (SEM). In SEM study, the images were obtained using a VEGA (TSCAN, CHEC) scanning electron microscope. Fractured surface samples (prepared in liquid nitrogen) were mounted on an aluminum stand and coated with gold using a sputter coater prior to microscopy.

Contact Angle
Contact angles were measured with de-ionized water on a sheet of polyurethane urea at room temperature. The water was poured as a drop by an insulin syringe. Contact angles were measured by an Image Analyzer Software and images were acquired by a camera. The test was carried out on 5 sheets and 4 drops of water were applied for each sheet.

Mechanical Properties
Tensile tests were carried out with a Santam Universal testing machine. A 10 N load cell was used and the crosshead speed was 50 mm/min. The test specimens consisted of strips of 14 mm × 0.7 mm × 100 mm. The strips were dried at 100°C in a vacuum oven for 24 h. All samples were stored at room temperature for two weeks before testing. The reported results were the mean values of five measurements.

RESULTS AND DISCUSSION

Fourier Transform Infrared Spectroscopy
FTIR spectra of siloxane-based polyurethane-urea are displayed in Figure 1(a) and the magnified carbonyl regions of the FTIR spectra (1650-1780 cm^{-1}) of these polymers are displayed in Figure 1(b).

For synthesized copolymers, the absorption bond of NCO group around 2270 cm^{-1} is disappeared and the broad absorption bond of OH around 3300 -3500 cm^{-1} is narrowed and changed to NH absorption bond at 3280 cm^{-1}. The urethane and urea absorption bonds are emerged around 1729, 1645 cm^{-1}, respectively. These data confirm the completed reactions in polyurethane synthesis[12].

The absorption bands in a typical FTIR spectrum of siloxane-containing copolymer consist of 1260 cm^{-1}(sym. CH$_3$ bending), 1020 and 1100 cm^{-1}(Si–O–Si stretching), 803 cm^{-1} (CH$_3$ rocking), 3320 cm^{-1} (urea N–H stretch) and 1645 cm^{-1} (H-bonded urea C=O), which are assigned to the urea linkage, 3331 cm^{-1} (urethane N–H stretch), 1703 cm^{-1} (H-bonded urethane C=O), and 1080 cm^{-1} (C-O-C aliphatic ether stretching), 1600 cm^{-1} and 1500 cm^{-1} (C-C aromatic ring stretching). Three carbonyl absorption bands observed in the FTIR spectrum can be assigned as strongly hydrogen-bonded carbonyl groups near 1703 cm^{-1}, loosely (weak absorbance) hydrogen-bonded carbonyls near 1714 cm^{-1} and free (non-hydrogen bonded) carbonyl groups near 1727 cm^{-120}.

As shown in Figure 1(b), the intensity of free carbonyl groups in polyurethane-urea based PTMG is stronger than siloxane-based material. A close observation of the spectra at this region shows that by increasing the siloxane content in PUUs, the
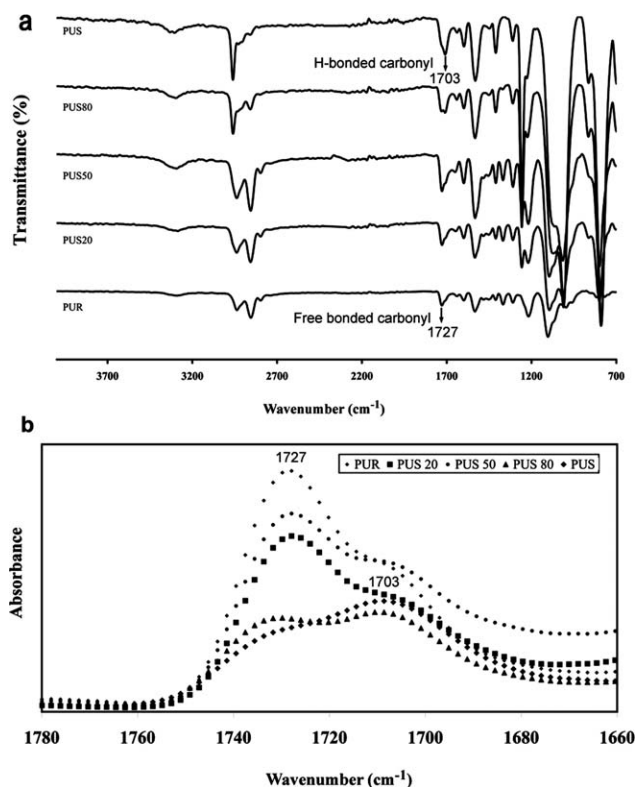
Figure 1. (a) Comparing FTIR spectra of urethanes-ureas and (b) FTIR spectra in the C=O stretching region from 1780 to 1660 cm^{-1} for polyurethane-ureas.

intensity of free carbonyl groups band decreases and the intensity of hydrogen-bonded carbonyl groups increases, i.e., by increasing PDMS content in soft segments, a large fraction of carbonyl groups participate in hydrogen bonding with N-H groups in the hard domain [21]. Therefore, PUS shows the highest intensity of hydrogen-bonded absorption in hard domain and better phase separation. This may be due to higher difference in solubility parameter of different segments.

NMR Spectroscopy

The ^{1}H-NMR spectra of PUS 20 as typical sample is shown in Figure 2. A chemical shift value at 0.059 ppm confirms the presence of siloxane related to Si-CH$_3$; the H aromatic at 7.341 and 7.079 ppm confirm the present of MDI and M-CDEA; the methylene groups in PTMG and butanediol appear at 3.367, 3.230, 1.480, and 1.440 ppm; -CH$_2$-COO- at 2.643 and 2.369 and chemical shifts related to urethane and urea appear at 9.519 and 9.390 ppm [9,22]. These data may confirm the structure of siloxane-based polyurethane-urea.

Differential Scanning Calorimetry (DSC)

DSC thermograms of polyurethane-urea copolymer samples are presented in Figure 3. PDMS-based polyurethane samples show glass transition at about -106 °C that is related to glass transition of PDMS soft segment. Each transition at about -60 °C observed for PUS80 and PUS20 is associated with a mixed phase including PTMG, PDMS and dissolved hard segments [20]. The assignment is confirmed with an observed increase in the heat capacity (ΔC_p changes from 0.048 J/g°k for PUS80 and
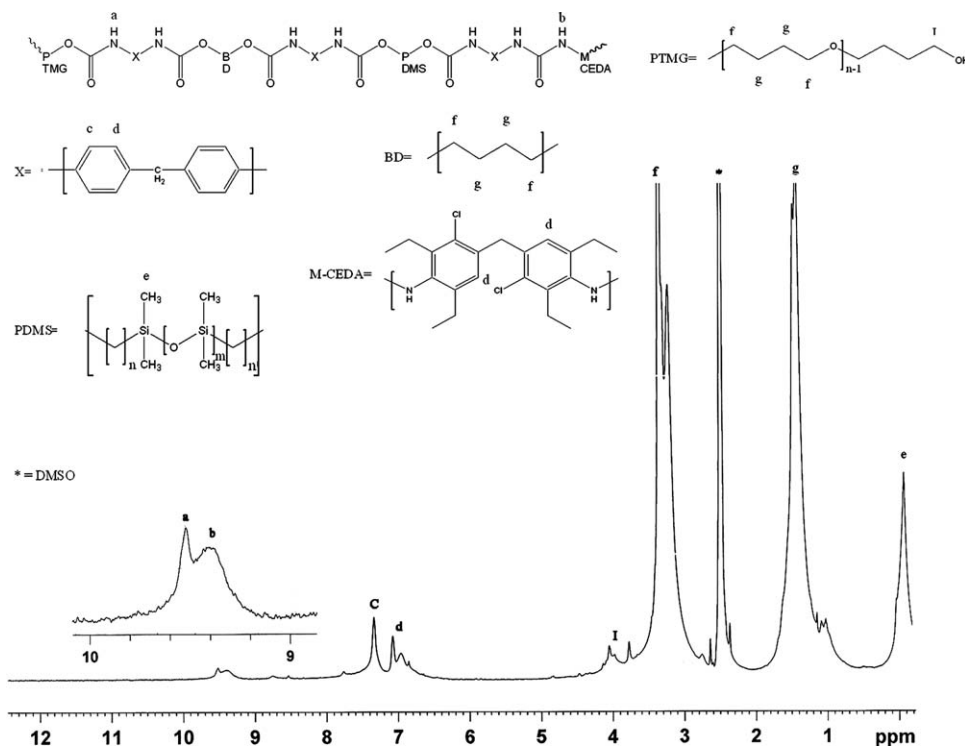

Figure 2. ^{1}H NMR spectrum siloxane-based polyurethane-urea (PUS20).
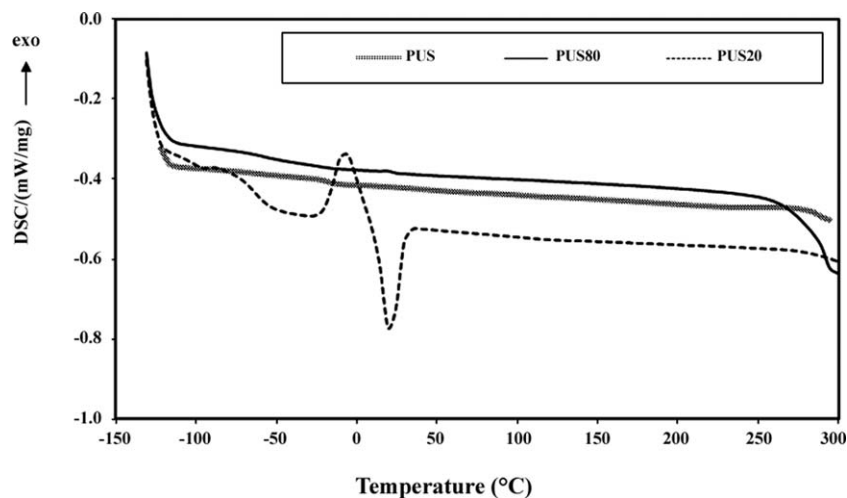
Figure 3. DSC Thermograms from the second heating after cooling.

0.236 J/g°k for PUS20) at the glass transition. The melt transition of PTMG soft segment in PUS20 also appears at about 20°C. However, the melting enthalpy has disappeared in DSC trace of PUS80. Therefore, it can be concluded that by increasing the PDMS content, crystallinity of the PTMG soft segments is greatly affected and the melting transition of PTMG segment is suppressed.

As shown in the polyurethane-ureas DSC thermogram, in PDMS containing polyurethanes, neither the hard domain T_g, nor any crystallization or melting transition were observed. This

behavior might be due to the prevention of crystallization procedure or fine sizes of crystals.

Thermogarvimetric Analysis (TGA)

The thermogravimetric analysis of the PUU and PDMS-based PUUs was carried out from 30 to 550°C in nitrogen and from 550 to 700°C in oxygen atmosphere. The TGA and DTG thermograms are given in Figure 4. Temperatures of 5% weight losses (T_5) as well as the remaining ash contents are deduced from the TGA curves and presented in Table II. The TGA curves of PDMS-based PUUs display three sharp weight loss regions at 250–340°C (Stage 1), 340–390°C (Stage 2), and 390–490°C (Stage 3).

It seems that incorporation of PDMS has positive effect on T5 (temperature at 5 wt % weight loss), and causes a shift in decomposition temperature onset from 297 to 310°C according to the amount of siloxane content in polymer backbone. This improvement may be due to synergistic effect of M-CDEA chain extender.

Notably, for PDMS-based PUUs, the TGA curves exhibit a high stability region at 390–490°C, which may be justified by the formation of stable cyclosiloxane species due to the interchange reaction.[23]

From TGA data, it can be concluded that after exposure to oxygen in thermogravimetric analysis, the PDMS-based PUUs show
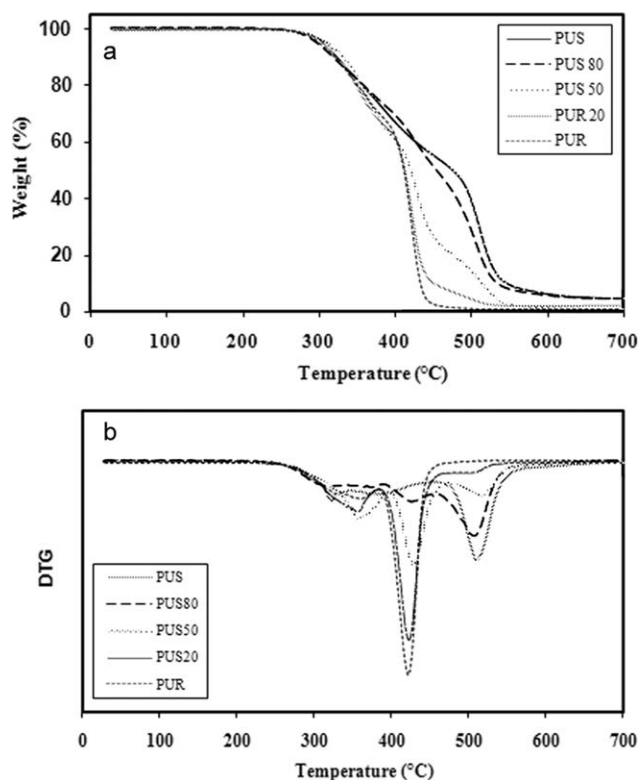

Figure 4. (a) TGA curves, (b) DTG curves, of polyurethane-ureas.

Table II. Thermal Properties of Polyurethane-Ureas

Sample	T_5 (°C)	T_{max1} (°C)	T_{max2} (°C)	T_{max3} (°C)	Ash content %
PUS	310	387	–	512	4.77
PUS80	303	378	430	509	4.67
PUS50	310	359	430	517	3.10
PUS20	307	359	424	514	2.26
PUR	297	361	424	–	0.70

[a] T_5, temperatures at 5 wt % decomposition of the elastomers; T_{max1}, temperature of maximum rate of degradation in stage 1; T_{max2}, temperature of maximum rate of degradation in Stage 2; T_{max3}, temperatures of maximum rate of degradation in Stage 3.
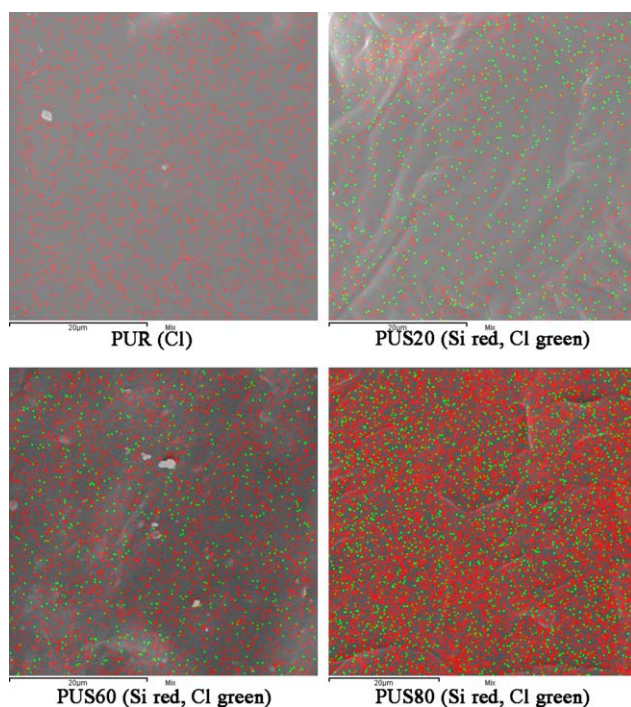
Figure 5. Si and Cl mapping of the surface of polyurethane-ureas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

smaller weight loss over a relatively wide range of temperatures. These samples also leave a larger amount of char in comparison with the polyether-based polyurethane (Table II).

This observation can be explained due to formation of a heat stable SiO_2 protective layer upon degradation. This also improves the fire resistance of the prepared polyurethane-urea, because SiO_2 can protect the remaining layers as an insulator, which retards further burning of the solid polymer.[18]

It is generally agreed that the weight loss at Stage 1 is related to the degradation of urethane/urea hard segments, while the weight loss at Stages 2 and 3 are associated with the degradation of soft segments.[24] It can be hypothesized therefore that the relative rates of degradation in Stages 2 and 3 are strongly dependent on PDMS:PTMG ratio of the soft segment composition.

UL 94 Flammability Tests

The flammability behavior of polyurethane-ureas was evaluated by performing UL 94 standard test method. The PUR sample burned with dripping and self extinguished by removing the fire source. This was categorized as V-2 grade. By incorporation of PDMS as part of the soft segment in polyurethane-urea, the self-extinguishing time, and dripping were reduced. This may imply that PDMS content has positive effect on extinguishing time. The PUS samples according to PDMS percentage are categorized as V-1 and V-0 grades.

Scanning Electron Microscopy (SEM)

Energy dispersive X-ray (EDX) analysis data and the corresponding elemental map for silicon and chlorine were performed to further verification of the microstructure of different

PU-urea polymers surfaces. Block copolymers with different contents of PDMS diol in soft segment have dissimilar surface topography. Figure 5, at 5000× magnification, shows distinct differences in EDX mapping.

Phase separation between the PTMG and PDMS chains inside the soft blocks is expected due to their intrinsic incompatibility.[2] The most important factor inducing the phase-separated morphologies is the low solubility parameter of the PDMS ($d = 7.3$–7.5 $cal^{1/2}$ $cm^{3/2}$) compared with the other components such as PTMG ($d = 8.9$ $cal^{1/2}$ $cm^{3/2}$ and MDI/BD: $d = 11.3$ $cal^{1/2}$ $cm^{3.2}$).[11]

The block copolymer of polyurethane-urea with PDMS promotes a silicone-rich surface due to the higher mobility and low surface energy of the PDMS.[25]

As shown in Si and Cl mappings (Figure 5), silicon and chlorine are distributed uniformly on the surface and by increasing of siloxane content in copolymer; the silicon-rich surfaces are increased. Elemental analysis of the surface of polyurethane-urea (Table III) illustrates higher silicon detection on the surface of the PUUs of higher soft PDMS content. This is well agreed with the TGA results. In other words, by increasing the siloxane content in the structure of polyurethane-urea, the heat stability of the copolymers is increased possibly due to higher silicon-rich surface formation.

Atomic Force Microscopy (AFM)

Surface roughness of siloxane-urethane copolymers with different siloxane contents were examined by AFM and their roughness were calculated. The roughness parameters are estimated by analyzing the topography scans taken from samples' surfaces (Figure 6). As shown in Figure 6, AFM phase images are affected by the silicon contents. The phase image of the film, in absence of PDMS, appears to have fewer features.

When PDMS concentration on surface of the sample is sufficiently high, the PDMS chains start to form aggregates.[26] This result is in accordance with EDX results, which shows a remarkable increase in Si content on the surface of PUS samples by increases in PDMS concentration.

The roughness parameters, S_a (average roughness) and S_q (the root mean square) are increased by increasing the siloxane diol content (Table IV). To summarize, the high roughness due to more siloxane contents in elastomer may affect the surface properties.

Contact Angle

Contact angle measurement is easily performed by establishing the tangent angle of a liquid drop with a solid surface at the base.

Table III. EDXs Elemental Analysis at the Surface of Polyurethane-Urea

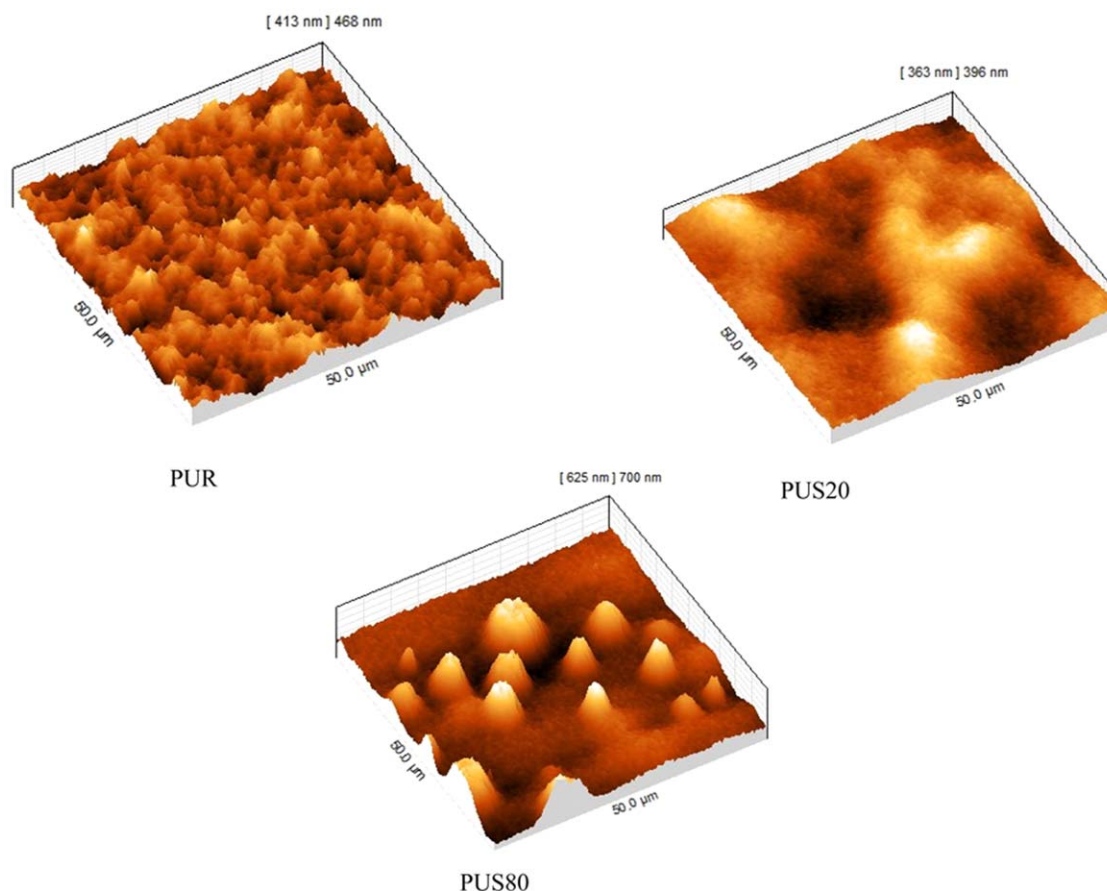| Sample	C (%)	O (%)	Si (%)	Cl (%)
PUR	78.81	20.21	–	0.98
PUS20	67.98	25.73	5.17	1.02
PUS50	62.60	26.35	9.46	1.09
PUS80	53.75	28.51	16.51	1.03

Figure 6. AFM images of polyurethane-ureas. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

It is affected by both roughness and hydrophilicity/hydrophobicity of the surface. The results of contact angle measurements are given in Table V.

The contact angle of PTMG based polyurethane-urea was 73°. By adding 20 wt % of PDMS soft segment in polyurethane-urea, the contact angle is raised significantly to 98° and for PUS with 100 wt % of PDMS it is 109°. This shows that

Table IV. Roughness of Polyurethane-Ureas by AFM

Sample	S_a (nm)	S_q (nm)
PUR	46.6	58.5
PUS20	57.5	71.3
PUS80	72.1	102

Table V. Contact Angle of Water on PUUs Surface

Sample	Contact angle (θ,°)
PUS	3 ±109
PUS80	103 ± 6
PUS20	98 ± 3
PUR	73 ± 4

hydrophobicity increases due to increasing of PDMS soft segment content of the prepared polyurethane-ureas. This observation indicates that hydrophobic nature of PDMS has a stronger effect than surface roughness (which is increased in presence of PDMS). The results of EDX, AFM and contact angle each may complement the others. The high hydrophobicity may be very helpful in designing marine biofouling-resistant coatings[27].

Dynamic Mechanical Thermal Analysis (DMTA)
The phase transitions of all materials were investigated using DMTA. The PDMS-based PUUs show a high degree of micro-phase separation between the PDMS and the PTMG soft domains and the urethane hard phase. The micro-phase separation is due to the thermodynamic immiscibility between the hard and soft segments. Factors that control the degree of micro-phase separation include copolymer composition, block length, crystallization of either segment, and method of sample fabrication.[22]

Storage modulus and damping factor of polyurethane-ureas are shown in Figure 7(a,b). The samples based on two polyols show two main transitions for the soft segments.

T_{g1} observed around $-110°C$ is associated with the segmental relaxation of PDMS and the T_{g2} around $-50°C$ is assigned to the segmental relaxation of PTMG soft phase. By variation in
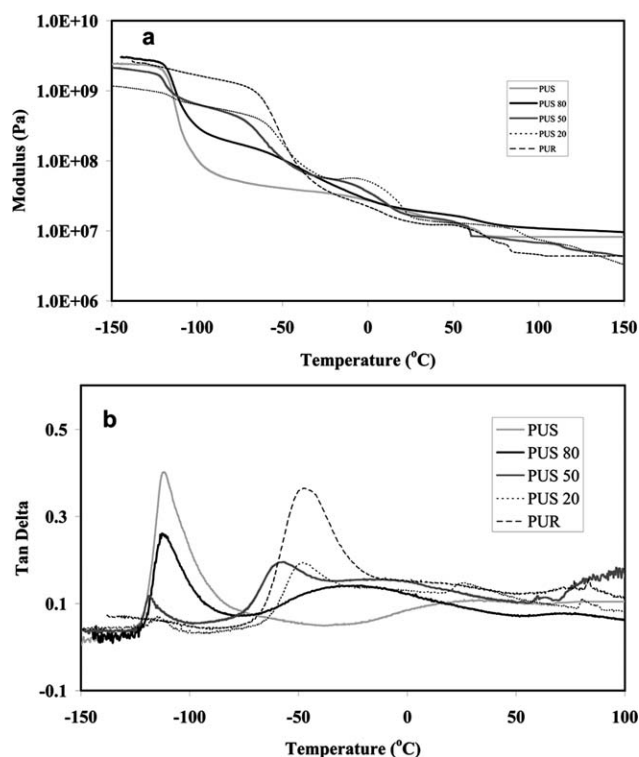
Figure 7. (a) DMTA storage modulus vs. temperature at 1 HZ and (b) the corresponding tan δ (damping) plot.

PDMS and PTMG percentages in the matrix, the tan δ peak height of these transitions is changed and for the PUS and PUR with single soft segment only one transition is observed.[20,28]

As shown in Figure 7(a), the storage moduli of PUS, PUS80, PUS50, and PUS20, drop in the region of −125 to −75°C, which correspond to the low glass transition temperature and percentage amount of the PDMS soft segments. These E' values for PUS and PUS80 drop sharply and for the other samples decrease slowly. The same behavior is shown for PUR in the region of −75°C to −50°C which drops sharply. After these transitions, all the polyurethane-ureas are in the rubbery state. Only a small drop occurs (about one order of magnitude) over
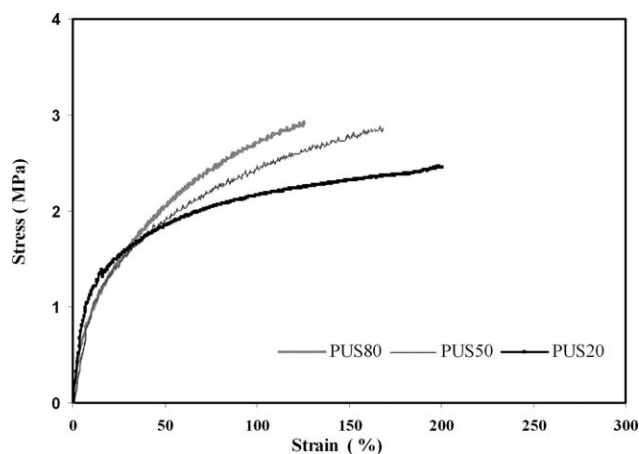

Figure 8. Tensile strength and elongation-at-break of polyurethane-ureas.

Table VI. Tan δ of Polyurethane-Ureas

	Tan δ	
PUR	–	−47
PUS 20	−114.9	−48
PUS 50	−118.4	−57.8
PUS 80	−112.1	−24.3
PUS	−111.5	–

the temperature range of 0–50°C, because intermolecular hydrogen bonding between the urethane hard segments supports the storage modulus in the rubbery state. Intermolecular hydrogen bonding between the urethane hard segments causes phase separation and by increasing the PDMS content in PTMG/PDMS mixed soft phase, the degree of micro-phase separation between the soft polyols and the hard urethane segments is increased.[29]

As it may be observed in FTIR spectra, stronger hydrogen bonding in PUS and PUS80 shows more phase separation. The appearance of two distinct tan δ in DMTA results is a confirmation of micro-phase separation in all PUUs copolymers (Table V).

Mechanical Properties

The mechanical properties of the siloxane-urethane copolymers with different compositions of soft segments are shown in Figure 8. The results clearly demonstrate that, by increasing the PTMG content, the elongation-at-break of the copolymers are increased, which may coincide with a reduction in the ultimate tensile strength.

Furthermore, PUS20 as the most extendable and PUS80 showed the highest tensile strength among all copolymers (mixed PDMS/PTMG comonomer system). In fact, the formations of hydrogen bonds (confirmed by FTIR studies) improve the mechanical and thermal properties of the elastomers which are related to siloxane content of the copolymers.

CONCLUSIONS

A series of segmented polyurethane-urea copolymers based on polydimethyl siloxane diol, as a soft segment, were synthesized by using mixed chain extenders of 1,4-butanediol and M-CDEA, via a two step solution polymerization. The prepared polymers were characterized and evaluated with different techniques.

Si-maps show that siloxane domain is distributed uniformly on the surface of synthesized PUUs. The AFM images show increases in roughness in relation to increases of PDMS content. This result is also confirmed by contact angle measurement. By increasing PDMS content in PUUs, contact angle is increased significantly. This is an evidence of hydrophobicity of the surface, which makes the material an appropriate candidate in marine biofouling-resistant coatings.

The TGA thermograms show that three distinct decomposition stages and that the thermal stability are controlled by hard

segments in the first stage and by PTMG and PDMS segments in the second and third stages, respectively.

UL 94 tests show that, PDMS content in M-CDEA chain extended polyurethane-ureas has synergistic effect on extinguishing time and by increasing PDMS content in PUS copolymer, they can be classified as V-1 and V-0 grades.

By increasing the PDMS content in soft segment, most of the carbonyl groups take part in H-bonding with N-H groups of urethane hard segments and so the mixing of hard and soft segments are minimized and further phase separation occurs.

The thermal stability of siloxane-based polyurethane-urea has improved. Introducing M-CDEA chain extender also has had positive effect on thermal stability and self- extinguishing characteristics of the prepared elastomers. This may be due to its aromatic chemical structure and chlorine moiety. Flexibility at low temperature has made these polymers more suitable for cryosystem applications.

ACKNOWLEDGEMENTS

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