Morphological Studies of Polyurethane Elastomers Extended with α,ω Alkane Diols

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A B S T R A C T

Polyurethane elastomers with improved crystallinity and hydrophilicity were synthesized by step growth polymerization techniques using poly(ε-caprolactone) (PCL) and 4,4′-diphenylmethane diisocyanate (MDI), extended with α,ω alkane diols (hydroxyl group attached with first and last methylene unit of an alkane chain). Structural characterizations were performed using FTIR, ^{1}H NMR and ^{13}C NMR techniques. Crystallinity of the polyurethane (PU) films was studied and discussed by using X-ray diffraction technique. For all the samples, the crystallinity and hydrophilicity were found to increase with increasing of the chain extender length. Optimum crystallinity and hydrophilicity were obtained from elastomer extended with 1,10-decane diol (DDO) in comparison to elastomers extended with 1,2-ethane diol (EDO). Contact angle measurement, water absorption and swelling behaviour of the synthesized polyurethane were affected by number of methylene units in the chain extenders in the resulted PU. Investigation of structure-property relationship for prepared elastomers showed that the main determining factors for observed properties were degree of crystallinity, hydrophilicity and chain extender length in the PU backbone.

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INTRODUCTION

Wettability of solid surface, especially those of polymeric materials, plays an important role in every daily life [1,2]. The ability to manipulate the water wettability is equally important in many unit operations of modern industrial processes and of course in end use properties of various commercial products. In determining the water wettability of solid surfaces, the type of material of which the solid surface is made becomes an important issue. Many synthetic polymeric materials have relatively hydrophobic surfaces which will repel water upon contact. It is possible to change such hydrophobic

surfaces to hydrophilic ones by employing chemical modification. It has been recognized for some time that polymeric materials which are soft and elastic tend always to have hydrophobic surfaces [3,4]. Various surface modification techniques are available to make solid surfaces wettable with water by increasing the intrinsic surface energy of solids. For example corona discharge and cold plasma treatments [5], wet chemical methods [6], and other photochemical methods [7] are used to enhance the wettability of the solid surfaces. Similar surface modification techniques are also used to enhance adhesion to plastic surfaces. In general, approaches are based on the introduction to the surface of chemical functional groups capable of interacting favourable with water. Polyurethanes have potential array of commercial applications as they can be moulded, injected, extruded and recycled [8]. They are used in almost every industrial as well as biomedical application. Polyurethanes are block copolymers with alternating soft and hard blocks or segments. Soft segments generally derive from a polyether or polyester polyol, whereas the diisocyanate in conversion to urethane linkages form hard segments. The urethane linkage (-NH-COO-) is a result of reaction between the isocyanate (-NCO) group of diisocyanate and hydroxyl group (-OH) of polyol. If a stoichiometric excess of diisocyanate is used, the resulting short typically diurethane chains are -NCO terminated and the product is called NCO-terminated prepolymer. Segmented polyurethanes (SPU), consisting of hard segments and soft segments, are known to have microphase separated structure [9-11], which brings SPU to be used in various ways such as adhesives, coatings, biomedical materials and elastomers. SPUs are used in many fields for a number of reasons: they effectively wet the surface of most substrates; they readily form hydrogen bonds to some substrates; their low viscosity allows them to permeate porous substrates; and they form covalent bonds with substrates that have active hydrogen. Furthermore, they also have good toughness, water and a broad range of chemical resistance.

It is important to note that a polymer tailoring for any required application should have better surface properties relevant to its end use. A deeper understanding of the microphase separation promises to realize new and improved properties of SPU. Surface

properties of SPU are also of importance, hence a lot of studies have been done in order to characterize and control them [12-14]. Several strategies have also been applied to modify the surface as well as the interfacial properties of SPU [15-19]. Increase in number of methylene units in alkane diol chain extender and resulting in final PU is considered to be the most useful method as chemical modification [20]. Depending on the types, the content, and the methods, the increase in number of methylene units in alkane diol chain extender can affect not only the bulk, but also the surface properties. The structure of the microphase separation is not only a function of the system thermodynamics, but also depends greatly on the ability of the hard segments to pack itself correctly to form a hard domain. It is well known that soft segment forms crystalline structure in the segmented polyurethane due to their long and ordered structure [21]. Attempts have been made to study the crystallinity [22,23] and hydrophilicity by determining contact angle [24], water absorption [25] and swelling behaviour [26] of different polymeric materials. Due to the absence of any report on the synthesis of SPUs, studying surface morphology with increase in number of methylene units in alkane diol chain extender, the effect of increase in -CH$_2$- units on the crystallinity and surface morphology is investigated and discussed in this paper. For this investigation polyurethanes were synthesized via a standard two-step reaction procedure; a prepolymer based on polycaprolactone diol (CAPA 225-molecular weight 2000) and 4,4′-diphenylmethane diisocyanate (MDI) was extended with a series of chain extenders having 2-10 methylene units in their structure. The effect of chain extender length on crystallinity, surface morphology and hydrophilicity was studied by X-ray studies and, by determining contact angle, density, water absorption (%), equilibrium degree of swelling and surface energy.

EXPERIMENTAL

Chemicals

4,4′-Diphenylmethane diisocyanate (MDI) was purchased from Sigma-Aldrich Chemical Co. Chain extenders (1,2-ethane diol (EDO), 1,3-propane diol

(PDO), 1,4-butane diol (BDO), 1,5-pentane diol (P′DO), 1,6-hexane diol (HDO) and 1,10-decane diol (DDO) were obtained from Merck Chemicals Co. Polycaprolactone diol, CAPA 225 (molecular weight 2000 from Introx Chemicals) and all the chain extenders used in this study were dried at 80ºC under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapours that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 225 was confirmed by applying the procedure reported in ASTM D-4274C [27]. MDI and all other materials were used as-received. All the reagents used in this work were of analytical grade.

Synthesis of Polymer (PU)

For this investigation a prepolymer was synthesized as predicted in our previous studies [28,29] by the step-growth polymerization of PCL and MDI, and extended with series of chain extenders. Into a four-necked reaction kettle equipped with mechanical stirrer, heating oil bath, reflux condenser, dropping funnel and N_2 inlet and outlet was placed PCL (31.25 g, 0.0156 mol). The temperature of the oil bath was increased to 60ºC. Then MDI (11.95 g, 0.047 mol) was added and the temperature was then increased to 100ºC. It almost took 1.0 h to obtain NCO-terminated prepolymer. The NCO contents of the prepolymer were determined and found close to the theoretical value (experimental value 9.31%; theoretical value 9.29%). Conversion of the prepolymer into the final PU was carried out by stirring the prepolymer vigorously, and then adding a previously degassed chain extender e.g., 1,2-ethane diol (1.94 g, 0.0313 mol). When homogeneity was obtained in the reactant mixture, the dispersion of chain extender was considered completely and the liquid polymer was cast into a

Teflon plate to form a uniform sheet of 2-3 mm thickness. The synthesized polymer was then placed in a hot air circulating oven at 100ºC and cured for 24 h. The cured sample sheets were then stored for one week at ambient temperature (25ºC) and 40% relative humidity before testing.

Prepolymer synthesis and film casting for other samples were preceded same as described briefly in the synthesis of SDPU1 (1,2-EDO). For each sample the prepolymer was extended with a weighed amount of alkane diol chain extender (0.0313 mol) as predicted in Table 1. All other parameters, temperature condition remained the same as described previously in the synthesis of SDPU1. Schematic illustration of chemical route for synthesis of EDO based polyurethane (SDPU1) is shown in Scheme I.
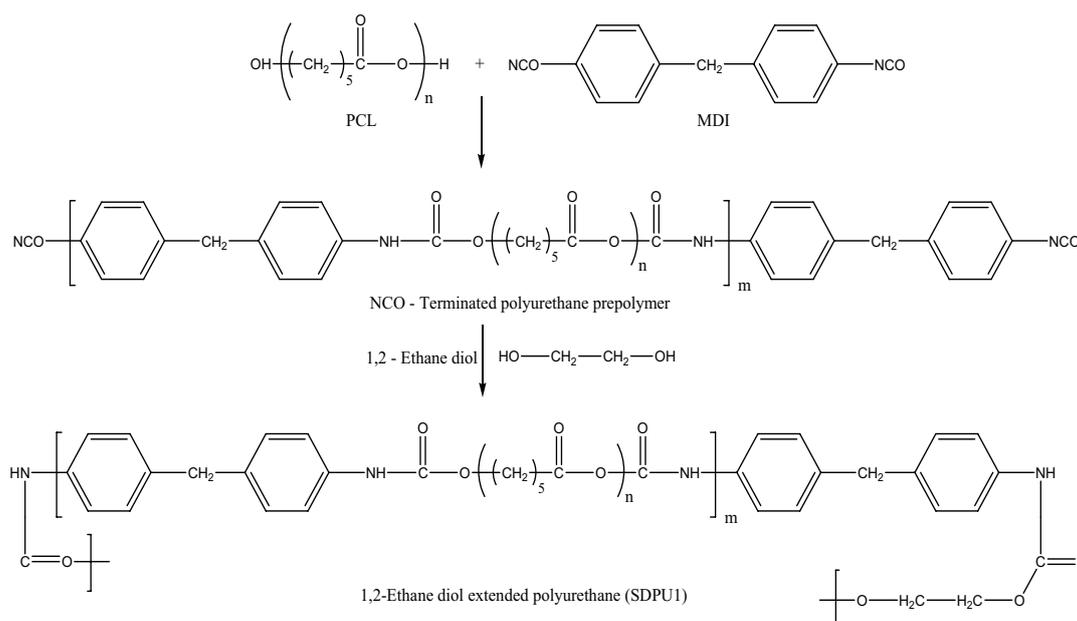
Measurements

FTIR Spectrum of the PU polymer films was obtained with a Bruker-IFS 48 Fourier transform infrared (FTIR) spectrophotometer (Ettlingen, Germany) over the range of 500-4000 cm^{-1} at room temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulphoxide (DMSO)-d$_6$ solution using a Bruker Advance 400 MHz Spectrometer. Chemical shifts (δ) were given in ppm with tetramethylsilane (TMS) as a standard. X-Ray diffractograms of the polymers were obtained in a Siemens D-5000 diffractometer with radiation Cu-Ka (λ = 15.405 nm, 40 Kv and 30 mA) at 25ºC. The relative intensity was registered in a dispersion range (2θ) of 5-40º. Kruss G10 contact angle measuring system was used for measurement of water droplet angle on polymeric film surface via sessile-drop experiment. Contact angle was measured using two test liquids (water and diiodomethane) for result precision. All the data pre-

Table1. Sample code designation and different formulations of PUs.

Sample number	Sample code	Prepolymer extended compound	Mass ratio of CAPA 225 : MDI : CE* with molar ratio 0.0156 mol : 0.047 mol : 0.0313 mol
1	SDPU1	1,2-Ethane diol (EDO)	31.25 g : 11.95 g : 1.94 g
2	SDPU2	1,3-Propane diol (PDO)	31.25 g : 11.95 g : 2.38 g
3	SDPU3	1,4-Butane diol (BDO)	31.25 g : 11.95 g : 2.82 g
4	SDPU4	1,5-Pentane diol (P'DO)	31.25 g : 11.95 g : 3.25 g
5	SDPU5	1,6-Hexane diol (HDO)	31.25 g : 11.95 g : 3.69 g
6	SDPU6	1,10-Decane diol (DDO)	31.25 g : 11.95 g : 5.44 g

* Chain extender

Scheme I. Chemical route for the synthesis of polyurethane elastomers (SDPU1).

sented were average of four measurements. Surface tension and their polar and dispersive portions were calculated applying two different methods (Owens-Wendt Method & Wu Method) for precision of the results.

Evaluation of Water Absorption

Bulk hydrophilicity of the polyurethanes was quantified by measuring the percentage amount of water that each polymer absorbed at 37ºC. The film of samples (10×10×1 mm) were placed in 100 mL Erlenmeyer flasks, containing deionized, degassed water and kept for 1, 2, 3, 4 and 5days in an incubator maintained at 37ºC. The samples were removed from water at predetermined time intervals, wiped gently with filter paper, and weighed immediately with an analytical balance. The sample mass change resulting from the water uptake (expressed as a percentage) was calculated according to the following formula:

$$\text{Water absorption}(\%) = \frac{m_w - m_d}{m_d} \times 100$$

where m_d and m_w are the masses of dry and wet polyurethane samples, respectively.

Equilibrium Degree of Swelling

The equilibrium degree of swelling of each elastomer was determined by immersing a small sample (20×20×2 mm) in 100 mL solvent (toluene) for 7 days at room temperature and reweighing after rapid surface drying with paper towels. The equilibrium degree of swelling was calculated using the following relations [30,31]:

$$\frac{1}{V_R} = \frac{v_R + v_S}{v_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{\omega_S}{\omega_R} = 1 + \frac{\rho_R}{\rho_S} \cdot \frac{\omega_{S+R} - \omega_R}{\omega_R}$$

where $1/V_R$ is equilibrium degree of swelling, v_R is volume fraction of elastomer component in the swollen sample, v_S is volume fraction of solvent in the swollen sample, ω_R is the weight of dry sample after swelling, ω_S is the weight of solvent contained within swollen sample, ω_{S+R} is the weight of swollen sample, ρ_R is density of dry sample before swelling, and finally ρ_S is density of solvent (0.876 for toluene). Density of the dry polymer samples (ρ_R) was measured according to method reported in ASTM D-1817 [27].

RESULTS AND DISCUSSION

The main aim of this research work was to study the effect of α,ω alkane diols on the properties of polyurethane elastomers. So the synthesis of polyurethane elastomer was considered following the

synthetic route as outlined in Scheme I. The reaction of one equivalent of polyol with three equivalents of MDI led to NCO-terminated polyurethane prepolymer, which was subsequently extended with two equivalents of chain extender to prepare final polyurethane.

Molecular Characterization

Structural characterization was performed using FTIR, ^{1}H NMR and ^{13}C NMR spectroscopic techniques. FTIR Spectroscopy obtained from the cast film is shown in Figure 1. This analysis was used to check the end of polymerization reaction, verifying the disappearance of the $\overline{v}$ NCO at 2265 cm^{-1} and the appearance of $\overline{v}$ N-H at 3000-3400 cm^{-1}. Presence of expected peaks implied that the reaction was completed and the predesigned PU was formed. FTIR Spectra obtained also contained all the related information of the primary structure of the final polymer. FTIR Spectra showed characteristic bands of urethane groups at 3330 cm^{-1} (N-H stretching). The peaks located at 2947 and 2810 cm^{-1} were assignable to CH symmetric and asymmetric stretching vibrations of CH$_2$ groups. The peaks observed at 1728, 1642, 1599, and 1529 cm^{-1} were due to C=O bond and NH deformations, respectively. The absorption bands at 1464, 1407, and 1311 cm^{-1} were attributed to CH$_2$ bending vibration, CH bending vibration, and CH$_2$ wagging, respectively. Peaks corresponding to the absorption of -NH, -CO, -CHN were observed at 3330, 1728 and 1464 cm^{-1} respectively, which indicated the new synthesized product having -NHCOO groups being formed. The observed N-H bending vibrations at 1529 cm^{-1}, C-O-C stretching absorption
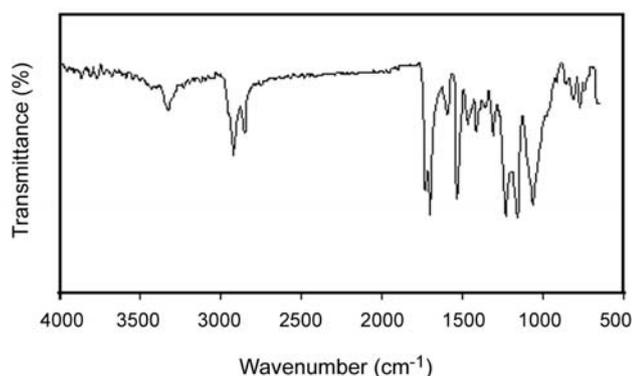
band corresponding to the ether oxygen of soft-segment at 1000-1150 cm^{-1} also provided a strong evidence for the formation of PU. It is worthwhile mentioning that the N-H group in polyurethane could form hard-hard segment H-bonding with the carbonyl oxygen and hard-soft H-bonding with the ether oxygen. The stronger hard-hard segment H-bonding acts as physical cross-links leading to difficult segmental motion of the polymer chain which results in a more significant phase separation between hard and soft segments. The phase separation improves the mechanical properties of polyurethanes but reduces their flexibility and solubility [32,33].

^{1}H NMR (400 MHz, DMSO-d$_6$) and ^{13}C NMR (400 MHz, DMSO-d$_6$) spectra of final synthesized polyurethane samples (SDPU1-6) were in accordance with proposed structures. ^{1}H NMR and ^{13}C NMR spectra of polyurethane extended with 1,3-propane diol (SDPU2) are shown in Figures 2a and 2b. The signal of urethane (NH) was observed at 8.45 ppm and peaks observed at 7.05-7.45 ppm could be assigned to proton of aromatic structure. Some other peaks at 1.29-4.08 ppm which could be assigned to proton of CH$_2$, CH$_2$OCO supported the formation polyurethane. In ^{1}H NMR spectra (Figure 2a), the observed peaks were assigned as: 8.46 ppm (s, NH); 7.3-7.2 (m, 4H); 7.08-7.02 (m, 4H); 4.05-3.93 (broad, 4H); 3.77-3.73 (s, 2H); 3.36 (m, 2H); 2.47 (DMSO); 2.21 (m, 2H); 1.48-1.35 (m, 2H); 1.34-1.24 (m, 2H) and regarding ^{13}C NMR spectra (Figure 2b); observed peaks were assigned as: 173.2, 154.8 ppm (C=O); 138.6, 136.9 (aromatic C); 129.2, 118.7 (aromatic CH); 64.4, 63.9, 61.0, 40.7, 40.6, 40.4, 40.1, 39.9, 39.7, 39.5, 39.3, 34.9, 33.8, 28.9, 25.5, 25.4, 24.6, 25.5 (CH$_2$).

X-Ray Diffraction Studies

Degree of crystallinity of the PU samples was estimated multiplying the ratio of the crystalline peak area to total peak area by 100. The d-spacing of different samples was determined by Debye-Scherrer (powder) method using Bragg's relation [34,35]

$$n\lambda = 2d \sin \theta$$

where, n is an integer, λ is the wavelength of the X-ray which is 1.54 Å for Cu target, d is the inter-planar spacing also called d-spacing, θ is the angle between the planes and the direction of the beam.

Figure 1. FTIR Spectrum of polyurethane film (SDPU6).
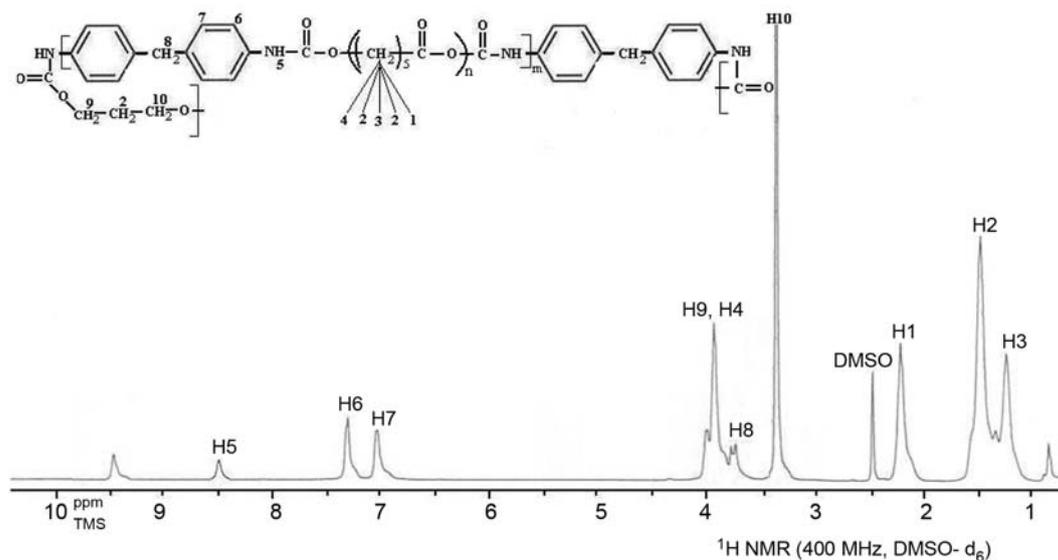
(a)
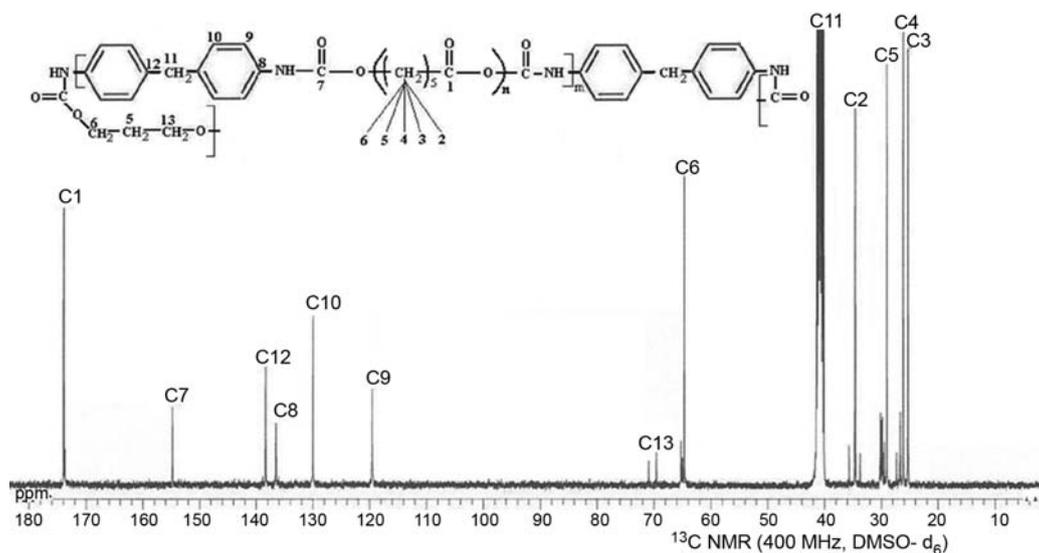
(b)

Figure 2. NMR Spectra of polyurethane (SDPU2): (a) ^{1}H NMR and (b) ^{13}C NMR.

In segmented PUs, phase separation of soft segments and hard segments may take place depending on their relative contents, structural regularity and thermodynamics incompatibility. The X-ray diffraction studies showed that crystallinity much depends on the number of methylene units in the polyurethane backbone and crystallinity increases as the chain extender length in the final PU increases (Table 2 and Figure 3). We can observe that the increase in chain extender length favours the formation of more ordered structure. There is an increase in intensity of

the peak localized at $2\theta=21.5^\circ$ with increase of -CH$_2$- units in the formulation, generating better defined peak. We can conclude that PU extended with DDO (SDPU6) has shown the higher peak intensities leading to higher chain orientation degree. These results confirm the hypothesis that the increase in chain extender length tends to increase in phase segregation and consequently to soft segment mobility. This increase in mobility would be responsible for an increase in the chain orientation degree. It can be seen that the sample SDPU1 has shown a lower diffraction

Table 2. The *d*-spacing and degree of crystallinity of PU samples extended with series of chain extender (calculated from X-ray diffraction peaks).

Sample number	Sample code	d_a (A°)	PC_a (%)	d_b (A°)	PC_b (%)	TC (%)
1	SDPU1	4.38	6.3	13.52	20.4	26.7
2	SDPU2	4.37	6.9	13.52	22.8	29.7
3	SDPU3	4.35	7.0	13.01	25.0	32.0
4	SDPU4	4.32	7.2	12.55	26.5	33.7
5	SDPU5	4.30	7.8	12.37	27.5	35.3
6	SDPU6	4.28	8.1	11.80	29.7	37.8

d_a (A°), d_b (A°) are the d-spacing of peaks a and b in (A°); PC_a (%), PC_b (%) are the percentage of crystallinity of the peaks a and b; TC (%) is the total percentage of crystallinity.

peak height and broader upper half peak area which indicate that this sample has smaller crystal particles resulting in diminished crystallinity.

Previous studies [36,37] have concluded that the crystallinity of PU elastomers is provided by the soft segments. As the hard segments have higher polarity than soft segments, they interact with each other faster than the soft segments, and thus, the part of the PU structure due to the hard segments would be less crystalline than the one due to the soft segments, which

Figure 3. X-Ray diffractograms of: (a) SDPU1; (b) SDPU2; (c) SDPU3; (d) SDPU4; (e) SDPU5; and (e) SDPU6.

are able to reorganize themselves until they reach a more stable disposition before interacting with each other, and hence, give a structure with maximum crystallinity. Only when the hard segments are annealed, they are able to reorganize themselves before crystallization, thus leading to crystalline thermoplastic polyurethane structure. It is worthwhile to mentioning that hard segment, when present at higher concentration, presents diffraction peak in a range of $2\theta = 11.12°$. So that crystallinity in the present study is due to soft segment itself. As the crystallinity of the PUs in this study is considered mainly due to the presence of soft segments, interrelations with the phase separation and structural organization must be expected. In general, the lower the melting enthalpy (reduced structure organization), the lower the crystallinity. Considering that a lower melting enthalpy can be associated to a lower degree of phase separation, the lower crystallinity can be related to a smaller degree of phase separation.
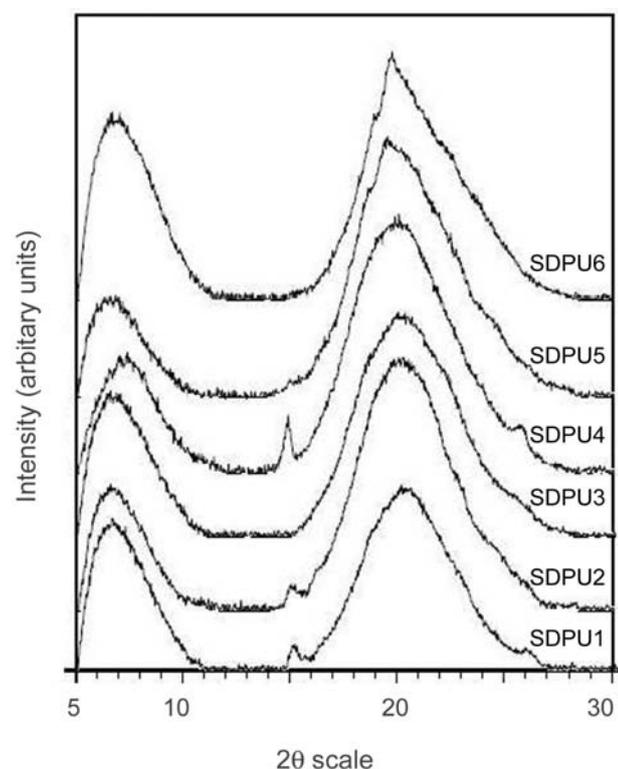
Surface Morphological Studies
Contact Angle Measurement
Hydrophilicity was evaluated by measuring the contact angle formed between water or diiodomethane drops and surface of the PU films using contact angle measuring devices (G-10 KRUSS). In the present study the contact angle was measured using two different test liquids for obtaining results with highest precision. The values of contact angle using water as test liquid change from 81.6° to 66.66° as the number of methylene units in the PU backbone vary from 02 to 10 (Table 3). Similar behaviour of decreasing in contact angle values (52.0° to 36.06°) was observed

Table 3. Variation of contact angle with different test liquids and chain extender.
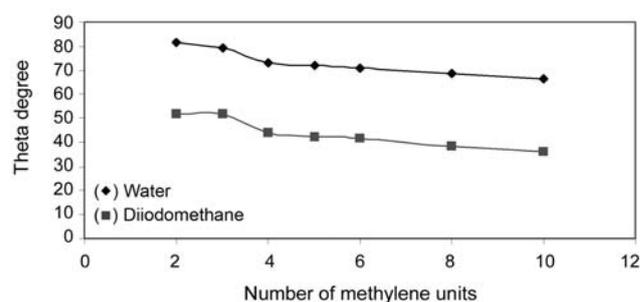
Sample number	Sample code	Contact angle (θ) with water and diiodomethane	
		Water	Diiodomethane
1	SDPU1	81.6	52.0
2	SDPU2	79.1	51.6
3	SDPU3	73.1	43.8
4	SDPU4	72.0	42.0
5	SDPU5	70.6	41.4
6	SDPU6	66.6	36.0

using diiodomethane test liquid (Figure 4). As it can be observed, there is a remarkable difference between the contact angle degree values of SDPU1 to SDPU6 with both the test liquids. This means hydrophilicity of the final PU film increases by increasing the chain extender length. This phenomenon might be due to fact that the hard segment carrying polar group is connected with short chain extender (SDPU1) resulting the movement of the hard segment to be more restricted as it does not have freedom to come on the surface. On the other hand when it is connected to a long flexible chain carrying 10 methylene units (SDPU6), more conformation freedom is incorporated in PU and therefore it does not restrict the movement of the hard segments and it can easily move towards the surface. While during the casting process, the polymer is ultimately made of hydrophilic because of the relative abundance of the polar group present. This further increases the hydrophilicity of the PU film as chain extender length increases. Moreover, the decrease in water wettability of solid surfaces is attributed to the thermodynamic driving force to minimize the surface free energy. It is believed that chemical functional groups, responsible for the enhanced wettability, gradually migrate away from the surface exposed to dry air towards the interior of polymeric material. The migration of the functional groups to minimize the solid surface energy is facilitated by the local segmental motion of polymers.

Surface Free Energy
Surface tension and their polar and dispersive portions were calculated by application of two different

Figure 4. Contact angle of PU film as a function of chain extender length.

Table 4. Total surface energy calculated data with Owens-Wendt and Wu methods.

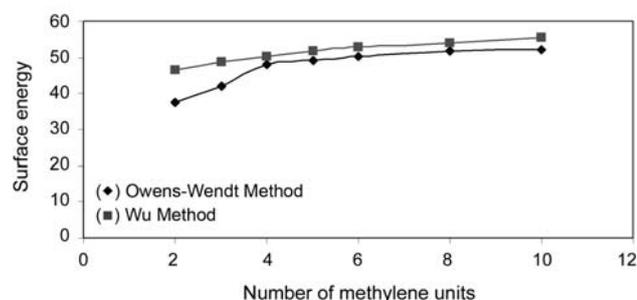| Sample number	Sample code	Owens-Wendt Method			Wu Method		
		Disperse portion (mN/m)	Polar portion (mN/m)	Total surface energy (mN/m)	Disperse portion (mN/m)	Polar portion (mN/m)	Total surface energy (mN/m)
1	SDPU1	33.37	4.25	37.62	37.34	9.31	46.65
2	SDPU2	35.20	6.62	41.83	41.92	6.71	48.63
3	SDPU3	39.14	8.73	47.86	38.40	11.78	50.19
4	SDPU4	44.18	5.13	49.31	42.70	9.15	51.86
5	SDPU5	47.13	2.96	50.10	43.86	9.01	53.01
6	SDPU6	49.97	2.14	52.11	47.20	8.47	55.66

Table 5. Hydrophilicity and swelling data of samples.

Sample number	Sample code	Density (g/cc)	Water absorption (%)						Equilibrium degree of swelling
			1st day	2nd day	3rd day	4th day	5th day	7th day	
1	SDPU1	1.008	2.08	2.10	2.11	2.12	2.13	2.13	9.52
2	SDPU2	1.018	2.28	2.31	2.32	2.32	2.33	2.33	10.10
3	SDPU3	1.021	2.64	2.68	2.69	2.69	2.69	2.69	14.39
4	SDPU4	1.022	2.98	3.00	3.02	3.02	3.03	3.04	15.10
5	SDPU5	1.024	3.64	3.68	3.69	3.70	3.70	3.71	15.21
6	SDPU6	1.025	3.79	3.82	3.84	3.85	3.85	3.85	21.16

methods (Owens-Wendt Method and Wu Method) for precision and validation of the results. It was found that surface energy increases as the number of methylene units in the final PU backbone increases (Table 4). This behaviour was confirmed from the results of both applied method (Figure 5). This phenomenon is due to that fact that decrease in contact angle values leads to increase in surface energy. The contact angle of a liquid with a solid surface is related to the solid surface energy, γ_S, liquid surface tension, γ_L, and solid-liquid interfacial tension, γ_{SL}, by the well known Young's equation [38].

$$\cos\theta = \frac{\gamma_S - \gamma_{SL}}{\gamma_L} \qquad (1)$$

This shows that higher the solid surface energy, γ_S, or the lower the liquid surface tension, γ_L, the lower the contact angle would become. In other words, one can make a solid surface more wettable either by lowering the surface tension of the liquid or by increasing the surface energy of the solid [39]. It is well known that increase in chain extender length results in decreasing free volume and chain mobility in the PU membrane.

This would increase the surface free energy. In addition to this, it was also observed that with increasing chain extender length, the polar component steadily decreases and the dispersive part is increased.

Evaluation of Water Absorption (%) and Swelling Behaviour

Physical properties of PU such as density, water absorption (%), equilibrium degree of swelling were determined (Table 5). Also as these polymers can be used to perform and degrade in biological environments because of their hydrolysable soft segments such as poly(ε-caprolactone) (PCL) on their backbone. So bulk water absorption ability plays an important role on their degradation rate. Water absorption as a function of time and type of samples are collected in Table 5. There was no considerable difference in the amount of absorbed water as a function of time. The chain extender length was the main factor in controlling the amount of absorbed water. The results obtained clearly show that water absorption of samples is increased with increasing $-CH_2-$ into the final PU samples (Figure 6). In addition the swelling

Figure 5. Surface free energy of PU film as a function of number of methylene units in chain extender.
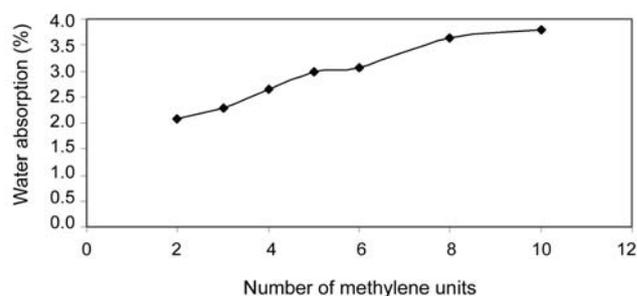
Figure 6. Water absorption of PU film as a function of chain extender length.

behaviour was also in accordance with water absorption. The swelling ability of final PU steadily increases as the chain extender length increases. It has been found that SDPU1 has better solvent resistance as compared to SDPU6, and this resistance continuously decreases as the number of methylene units in PU increases. This effect can be elucidated by the degree of physical cross-linking and hydrogen bonding in polyurethane.

CONCLUSION

Polyurethane elastomers with tunable crystallinity and hydrophilicity were synthesized by step growth polymerization techniques using poly(ε-caprolactone) (PCL) and 4,4′-diphenylmethane diisocyanate (MDI), extended with α,ω alkane diols. The conventional spectroscopic characterization of the samples with FTIR was in accordance with proposed polyurethane structure. Crystalline behaviour of the polyurethane film was studied and discussed by using X-ray diffraction technique. For all the samples, the crystallinity and hydrophilicity were found to increase with increasing of chain extender length. Optimum crystallinity and hydrophilicity were obtained from elastomer extended with DDO in comparison to elastomers extended with EDO. It was concluded that by increasing the chain extender length into the PU formulation, the crystallinity of the samples increases. The interactions of the final PU films with water and diiodomethane on the surface were clearly related to the number of -CH$_2$- units. Contact angle measurement, water absorption and swelling behaviour of the synthesized polyurethane were affected by number of methylene units in the chain extender of the PU. Investigation of structure-property relationship for prepared elastomers showed that the main determining factors for observed properties were hydrogen bonding, crystallinity, hydrophilicity and chain extender length in PU backbone.

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