

Synthesis and Characterization of Polyurethane Elastomers Based on Chitosan and Poly(ϵ -caprolactone)

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ABSTRACT: Biodegradable polyurethane (PU) elastomers with potential for biomedical and industrial applications were synthesized by the reaction of poly(ϵ -caprolactone) (PCL) and isophorone diisocyanate (IPDI), extended with different mass ratio of chitosan and 1,4-butanediol (BDO). Their chemical structures were characterized using FTIR, ¹HNMR, and ¹³CNMR, and thermal properties were determined by TGA and DMTA. Incorporation of chitosan contents into the polyurethane backbone caused improvement in thermal stability and thermal degradation rate. Optimum thermal properties

and degradation profile were obtained from elastomer extended with chitosan. The crystallinity and hydrophilicity of the prepared polymers were also examined by X-ray and contact angle measurements. The results showed that hydrophilicity decreased and crystallinity increased with increasing of chitosan content in polyurethane backbone. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3157–3165, 2009

Key words: chitosan; poly(ϵ -caprolactone); polyurethane; synthesis; biodegradable

INTRODUCTION

Polysaccharides are widely distributed in nature. Their molecular structure and hence their properties vary over a broad range. These natural polymers will therefore become increasingly important in various fields as they possess unique structures and characteristics that are quite different from those of typical synthetic polymers.¹

Among many kinds of polysaccharides, cellulose and chitin are the most important biomass resources. Cellulose is synthesized mainly in plants, whereas chitin is synthesized mainly in lower animals. Although cellulose has been studied extensively, only limited attention has been paid to chitin, principally from its biological properties.² Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide groups at the C-2 positions instead of hydroxyl groups comparing with cellulose. In addition to its unique polysaccharide architecture and the presence of amine groups (5–15%) in chitin^{3,4} are highly advantages for providing distinctive biological functions and for conducting modification reactions.^{5,6} Chitosan is the *N*-deacetylated derivative of chitin, although this *N*-deacetylation is almost never complete. Flash treat-

ment of the alkali impregnated chitin at 140–190°C has been reported to be efficient to give highly deacetylated chitosan over a short time period.⁷ Chitosan is also structurally similar to cellulose, but it is an amino polysaccharide having amine group at the C-2 position in place of hydroxyl group (Fig. 1).

In the past 30 years, substantial progress has been made on fundamental and applied research in chitosan technology. This natural polymer has excellent properties such as biocompatibility, biodegradability, nontoxicity, and adsorption properties, which have drawn extensive attractions in recent years.⁸ It is recommended as a suitable functional material for further polymerization. Chitosan has a wide range of applications in many fields. It may be used in membranes,⁹ for removal of metal ions from waste water,¹⁰ drug delivery systems,¹¹ biological applications,¹² tissue engineering,¹³ biosensors,¹⁴ scaffolds,¹⁵ and packaging.¹⁶ In addition, chitosan also provides bacteriostatic and fungistatic activities.^{17–19} For these reasons, chitosan has been one of the important biomaterials for wound management in recent years.²⁰

Polyurethanes on the other hand are used widely in biomedical applications because of their good physical and mechanical properties together with their biocompatibility characteristics, such as heart valves, aortic grafts, dialysis membranes, pacing leads insulation, indwelling catheters, intra-aortic balloons, and mammary implants.^{21,22}

In spite of the many properties of chitosan, the low mechanical strength of this material sometimes limits its further applications.²³ Recent studies have

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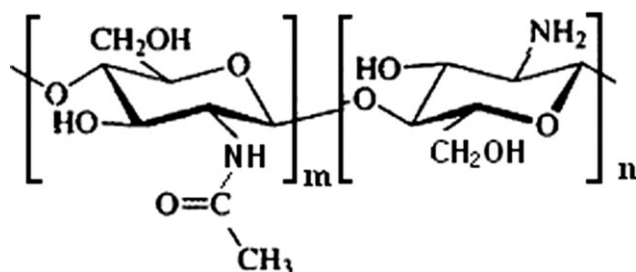


Figure 1 Structure of chitosan.

reported on the enhancement of mechanical strength for biomedical applications by blending or interpenetrating the network with other synthetic or natural polymers.^{24–27} The synthesis and characterization of starch and chitin-based polyurethane have been examined in our previous studies.^{28,29} It was suggested that molecular rigidity, strength, and heat resistance increase by incorporating chitin and starch contents in the PU backbone.

In this study, to obtain biodegradable polyurethanes with good mechanical properties, a new method for the preparation of chitosan-based polyurethanes was designed using polycaprolactonediol, isophorone diisocyanate, 1,4 butanediol, and chitosan. The bulk structures and properties were characterized by FTIR, NMR, DMTA, TGA, and XRD techniques.

EXPERIMENTAL

Materials

Polycaprolactone diol (PCL) with molecular weight of 2000 was obtained from Solvay Chemicals, UK. Isophorone diisocyanate (IPDI), 1,4 butanediol, (1,4-BDO), hydrogen peroxide 30%, dimethyl sulfoxide (DMSO), and acetone were purchased from Merck, Germany. PCL and 1,4-BDO were dried at 60°C under vacuum for 24 h before use to ensure the removal of all air bubbles and water vapors that may otherwise interfere with the isocyanate reactions. Low molecular weight chitosan ($M_v = 3.5 \times 10^5$, DD = 80%) was purchased from Aldrich and treated with H_2O_2 before use.

Ipdi and all other materials were used as-received. All the reagents used in this work were of analytical grade.

Treatment of chitosan

A mixture of distilled water with H_2O_2 was prepared with volume ratio of 3/1 and proper amount of chitosan was added to this mixture followed by stirring at room temperature for 48 h. During this period, the chitosan will dissolve in the mixture and breakage of 1,4- β -D-glucoside bonds of chitosan leads to the depolymerization and formation of oli-

gosaccharides.^{30,31} The resulting solution of oligosaccharides was added to the acetone as a nonsolvent. The precipitated solid was collected and dried under vacuum over night. The treated chitosan will dissolve in DMSO after 24 h and can be used for preparation of polyurethane elastomer in solvent media.

Synthesis of PU extended with chitosan

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 (20 g; 0.01 mol), and the temperature of the oil bath was increased to 60°C. Then, IPDI (6.77 g; 0.03 mol) was added drop wise, and the temperature was increased to 100°C. It almost took 4.0 h to obtain NCO terminated prepolymer. Conversion of the prepolymer into the final PU was carried out by adding a previously degassed chain extender solution to the reactor and stirring was continued at least for another 6 h. The overall PCL/IPDI/chain extender molar ratio 1/3.05/2 was used for synthesis purposes. The equivalent weight of chitosan was selected as 56.4. It was calculated as follows: $[(161/3) \times 0.8 + (203/3) \times 0.2] = 56.4$ where 161 and 203 are molecular weight of chitosan and chitin, respectively.

When color homogeneity was obtained in the reactant mixture, the dispersion of chain extender was considered complete, and the liquid polymer was cast into a Teflon plate to form a uniform sheet of 2–3 mm thickness.³² The synthesized polymer was then placed in a hot air circulating oven at 100°C and cured for 24 h. The cured sample sheets were then stored for 1 week at ambient temperature (25°C) and 40% relative humidity before testing.³² Samples were prepared with different proportions of chitosan/BDO. The compositions of the prepared polyurethanes are given in Table I, and the reaction route of polymer synthesis is also shown in Figure 2.

Measurements

Infrared measurements were performed on a Bruker-Equinox 55 Fourier transform infrared (FTIR) spectrometer (Ettlingen, Germany) by H.ATR

TABLE I
Sample Code Designation and Different Formulations of PU's (g)

Sample code	Capa 225	IPDI	1,4 butanediol	Chitosan
PU1	20	6.77	1.8	0
PU2	20	6.77	1.44	0.45
PU3	20	6.77	1.08	0.90
PU4	20	6.77	0.72	1.35
PU5	20	6.77	0.36	1.80
PU6	20	6.77	0	2.25

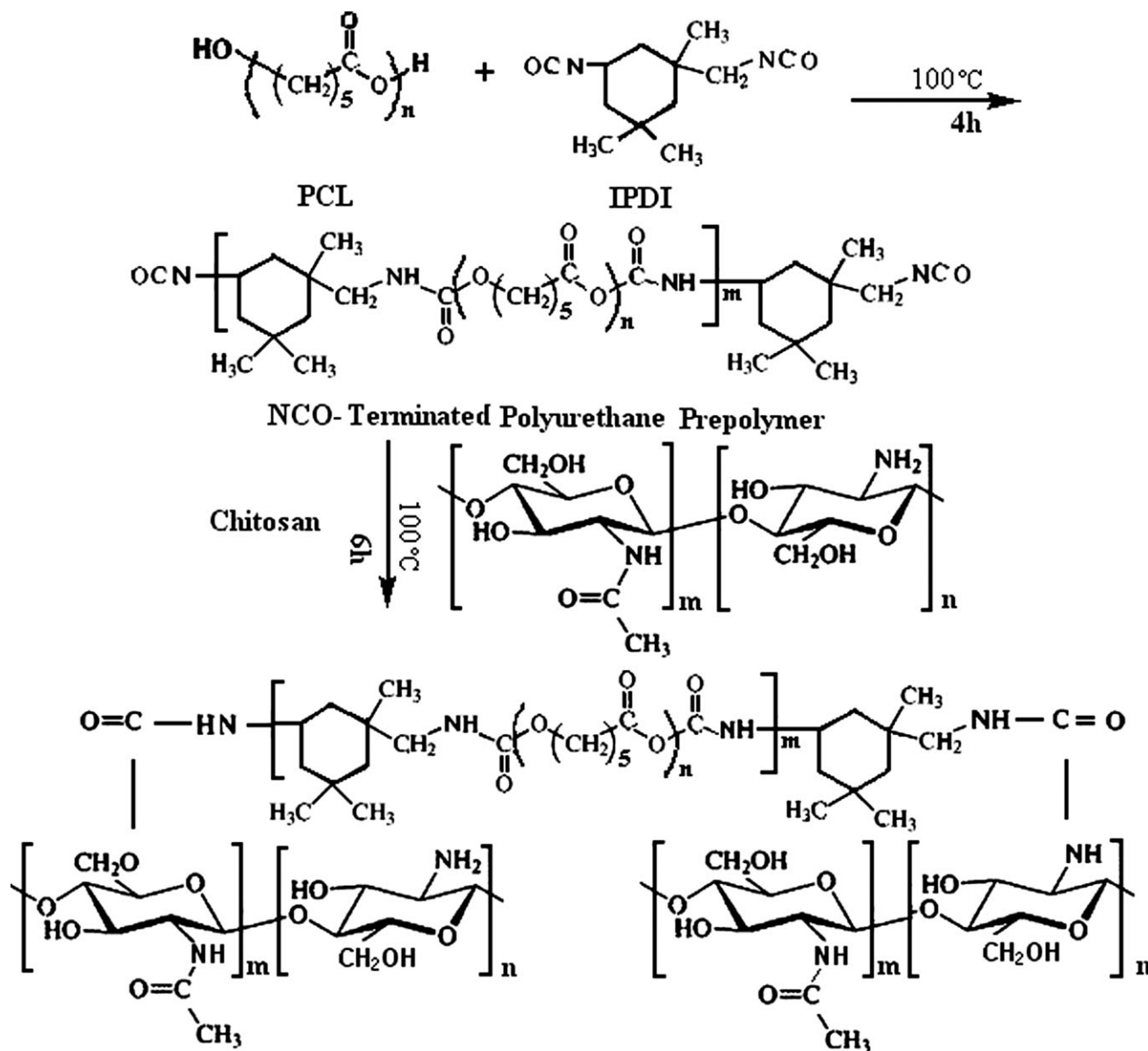


Figure 2 Chemical route for synthesis of chitosan-based polyurethane elastomers.

accessories equipped with ZnSe crystal. The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded in deuterated dimethyl sulfoxide ($\text{DMSO}-d_6$) solution using a Bruker Advance 400 MHz Spectrometer (Germany). Chemical shifts (δ) were given in ppm with tetramethylsilane (TMS) as a standard. Thermogravimetric analysis (TGA) was recorded on a Polymer Lab TGA-1500 (London, UK) under nitrogen atmosphere from room temperature up to 650°C with heating rate of $10^\circ\text{C}/\text{min}$. The dynamic mechanical measurements (DMTA) were performed on a Triton Tritic 2000 instrument over a temperature range of -100 to 200°C at heating rate of $10^\circ\text{C}/\text{min}$ and frequency of 1 Hz. The dimensions of samples were $30\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$. The value of storage modulus versus temperature was recorded for each sample.

Contact angle was measured at room temperature by G10 (Kruss)(Hamburg, Germany) instrument through sessile drop method and the X-ray diffractograms of the polymers were obtained with a Siemens D5000 diffractometer (λ -15.405 nm, 40 KV, and 30 mA) at 25°C . The relative intensity was registered in a dispersion range (2θ) of 5 – 70° .

RESULTS AND DISCUSSION

Synthesis and characterization

This study was focused on preparation of a new biodegradable biocompatible polyurethane elastomer with improved physical, mechanical, and thermal properties. So, synthesis of chitosan-based polyurethane was considered following the synthetic route

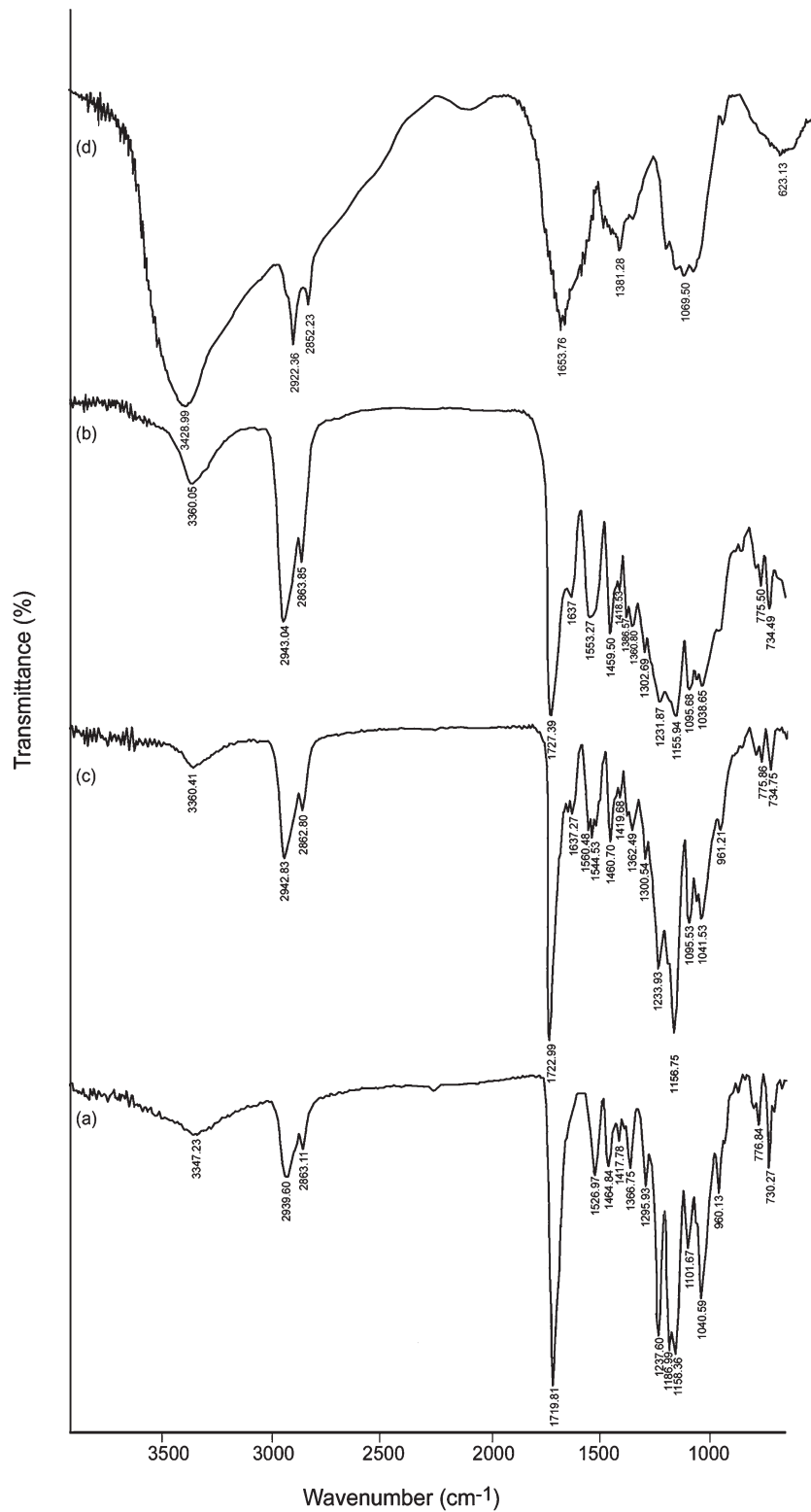


Figure 3 FTIR spectra of (a) PU extended with 0% chitosan; (b) PU extended with 60% chitosan; (c) PU extended with 100% chitosan; and (d) original chitosan.

as outlined in Figure 2. The reaction of one equivalent of polyol with three equivalents of IPDI leads to NCO-terminated polyurethane prepolymer, which

was subsequently extended with two equivalents of chain extender with different proportions of chitosan/1,4-BDO to prepare final polyurethane.

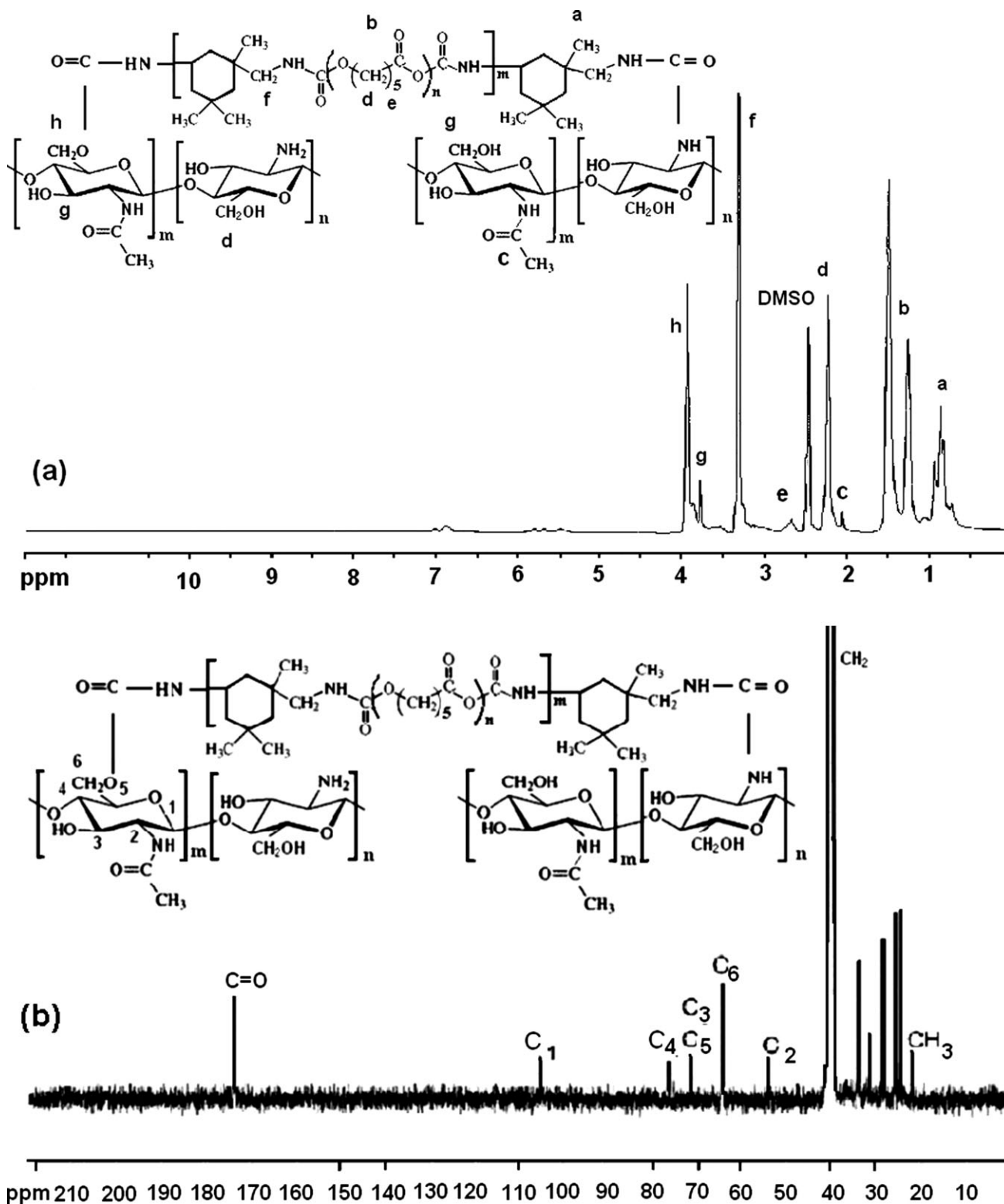


Figure 4 (a) $^1\text{H NMR}$ spectrum of chitosan-based polyurethane (PU6). (b) $^{13}\text{C NMR}$ spectrum of chitosan-based polyurethane (PU6).

IR spectroscopy

FTIR spectra of polyurethane extended with 0.0, 60, and 100% chitosan are shown in Figure 3. FTIR spectrum of original chitosan [Fig. 3(d)] showed that

broad OH stretching vibration bands appeared at 3443 cm^{-1} . The N-H stretching vibration bands appeared at 3360 cm^{-1} . The C-H symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2943 and 2863 cm^{-1} , respectively.

The faint absorptions at 1727, 1637, and 1563 cm^{-1} are due to C=O bond and N—H deformations. The absorption bands at 1458, 1360, and 1302 cm^{-1} were attributed to CH_2 bending vibration, C—H bending vibration, and CH_2 wagging, respectively. The broad intense band at 1020–1220 cm^{-1} was attributed to the ring and bridge C—O—C vibrations of chitosan-ether-type absorption.

FTIR spectrum of PU6 [Fig. 3(c)] showed a stronger absorption peak of N—H stretching vibration at 3360 cm^{-1} comparing with PU4 [Fig. 3(b)] and PU1 [Fig. 3(a)]. The C—H symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2943 and 2863 cm^{-1} , respectively. The other peaks were assigned as: 1727, 1637 cm^{-1} (C=O bond); 1553 cm^{-1} (N—H deformation); 1459 cm^{-1} (CH_2 bending vibration); 1418 cm^{-1} (C—H bending vibration); 1302 cm^{-1} (CH_2 wagging). By extending prepolymer with different proportions of chitosan/1,4-BDO, the FTIR spectrum showed a very strong, new peaks at about 1722 cm^{-1} , which were assigned to C=O stretching of soft segment of PCL and urethane bonds. Another new peak was also observed at about 1460 cm^{-1} , which was assignable to urethane C—N bonds. It was observed that the intensity of hydrogen-bonded C=O increased as the chitosan content increased (1637 cm^{-1}), suggesting the formation of new hydrogen bonds between chitosan and polyurethane. Moreover, with increasing chitosan content, the peak of urethane carbonyl groups at around 1727 cm^{-1} (PU1-1719 cm^{-1} ; PU4-1722 cm^{-1} PU6-1727 cm^{-1}) decreased. This implies that stronger interchain interactions between chitosan and PU in chitosan-based PU than BDO-based PU. The intensity of N—H stretching vibration bands appeared at 3360 cm^{-1} was also increased by increasing of chitosan content in formulation. From Figure 3(d), it can be noticed that a broad band appeared at 3428 cm^{-1} in original chitosan has been disappeared in the final polyurethane extended with chitosan. This provides the evidence that all of the chitosan has been consumed and there is no free chitosan in the final polyurethane sample. It is worse to mention that all the chemicals were selected stoichiometrically.

NMR spectroscopy

NMR spectrum of polyurethane extended with 100% chitosan is shown in Figure 4. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) and ^{13}C NMR (400 MHz, $\text{DMSO}-d_6$) spectra of final synthesized polyurethane samples were in accordance with proposed structures. Methylene groups of isophorone diisocyanate were observed at 0.54–0.94 ppm. Central methylene groups of polycaprolactone were observed at 1.1–1.4 ppm. Acetyl group was appeared as a peak at 2.05 ppm. CH_2O —

TABLE II
The Variation of Contact Angle with Different Contents of Chitosan

Sample no.	(chitosan/1,4BDO) % by mass	Contact angle (°)
PU1	0/100	77.4
PU2	20/80	77.9
PU3	40/60	81.4
PU4	60/40	84
PU5	80/20	90.7
PU6	100/0	98

and CH_2CO — of polycaprolactone appeared at 2.22 and 2.65 ppm, respectively. CH_2 -ofisophorone diisocyanate was observed at 3.32–3.49 ppm. CH_2OH and — CHOH of chitosan were detected at 3.78 and 3.93 ppm. CH_2O attached to chitosan ring and urethane carbonyl was observed at 3.95 ppm and weak peaks appearing at 6.85–7.12 ppm were attributed to chitosan and urethane NH groups [Fig. 4(a)].

^{13}C NMR spectrum [Fig. 4(b)]: 173.2 ppm (C=O); 104.1 (C1-chitosan); 77.5 (C4- chitosan); 75.7, 73.3(C3 and C5 -chitosan); 65.3, (C6- chitosan); 55 (C2-chitosan); 65.3, 40.8, 40.4, 40.2, 39.5, 39.3, 34.9, 33.8, 28.7, 28.3(CH_2); 25.3, 24.5, 22.8(CH_3). Appearance of new peaks in ^1H NMR spectrum at 2.05 ppm (assigned to the proton of acetyl group (CH_3CO)) and in ^{13}C NMR spectrum at 22.8 ppm (attributed, to the methyl group of chitosan) provides evidence of involvement of chitosan in final polyurethane structure. Moreover, peaks located at about 55, 65.3, 73.3, 75.7, 77.5, and 104 ppm were attributed to C2, C6, C3, C5, C4, and C1 position of chitosan, respectively.

Contact angle

Hydrophilicity of the samples with different weight percent of chitosan were evaluated by measuring the contact angle formed between water drops and surface of the samples. For this purpose, the drops of water were placed on five different areas of the surface using a micro syringe. Results presented in Table II and Figure 5 is the mean value of five measurements.

As it can be seen, there is a remarkable difference in contact angle between different weight percent of chitosan in polyurethane backbone as a chain extender, where increases from 77.4 with 0% chitosan to 98 with 100% chitosan. This means that hydrophilicity decreases with increasing of chitosan in polyurethane structure. Decreased hydrophilicity of polyurethanes may be due to chain rigidity of polymer which arises due to incorporating of chitosan in polyurethane chain. However, the results confirm that chain flexibility is a more significant factor in

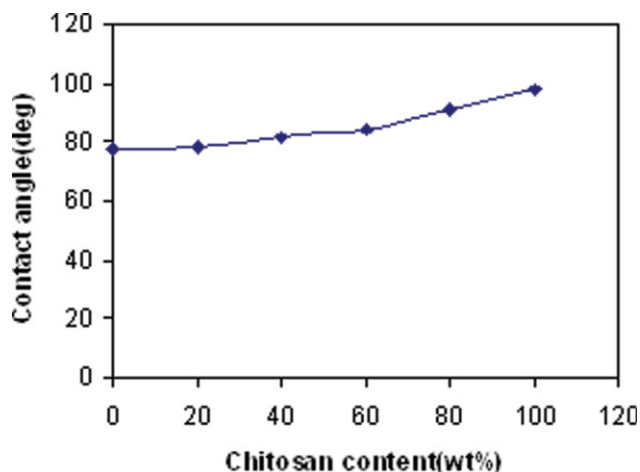


Figure 5 Contact angles of the samples versus chitosan content. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

controlling the contact angle. Chain rigidity does not allow the polar groups to come to the polymer surface and increase hydrophilicity.

X-ray studies

Chitosan has a highly ordered crystalline structure. X-ray diffraction analysis was carried out to find the changes of the crystalline structure on the substitution reaction with NCO terminated prepolymer. In segmented polyurethanes, phase separation of soft and hard segments can take place depending on their relative contents, structural regularity, and thermodynamics incompatibility. The X-ray diffraction studies showed that crystallinity much depends on the concentration of chitosan in the polyurethane backbone, crystallinity increased as the concentration of chitosan in to the final PU increased [Fig. 6(a) PU1, (b) PU3, and (c) PU6]. It can be seen that the presence of chitosan favor the formation of more ordered structure. There is an increase in intensity of the peak localized at $2\theta = 21.5^\circ$ confirming that the polymer tend to crystallize with increase of chitosan contents in the formulation, generating better defined peak. We can conclude that PU extended with 100% chitosan (PU6) and with combination of chitosan/1,4-BDO showed the higher peak intensities leading us to conclude that these samples present the higher chain orientation degree. These results confirm the hypothesis that the presence of chitosan increase in phase segregation and as consequence the soft segment mobility. This increase in mobility would be responsible for an increase in the chain orientation. On the other hand, chitosan itself is a crystalline polymer and higher intensity of crystallinity in the final PU may be due to chitosan itself. From the evaluation of the X-ray studies, we can

state that by the involvement of chitosan in the PU formulation, the crystallinity of the final polyurethane is improved.

Thermal properties

TGA studies

Thermal stability of prepared polymers with different amount of chitosan was evaluated by TGA technique. The thermal decomposition of all the PU samples was evaluated at different percent of weight loss (i.e., 5, 10, 50% and maximum), and results are presented in Table III and Figure 7. The most valuable criterion for thermal stability, that is, at 10% weight loss was found in the range of $314\text{--}332^\circ\text{C}$. Temperature of maximum decomposition rate was in the range of $575\text{--}603^\circ\text{C}$. It is quite clear that samples extended with 100% chitosan (PU6) are more thermally stable than samples extended with 100% 1,4-BDO (PU1). This is due to the higher thermal stability of chitosan polymeric structure in comparison to 1,4-BDO molecular structure because the molecular chain of chitosan composed of D-glucosamine monomers (Fig. 1). The linked glucosamine rings on chitosan had better miscibility with linked alicyclic ring in the hard segment of PU and can establish the formation of H-bonds between soft segment and NH group in the hard segment. Therefore intensity of crystallinity and shift of thermogravimetric values for 100% chitosan-PU (PU6) is more obvious than that of 100% BDO-PU (PU1). This behavior may also imply that chitosan; a crystalline polymer of D glucosamine with contents of N-acetyl-D glucosamine in

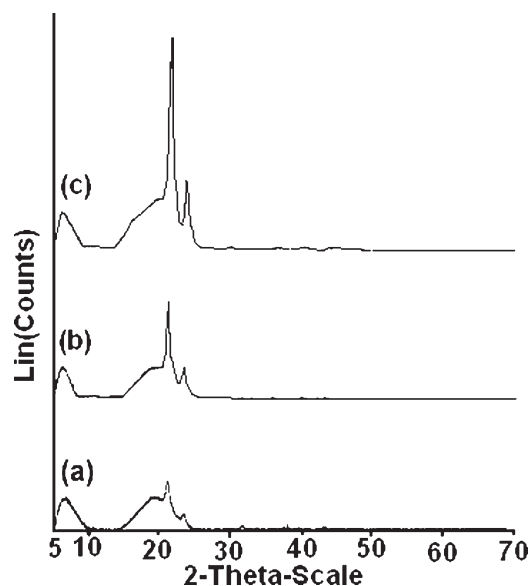


Figure 6 XRD spectra of the samples: (a) PU1, (b) PU3, and (c) PU6.

TABLE III
Thermal Stability and Dynamic Mechanical Analysis Data of the Samples

Sample code	T_5^a (°C)	T_{10}^a (°C)	T_{50}^a (°C)	T_{max}^b (°C)	First transition T_g (°C)	Second transition (°C)
PU1	281.6	314.5	373.7	465.06	-50.8	31.8
PU2	283.4	320.5	391	474.83	-49.5	32.5
PU3	283.7	324.4	398.6	478.08	-40.4	32.9
PU4	288.7	324	402.4	477.85	-35.4	50.5
PU5	300.2	325.8	402.4	484.60	-33.2	52.0
PU6	302.8	332.2	400.4	494.25	-33.0	52.3

^a Temperature of 10, 20, and 50% weight losses obtained from TGA.

^b maximum decomposition temperature obtained from TGA.

^c Transition related to soft segment.

^d Transition related to hard segment.

the range of 0–10% do not melt but degrade at elevated temperature³³ and can play a role in enhancement of thermal properties. The investigation of Table III data showed that for samples PU1–PU6, the thermal stability increased with the increasing of chitosan content.

DMTA studies

The viscoelastic properties of prepared samples were studied by means of dynamic mechanical thermal analysis. DMTA allows different types of transitions and relaxations to be detected and related to the structure and morphology of the samples. The storage modulus (E'), as a function of temperature is shown in Figure 8, the data of thermal transition are also collected in Table III. It is obvious from the Figure 8, that increase in chitosan contents results to change the thermal transition behavior of the final PU. From DMTA curves, all samples PU1–PU6 showed two thermal transitions. The lowest thermal transition is attributed to the glass transition temperature, which is related to soft segment, and the second thermal transition is related to hard segment. By increasing the amount of chitosan, both transition temperatures increase. This behavior implies that increase in chitosan contents in the PU backbone results to increase in hydrogen bonding, which acts

as physical crosslinking and improving polymer rigidity. The molecular rigidity of PU6 is higher than all the other samples and can play a significant role in determining the physical properties. From these results, it can be successfully concluded that the thermal history of these polymers is very much dependent on the chitosan contents in the polymer composition.

CONCLUSIONS

Chitosan-based biodegradable thermally stable polyurethane elastomers based on PCL and IPDI, extended with different mass ratio of chitosan and 1,4-BDO were synthesized. The conventional spectroscopic characterization of the samples with FTIR, ¹HNMR, and ¹³CNMR were in accordance with proposed polyurethane structure. For all the samples, the crystallinity was found to increase with increasing of the chitosan content. It was concluded that by increasing the chitosan contents in the polyurethane formulation, the crystallinity of the samples increases. TGA data showed that thermal stability increased with increasing chitosan contents of

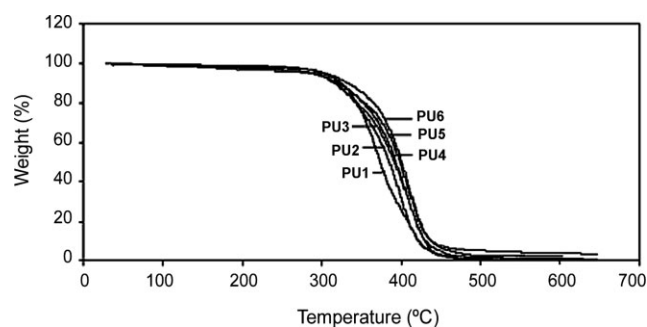


Figure 7 TGA thermograms of polyurethanes.

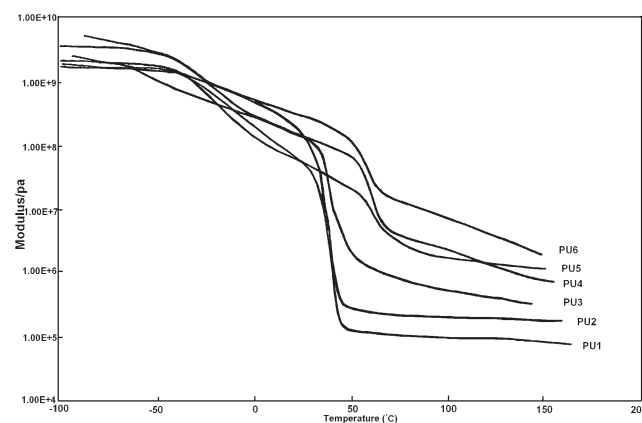


Figure 8 Storage modulus versus temperature curves of PU samples.

mixture. DMTA data showed much higher glass transition temperature for higher content of chitosan in polyurethane structure. It was concluded that by increasing the chitosan contents in the polyurethane formulation, the stiffness of the samples increases and this behavior was strongly supported by DMTA study. Contact angle is also increased by increasing the amount of chitosan. The increased contact angle is ascribed to the decrease of the hydrophilicity of the polyurethanes. Finally, it was concluded that these polymers have good thermal properties for further processing, and it can be reasonably claimed that they can be utilized in a number of potential applications, offering the unique properties of these two polymers, that is, polyurethane and chitosan.

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