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Study on thermal stability of polyurethane-urea based on polysiloxane and polycaprolactone diols

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Abstract−Different grades of segmented polyurethane-urea were synthesized through two-step solution polymerization of polydimethylsiloxane (PDMS) and polycaprolactone (PCL) polyols with methylene diphenyl diisocyanate (MDI) and mixture of 1,4-buthanediol and 4,4-methylene bis (3-chloro 2,6-diethylaniline) in toluene/tetra-hydrofuran media. Structural characterization of the synthesized samples was conducted using Fourier transform infra-red spectroscopy. X-ray diffraction, dynamic mechanical thermal analysis, thermal gravimetric analysis, and differential scanning calorimetry techniques were utilized to assess material characteristics. The results showed a relationship between PDMS content and thermal stability, morphology and mechanical properties of the urethane-urea samples. Onset degradation temperature was increased by increasing the PDMS content in the polyurethane backbone where the crystallinity was varied versus PDMS content. Strong interaction established between hard and soft segments resulted in a positive shift in PCL glass transition temperature. Tracking E′, E″ and damping factor in DMTA measurements confirmed the two-phase morphology. Hydrophobicity of polymer surfaces was traced by contact angle measurement.

Key words: Stability Thermal, Polyurethane-urea, Polydimethylsiloxane, Polycaprolactone

INTRODUCTION

Polyurethane elastomers (PU), composed of miscellaneous multisegmented copolymers, present excellent elastic dampening property, good mechanical and physical properties even at low temperatures including good hardness and high abrasion, high chemical resistance, and low thermal conductivity, finding applications in protective packaging, gaskets, artificial leather, elastic textile fibers, protective and cushioning in automobiles [1,2]. However, poor fire resistance restricts some of their applications. Some routes such as introduction of halogen-containing fire retardants into polyurethanes were introduced but encountered global prohibitions due to the release of environmental hazardous materials such as HX and other corrosive gases when burned [3,4]. Thereafter, siloxane modifiers, regarding their high fire points, were utilized to smoulder the ignition of polyurethanes by reducing heat release characteristics [5,6].

Polydimethylsiloxane copolymers, mainly due to their unique properties such as low glass transition temperature (−123 °C), low surface energy, high permeability to gases, good insulating properties, and very good thermal stability arisen from the nature of Si-O siloxane bonds have found many applications. Although physical properties of PDMS are constant in a wide range of temperatures, mechanical properties are usually low at ambient temperature, unless reinforced. Very high molecular weight polydimethylsiloxanes are often required to give favorable effects.

To improve the fire resistance of polyurethanes without sacrificing the mechanical properties PDMS could be used as a reactive soft segment in polyurethane backbone. However, several methods are suggested for the synthesis of segmented polyurethanes based on polydimethylsiloxane [7-10]. Living anionic polymerization is a suggested method for synthesis of controlled-morphology siloxane copolymers with styrene, methyl methacrylate and other vinyl monomers [11]. Hydrosilation reactions have been recently used to synthesize segmented copolymers containing siloxane blocks such as siloxane-alkyl oxide copolymers as emulsifier/stabilizer [12]. Ring-opening polymerization has also been reported for the synthesis of siloxane-based block copolymers with oligomers, functional terminal groups or several cyclic monomers. Yilgor [13] synthesized triblock polycaprolactone-*b*-polydimethylsiloxane copolymers via tin-catalyzed ring-opening polymerization of ε-caprolactone monomer by using organofunctionally terminated PDMS oligomers as initiators and comonomers.

Although living anionic polymerization is capable of producing a siloxane-containing copolymer with the favorable structure, step growth polymerization, due to the availability of a wide variety of siloxane oligomers with different reactive terminal groups, is the most common technique used for the synthesis of segmented multiphase copolymers containing siloxane. Manipulation of the siloxane soft segments or the plastic hard segments would result in copolymers with variety of properties.

A critical factor in this type of reaction is the proper choice of the reaction solvent since it would be extremely important in obtaining a high molecular copolymer with useful mechanical properties. Regarding the non-polar nature of siloxane, it is not soluble in the polar conventional solvents of polyurea and polyurethane, i.e., as dimethylacetamide, dimethylformamide, and *N*-methyl-2-pyrrolidone. High molecular weight polyureas are obtained in 2-ethoxyethyl ether and tetrahydrofuran solvent media. The type of diisocyanate may determine the best solvent for polymerization [14].

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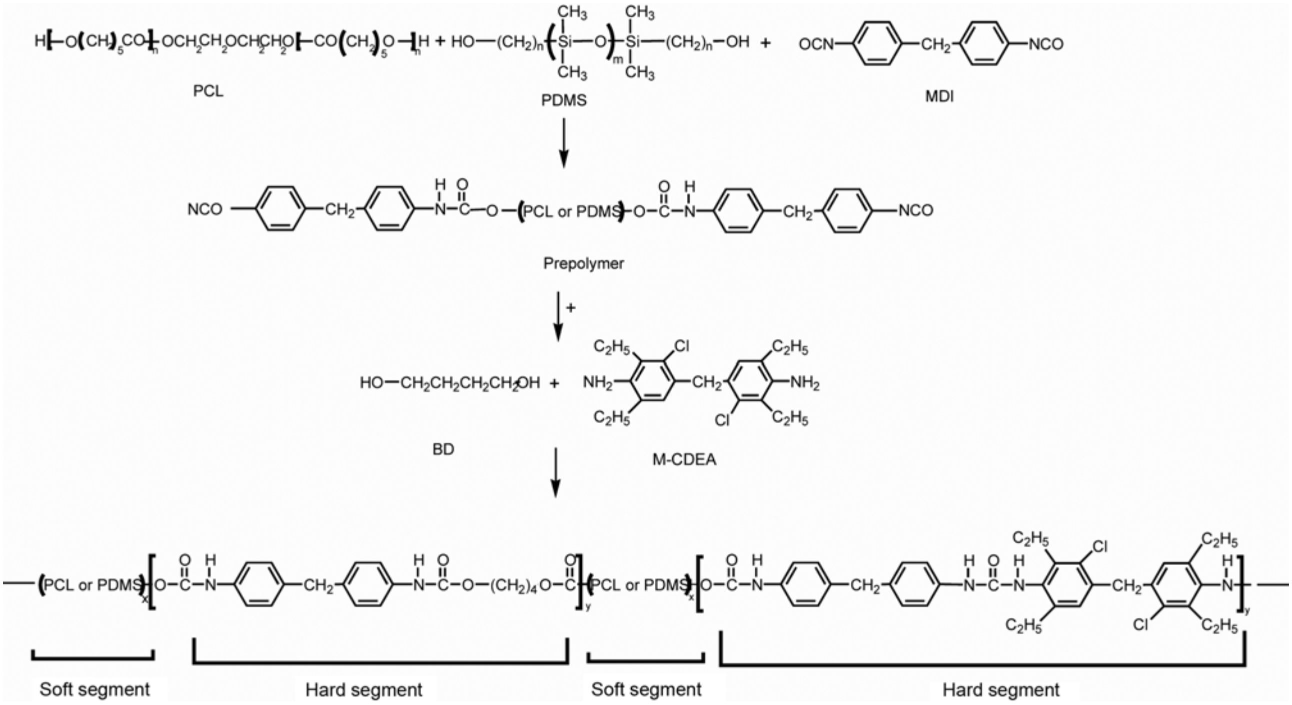

Scheme 1. Chemical structure of polyurethane-urea synthesis constituents.

Two major problems are usually encountered in the synthesis of segmented polyurethane-PDMS. The first is the thermal instability of hydroxyalkyl (primary hydroxyl) end groups on the siloxane oligomer. When heated, hydroxypropyl end groups undergo cyclization reactions, which leads to loss of functionality/reactivity. The second problem is the significant difference between the solubility parameter of PDMS and urethane, making it difficult to select a suitable solvent.

Yilgör also suggested a two-step procedure for synthesizing high molecular weight, high mechanical property siloxane-urethane copolymers. It has been shown that contribution of a large molecule in the soft segment of polydimethylsiloxane diol based polyurethane copolymers would significantly improve the mechanical properties of final product [15]. Madhavan et al. [16,17] investigated the effect of hard segment and diisocyanate type on the properties of segmented siloxane-based synthesized polyurethane. They showed that due to higher cohesion energy and large molecular size, 4,4′-methylene diphenyl diisocyanate leads to better mechanical properties. Yen and Tsai [18] blended segmented siloxane based polyurethane with polyurethanes containing a variety of ester- or ether-based soft segments with different concentrations to investigate the crystallization, thermal, and physical properties of the membrane formations.

As a kind of material with excellent mechanical properties, crystallization and thermal stability of polyurethane-urea is dependent on the structure of amine chain extenders, i.e., chain length, molecular volume, functionality and molecular arrangement of hard segments [18]. Physical and mechanical properties of these kinds of elastomers depend on the molecular structure. Comprehensive literature review shows that 1,4-butandiol is usually used as a diol chain extender in the synthesis of hydroxyl terminated polydimethylsiloxane based segmented polyurethane. Characteristics of polyurethane-urea synthesized using 4-methylene bis(3-chloro 2,6-diethylaniline) (M-CDEA) amine chain extender have not been investigated so far. M-CDEA chain extender (Scheme 1) is expected to form urethane-urea with higher thermal stability. Furthermore, chlorine in the molecular structure of chain extender would result in a self-extinguishing final product. Furthermore, good thermal stability, ozone and its wear resistance also lead to a variety of applications such as cable coating. Siloxane-containing polyurethane-urea copolymers are highly flexible at low temperatures (−110 °C), which are recommended for special coating applications. In the present research work, thermally stable polyurethanes urea based on polycaprolactone polyester and hydroxyl-terminated PDMS are synthesized using mixtures of diol and diamine chain extenders in toluene and tetrahyrofuran media followed by spectrometry, thermal decomposition (TGA, DSC and DMTA) and X-ray diffraction analysis. M-CDEA and 1,4-butanediol chain extenders are utilized to facilitate the process.

EXPERIMENTAL

1. Materials

Polydimethylsiloxane diol (M_n 2,500 g/mol), polycaprolactone (CAPA220; M_n=2,000 g/mol), 4,4-methylene bis(3-chloro 2,6-diethylene aniline) were supplied by Evonik (Germany), Solvay (England), Lonza (Switzerland), respectively. 1,4-butanediol, methylene diphenyl diisocyanate and all solvents were purchased from Merck (Germany). All diol compounds were dried in vacuum oven for 12 h at 80 °C. Toluene and tetrahydrofuran solvents were dried over sodium. Dimethylformamide was dried under calcium hydride and distilled under vacuum.

2. Characterization

FT-IR analysis was performed on a Bruker Equinox FTIR spectrometer (Germany) equipped with a Golden Gate single reflection ATR-FTIR attachment (attenuated total reflectance) accessory. The resolution was 4 cm^{-1} for all the infrared spectra and 16 scans were run for each spectrum. The test specimens were in the form of polymeric sheets. Intrinsic viscosity was measured from the flow time of a dilute solution through a simple glass capillary (Ubbelohde suspended-level viscometer). The viscosity measurements were made in *N*-methyl-2-pyrrolidone (NMP) at 60±0.01 °C. Four dilute polymer solutions between 0.5-2.0 g/dL concentrations were prepared. Flow time of pure solvent (t_0) and polymer solution (t) was measured. Where $t/t_0=\eta/\eta_0$, the specific viscosity was defined as $\eta_{sp}=(\eta/\eta_0)-1$ and reduced viscosity was defined as $\eta_{red}=\log(\eta/\eta_0)$. Both ($\eta_{sp}$/c) and ($\eta_{red}$/c), were plotted vs. c and extrapolated to zero concentration to obtain intrinsic viscosity [η].

Thermogravimetric analysis (TGA) measurements were performed with a Mettler Toledo thermal analysis system (Model DSC/TGA1, Switzerland). The mass loss of the dried samples was monitored under nitrogen gas inert atmosphere from ambient temperature to 500 °C at a rate of 10 °C/min and then heating was continued under oxygen gas up to 700 °C.

Dynamic mechanical thermal analysis (DMTA) was carried out under N_2 atmosphere with a “Triton” (Model Tritec 2000, England) in the tensile mode. The shear storage modulus (E′) and loss tangent (tan δ) of samples were measured at a frequency of 1 Hz with rectangular samples (0.1 mm×20 mm×50 mm) with a free length of 2 mm. The temperature was increased from −150 to 150 °C at a constant rate of 5 °C/min. X-ray diffraction (XRD) phase characterization analysis was accomplished employing a Siemens D5000 diffractometer (Germany) equipped with an FK 60-04 air insulated X-ray diffraction tube with an iron anode, the XRD spectra were taken with Fe Kα radiation (1.93604 nm) at 900 w, 35 kV and 25 mA.

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

Contact angles were measured with de-ionized water on a sheet of polyurethane urea at room temperature. The water was poured dropwise by an insulin syringe. Contact angles were measured by image analyzer software and the images were acquired by camera. The test was performed on five sheets, and four drops were applied on each sheet.

3. Synthesis

Polyurethane-urea copolymers were synthesized by polyol : isocyanate : chain extender with molar ratio of 1 : 2 : 1 via two-step solution polymerization technique. Details of materials and compositions are presented in Table 1.

Synthesis constituents were charged into a glass reactor immersed in an oil bath at 68-70 °C. Vacuum dried diols, as the soft segment, were added to the melted MDI after dissolving in a mixture of toluene and tetrahydrofuran. Butanediol chain extender and M-CDEA chain extender solution (in dry DMF) were introduced to the prepolymer based on isocyanate content after 2 h (Table 1). The content of diisocyanate in prepolymer was measured according to ASTM 2572. The viscous product was cured for 24 h at 100 °C after transferring to a Teflon mold. Scheme 1 shows the molecular structure of the materials used in the synthesis procedure.

RESULTS AND DISCUSSION

1. FTIR Spectroscopy

Fig. 1 shows FTIR-ATR spectra for polyurethane-urea samples containing different soft segment comonomers. Absorption peaks of NCO functionality disappeared at 2,270 cm^{-1} as well as the wide peaks related to diol hydroxyl groups at 3,300-3,500 cm^{-1}. Sharp absorption bands which appeared at 3,300, 1,729, 1,645 and 1,530 cm^{-1} were related to NH, urethane, urea and -CNH groups, respec-

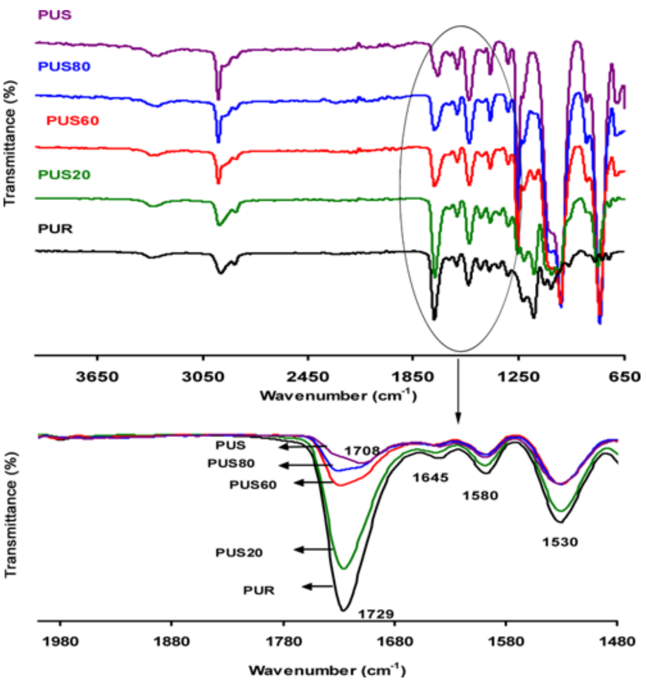

Fig. 1. ATR-FTIR patterns of synthesized segmented copolymer samples in 4,000-650 cm^{-1} and 2,000-1,480 cm^{-1}.

Table 1. Polyurethane-ureas, composition and nomenclature

Sample code	Diisocyanate (mol)	Chain extenders (mol)		Polyols (mol)		Hard segment content* (wt%)
	MDI	BDO	M-CDEA	PCL	PDMS	
PUS	2	0.5	0.5	.....	1	22.73
PUS20	2	0.5	0.5	0.8	0.2	25.94
PUS60	2	0.5	0.5	0.4	0.6	24.26
PUS80	2	0.5	0.5	0.2	0.8	23.45
PUR	2	0.5	0.5	1	…..	26.88

*HS content (wt%)=(MDI+BD+M-CDEA)/(MDI+BD+M-CDEA+PCL+PDMS)×100

Table 2. Intristic viscosity of polyurethane-urea in NMP at 60 °C

Sample code	[η] (dL/g)
PUR	0.670
PUS20	0.654
PUS60	0.310
PUS80	0.200
PUS	0.185

tively [19]. These results confirm the accomplished reaction between polyol and isocyanate.

Siloxane-containing samples depict absorption bands at 1,008 and 1,064 cm^{-1} which are related to the stretching vibrations of Si-O-Si bonds. Absorption peaks at 1258 and 805/860 are representatives of C-H (in $Si-CH_3$), C-H (in $Si-CH_3$) bending vibrations, respectively.

By exploring the spectral zone from 1,650 to 1,780 cm^{-1}, illustrated in Fig. 1, it is shown that in the structures obtained there are carbonyl groups involved in strong hydrogen bonding (1,708 cm^{-1}), free carbonyl (1,729 cm^{-1}) and weak hydrogen bonded carbonyl functionality (1,720 cm^{-1}). Increases in PDMS soft segments would intensify the peak intensities at wavenumber 1,708 cm^{-1} contrary to the wavenumber 1,729 cm^{-1}. This phenomenon is a typical suppression in the miscibility of dissimilar segments due to the considerable difference in the solubility parameters, which would result in phase separation. In other words, the contribution of carbonyl groups in hydrogen bonding with N-H functionalities of hard segments would be more probable in higher PDMS contents [20].

2. Viscosity Measurements

Five PDMS-containing polyurethane samples with soft segment portions of 73.12-77.27 wt% and variable PDMS content (0-100 wt%) were analyzed by an Ubbelohde capillary viscometer.

The intrinsic viscosity results, which are illustrated in Table 2, are considered highly important to provide a good estimation of viscosity average molecular weight (M_v) according to Mark-Houwink equation ($[\eta]=KM^{\alpha}$). This table shows that the intrinsic viscosity [h] decreases with increasing PDMS content in polyurethane-urea's structure. A similar result was reported by Feng Wang [11].

3. Thermogravimetric Analysis

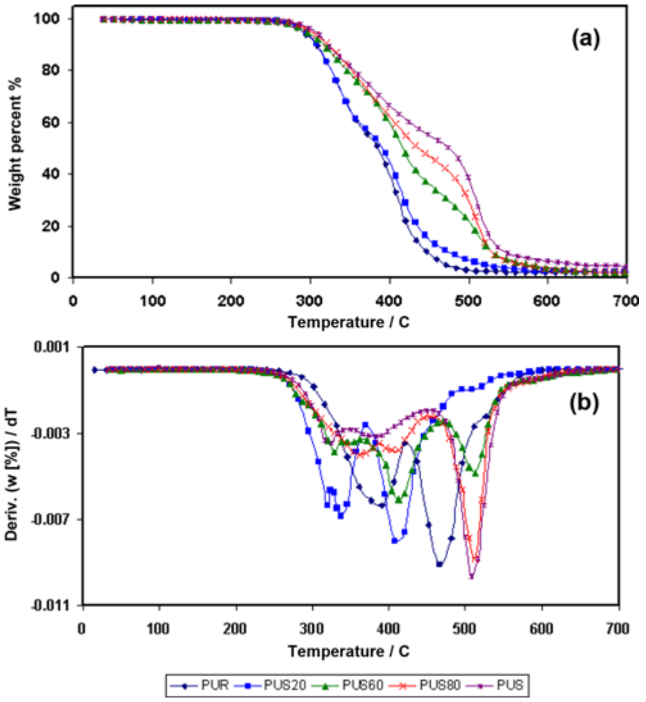

Fig. 2. Results of (a) thermogravimetry and (b) differential thermogravimetry analysis.

DTG and TGA thermograms of siloxane-based polyurethane-urea copolymers depict three main degradation steps (Fig. 2). Temperatures of 5% and 50% weight losses (T_5 and T_{50}) which were deduced from the TGA curves are also brought in Table 3. Depending on the siloxane content, the temperature of 5% weight loss (T_5) varies from 291 to 305 °C. Therefore, the initial degradation temperature of different siloxane-containing polyurethanes is varied by about 14 °C. In comparison with the Chuang studies (variation of 2-3 °C) [21], this temperature interval (i.e., 291-305) might be attributed to the presence of M-CDEA chain extender which synergistically acts with increasing siloxane content. The first degradation stage occurring at 250-375 °C could be attributed to the degradation of polyurethane bond and the subsequent depolymerization to hard and soft segment constituents [5]. The second (375-465 °C) and third (460-550 °C) stages are related to the polycaprolactone and PDMS degradations, respectively. According to DTG thermograms (Fig. 2(b)), the maximum degradation rate at the second and third stages is dependent on the respective PCL and PDMS content in soft segments. The higher thermal stability observed in the third stage could be due to the formation of cyclo-siloxane through interchange reactions. Siloxane formation observed at higher temperatures was also reported by other researchers [20,22].

The temperature interval for 50% weight loss (T_{50}) in PUR and PUS is approximately 90 °C. With increasing the siloxane content

Table 3. Thermal characteristics of prepared samples

Sample code	T_5%/°C	T_{50}%/°C	T_{max1}/°C	T_{max2}/°C	T_{max3}/°C	Ash content/wt%
PUR	291	385	.....	348	417	2.3
PUS20	293	391	321	343	417	2.6
PUS60	295	417	328	410	514	3.2
PUS80	301	437	323	417	511	3.8
PUS	305	475	325	.....	513	6.2

T_5%=Temperature at 5% weight loss, T_{50}%=Temperature at 50% weight loss, T_{max1}=Maximum degradation rate temperature at the first step, T_{max2}=Maximum degradation rate temperature at the second step, T_{max3}=Maximum degradation rate temperature at the third step

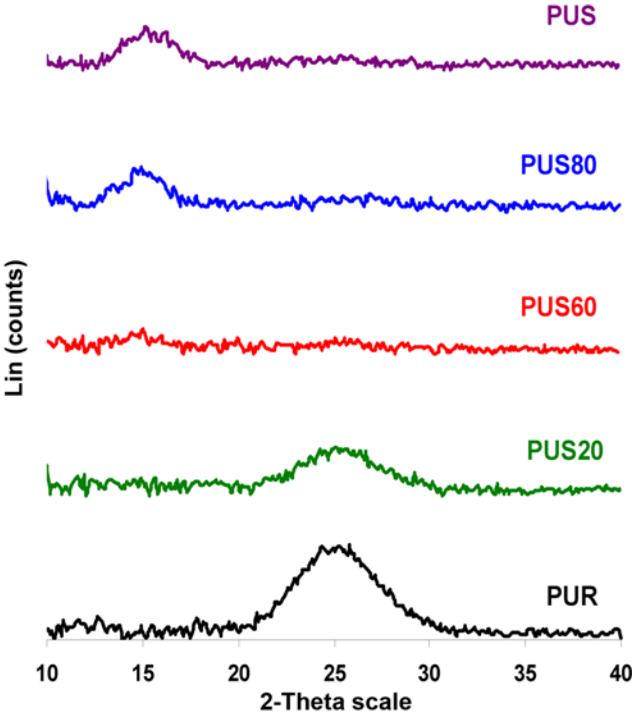

Fig. 3. X-ray diffraction patterns of prepared samples.

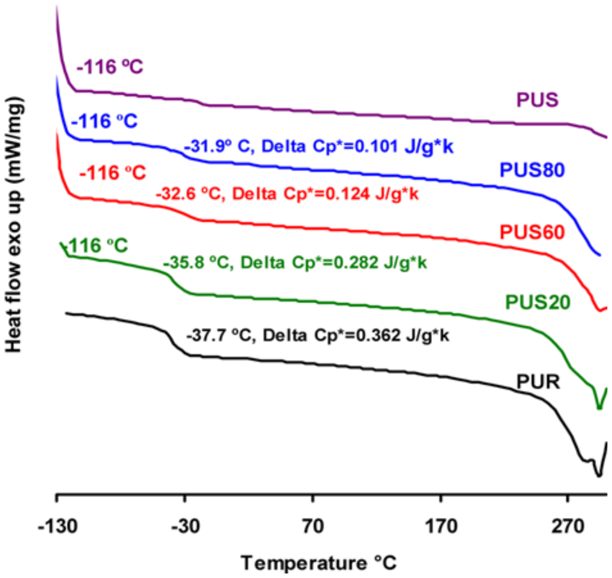

Fig. 4. DSC results of polyurethane-urea synthesized copolymers.

in polyurethane copolymer, T_{50} shifts to higher temperatures. Ash content values also increase with PDMS content. Formation of silicate complexes has been reported for PDMS when exposed to oxidation. This phenomenon might improve fire resistance since it may cover the surface as a protective insulating layer that would retard the polymer ignition process [20].

4. X-ray Diffraction

XRD patterns of polyurethane copolymers with different siloxane contents are illustrated in Fig. 3. Crystallization peaks appear at 25 °C and 15.5 °C for PUS and PUR respectively. With increasing the PDMS soft segment in polyurethane soft segments, crystallinity falls to a minimum for PUS 60 followed by an increasing trend. In fact, hard segments begin to crystallize as the phase separation advances; overall this would increase the crystallinity of polyurethane [23]. As mentioned before [18], crystallization in ester-based polyurethane copolymers is more probable compared to the ether-based types due to the stronger hydrogen bonds between the hard and soft segments. The higher crystallinity of the synthesized PUS sample compared to similar reported copolymers [18] might be due to the phase separation originating from the synergistic effect of M-CDEA and butane diol chain extenders promoting hydrogen bonding phenomenon [18].

5. Differential Scanning Calorimetry

DSC thermograms of polyurethane-urea copolymer samples are presented in Fig. 4. PDMS-based polyurethane samples show glass transition at about −116 °C. Glass transition temperature of PCL soft segment also appears between −37 up to −32 °C, indicating PDMS/PCL and hard segment phase separation. Appearance of a broad peak, as observed here, is typical of two-phase morphology [11]. Glass transition of the phase containing PCL, PDMS terminated ester segments and the hard segment soluble in this phase shifts to higher temperatures with increasing PDMS soft segment content. Increasing PCL content leads to an increase in the heat capacity fluctuations in glass transition (T_g). Accordingly, the transition observed in sample PUR is related to the glass transition temperature of a mixture phase containing PCL and the hard segment soluble in it [20]. DSC thermograms of segmented polyurethanes usually display hard segment melting peaks at 50-250 °C, but the absence of such peaks could not be necessarily ascribed to the copolymer homogeneity. This behavior might be due to the prohibition of crystallization procedure or fine size of crystals [24,25].

6. Dynamic Mechanical Thermal Analysis

Fig. 5 illustrates DMTA results for the prepared samples. Storage modulus (E′) (Fig. 5(a)), loss modulus (E'') (Fig. 5(b)) and damping factor ($\tan\delta$) (Fig. 5(c)), all confirm the two-phase structure of segmented polyurethane-urea copolymers. The main factor in producing a two-phase structure in soft segment is the lower solubility of PDMS compared to other constituents involved [23]. Only one transition appears in PUR (–30 °C) and PUS (–111 °C) samples, where in copolymer samples two distinct glass transitions −118 °C to −109 °C and −27 °C to −9 °C are distinguished. First transition peak position (T_{g1}) ascribed to the PDMS segmental motions does not considerably change with increasing PDMS content contrary to the second transition (T_{g2}) which shifts to higher temperatures. This could be attributed to the phase mixing in PCL soft segments [26].

Peak amplitude diminishing in secondary transition with higher PDMS content could be ascribed to the decrease in polyester comonomer. Similar behavior was observed by Yeh et al. [20] for samples containing polyether comonomers.

The decrease in storage modulus begins from −100 °C with increasing PDMS soft segment content into the copolymer, so PDMS based polyurethanes have found flexibility and application in a wide range of temperatures. Also at ambient temperature (15-35 °C), the storage modulus decreases in PUR, PUS, PUS20, PUS60, PUS80, respectively. PUR with higher content of hard segment, shows the higher storage modulus value at ambient temperature [27]. In siloxane-containing polyurethane-urea, depending on the siloxane content, higher modulus may be accounted for the hard segment immisci-

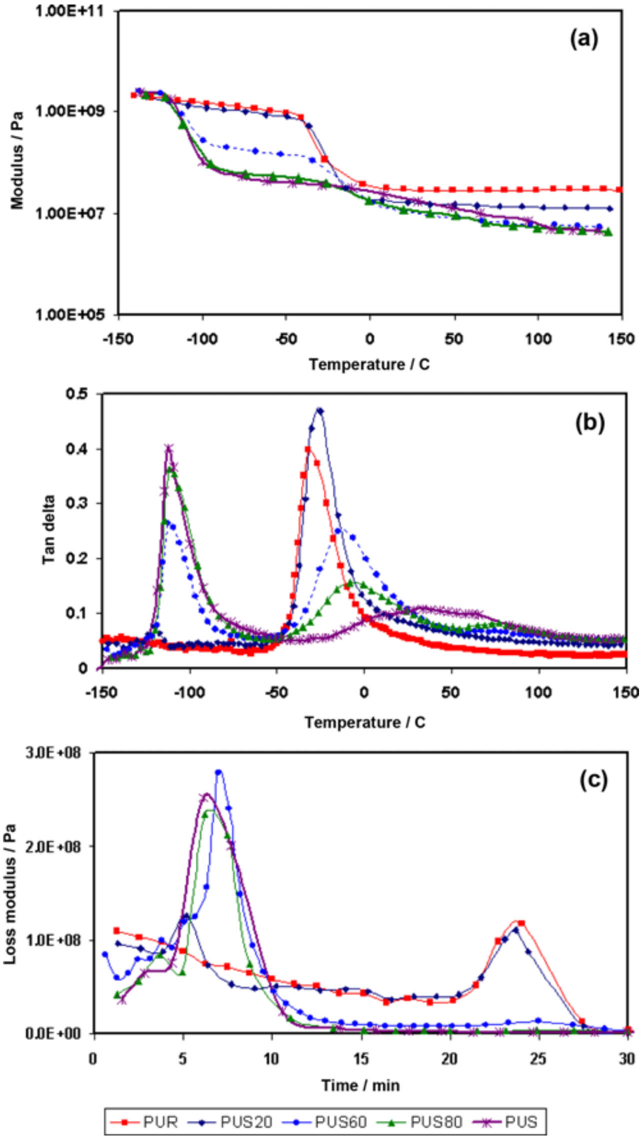

Fig. 5. Storage modulus (a) damping factor (tanδ) (b) and loss modulus (c) of synthesized samples.

bility resulting in two-phase structure.

According to Fig. 5(c), in loss modulus versus time profile, the relaxation times of PCL soft segment and PDMS are 18-32 and 1.5-15 min, respectively.

7. Contact Angle

Contact angle is easily measured by the tangent (angle) of a liquid drop with a solid surface at the base. The value of contact angle of PCL based polyurethane-urea was about 73°±4. By adding 0.2 mole of PDMS soft segment in polyurethane-urea, the contact angle increased significantly to 96°±3, and by increasing of PDMS content from 0.6 mole to 1 mole it changed from 107±4 to 109°±3. The trend observed for the contact angles strictly reflects the qualitative order of increasing hydrophobicity [28].

CONCLUSION

Polyurethane-urea copolymer was synthesized through a two-step solution polymerization in toluene/tetrahydrofuran medium. A two-phase structure was observed due to the inherent thermodynamical incompatibility between the hard and soft segments. Phase separation was intensified with increasing PDMS soft segment content due to the hydrogen bonding of carbonyl groups with N-H functionalities of hard segment. Siloxane-based polyurethane-urea samples exhibited higher thermal stability, and the onset degradation temperature increased with copolymer siloxane content. Synergistic effect of M-CDEA on siloxane content seemed to be an effective factor in thermal stabilization. Crystallinity of synthesized copolymers decreased with increasing PDMS soft segment content and PUS60 displayed the lowest value. By increasing PDMS content in PUUs, contact angle was increased significantly. This is evidence of hydrophobicity of the surface.

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