

# Synthesis and Characterization of Novel, Biodegradable, Thermally Stable Chitin-Based Polyurethane Elastomers

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**ABSTRACT:** Biodegradable polyurethane (PU) elastomers with potential for biomedical and industrial applications with tunable thermal properties were synthesized by the reaction of poly( $\epsilon$ -caprolactone) and 4,4'-diphenylmethane diisocyanate and extended with different mass ratios of chitin and 1,4-butane diol (BDO). Their chemical structures were characterized with Fourier transform infrared, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopy, and the thermal properties were determined by thermogravimetric analysis, differential scanning calorimetry, and dynamic mechanical thermal analysis techniques. The incorporation of chitin contents into the PU backbone caused improvements in the thermal stability and degradation rate. Opti-

mum thermal properties and degradation profile were obtained from elastomers extended with chitin, whereas elastomers extended with BDO displayed the worst properties. The investigation of the structure–property relationships of the prepared elastomers showed that the main determining factors for the observed properties were the physical effective crosslink density, hydrogen bonding, thermal stability, and content of chitin in the PU backbone. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 769–776, 2008

**Key words:** biodegradable; block copolymers; FT-IR; polyurethanes; thermal properties

## INTRODUCTION

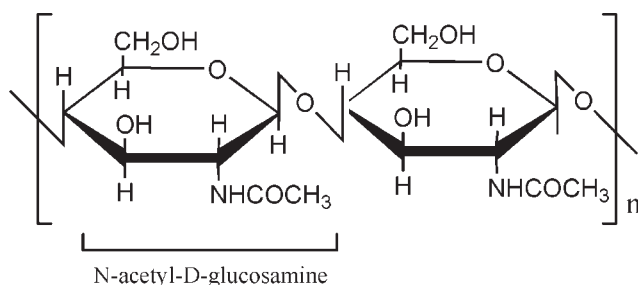
An increasing research interest in biodegradable polymers over the past 2 decades has led to the availability of a large variety of novel polymers with claims of biodegradability.<sup>1,2</sup> A large number of biodegradable polymers have been used in biomedical and industrial applications. Among these polymers, polyurethanes (PUs) are a unique class of polymers because a large variety of PUs with widely varying physical and chemical properties can be synthesized.<sup>3</sup> Biodegradable PU elastomers are expected to be suitable for any biomedical or industrial application.<sup>4</sup> Biodegradable PU is generally achieved by the incorporation of labile moieties susceptible to hydrolysis in the polymer chain. The most common method of introducing these hydrolysable linkages into PUs has been the incorporation of hydrolysable soft segments such as poly( $\epsilon$ -caprolactone) (PCL)

into the backbone.<sup>5,6</sup> PCL is a biodegradable, semi-crystalline, aliphatic polyester polyol.<sup>7</sup> It is hydrophobic and insoluble in water but degradable through the hydrolytic attack of the ester bond. The degradation rate of PCL-based PU is very slow in most cases. On the other hand, the introduction of a polysaccharide chain extender/crosslinker such as chitin can accelerate the degradation rate. Polysaccharides (cellulose, starch, chitin, etc.) are naturally occurring polymers obtained from renewable sources. They are readily biodegradable and tend to degrade in biologically active environments such as soil, sewage, and marine locations where bacteria are active.<sup>8</sup> As a biopolymer from agricultural resources, chitin and its derivatives with hydroxyl and acetamide groups have been considered alternative materials in the development of degradable elastomers because of their biodegradability, derivability, availability, and low cost.<sup>9–11</sup> Chitin [(C<sub>8</sub>H<sub>13</sub>O<sub>5</sub>N)<sub>n</sub>], having a cellulose-like rigid structure composed of (1,4)-2-acetamido-2-deoxy- $\beta$ -D-glucose units, is one of the most abundant natural polymers and is widely distributed in nature as the skeletal material of crustaceans insects and mushrooms and as the cell walls of bacteria.<sup>11</sup> Chitin is structurally similar to cellulose, but it is an amino polysaccharide with an acetamide group at the C-2 position in place of a hydroxyl group (Fig. 1).

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**Figure 1** Structure of chitin.

Attempts have been made to increase the thermal stability of PU through the chemical modification of its structure via, for example, the incorporation of silicone,<sup>12</sup> imide,<sup>13</sup> or thermally stable heterocyclic groups<sup>14</sup> such as furanic diol.<sup>15</sup> 4,4'-Dihydroxydiphenylsulfone (bisphenol-S) as a chain extender has also been used to obtain better thermal stability.<sup>16</sup> Furthermore, aliphatic diols,<sup>17,18</sup> diamine chain extenders, have been used and have included hydrazine or aliphatic,<sup>19</sup> aromatic,<sup>16</sup> and heterocyclic diamines.<sup>20</sup> In our previous study<sup>21</sup> with polysaccharide in PU, corn starch was reacted with a urethane prepolymer to modify starch and to prepare new hydrophobic copolymers. Because of the unique and novel characteristics of chitin, this article reports the synthesis and characterization of novel biodegradable thermally stable PU elastomers based on chitin and 1,4-butane diol (BDO). The hydroxyl and acetamide functionalities of this biopolymer allow chemical reactions with conventional diisocyanates or urethane prepolymers. For this investigation, a prepolymer was synthesized as described in our previous articles<sup>17,18</sup> by the step-growth polymerization of PCL and 4,4'-diphenylmethane diisocyanate (MDI) and extended with different proportions of chitin and BDO. After characterization, the intended beneficial effects on the samples' (CPU2–CPU5) thermal stability and degradation, as compared to when pure aliphatic diol (CPU1) was used as a chain extender, were studied. We expected that these compounds would take advantage of the thermal properties and degradation provided by the chitin-based PUs.

## EXPERIMENTAL

### Chemicals

Chitin (viscosity-average molecular weight =  $6.067 \times 10^5$ ) was kindly supplied by Iran Polymer and Petrochemical Institute (Tehran, Iran). Its molecular weight was deduced from the intrinsic viscosity, as described in the literature.<sup>22</sup> Chitin was purified according to already established methods in literature.<sup>23</sup> MDI and BDO were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Polycaprolactone polyol, CAPA 225 (molecular weight = 2000, Solvay Chemicals,

Cashier, England), and BDO were dried at 80°C *in vacuo* for 24 h before use to ensure the removal of all air bubbles and water vapors that may have otherwise interfered with the isocyanate reactions. The molecular weight of CAPA 225 was confirmed by the application of the procedure reported in ASTM D 4274C. MDI and all other materials were used as-received. All the reagents used in this work were analytical grade.

### Synthesis of PU extended with BDO (CPU1)

An overall PCL/MDI/chain extender molar ratio of 1 : 3 : 2 was used for synthesis purposes. Into a four-necked reaction kettle equipped with a mechanical stirrer, heating oil bath, reflux condenser, dropping funnel, and N<sub>2</sub> inlet and outlet was placed PCL (31.25 g, 0.0156 mol), and the temperature of the oil bath was increased to 60°C. Then, MDI (11.95 g, 0.047 mol) was added, and the temperature was increased to 100°C. It almost took 1.0 h to obtain the NCO-terminated prepolymer. We carried out the conversion of the prepolymer into the final PU by stirring the prepolymer vigorously and then adding a previously degassed chain extender, BDO (2.81 g, 0.031 mol). When color homogeneity was obtained in the reactant mixture, the dispersion of chain extender was considered complete, and the liquid polymer was cast onto a Teflon plate to form a uniform sheet 2–3 mm thick. The synthesized polymer was then placed in a circulating hot-air 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.

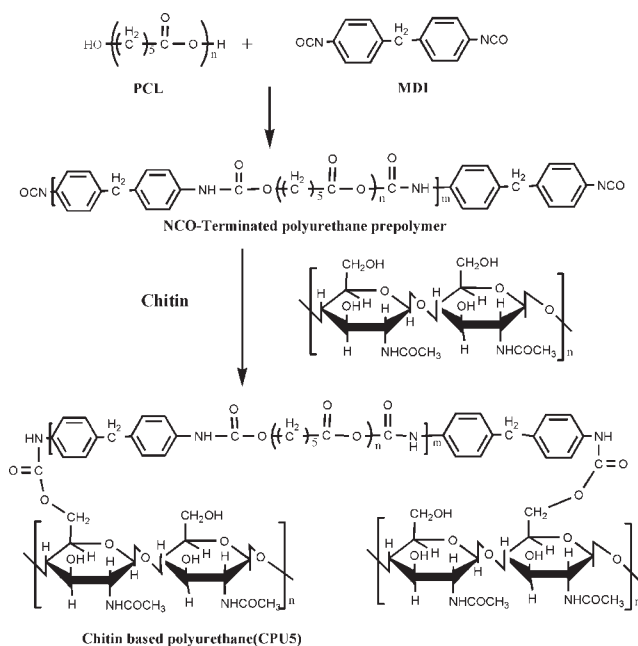
### Synthesis of the PUs extended with a mixture of chitin and BDO (CPU2–CPU4) and pure chitin (CPU5)

The prepolymer synthesis and film casting of the PU samples extended with mixture of chitin and BDO (CPU2–CPU4) was done according to the procedure described earlier for the synthesis of CPU1. A weighed amount of chitin according to molar ratio

**TABLE I**  
Sample Code Designations and Different Formulations of PUs

| Number | Sample code | Chitin/BDO composition (mass %) | CAPA 225/MDI/chitin/1,4-BDO molar ratio <sup>a</sup> |
|--------|-------------|---------------------------------|--|
| 01     | CPU1        | 0/100                           | 1 : 3 : 0 : 2  |
| 02     | CPU2        | 25/75                           | 1 : 3 : 0.5 : 1.5                                    |
| 03     | CPU3        | 50/50                           | 1 : 3 : 1 : 1  |
| 04     | CPU4        | 75/25                           | 1 : 3 : 1.5 : 0.5                                    |
| 05     | CPU5        | 100/0                           | 1 : 3 : 2 : 0  |

<sup>a</sup> In whole numbers.



**Figure 2** Chemical route for the synthesis of the chitin-based PU elastomers.

as predicted in Table I was dissolved in the solvent [a mixture of *N*-methyl-2-pyrrolidone and dimethyl sulfoxide (DMSO) with a ratio of 2 : 1].<sup>24</sup> For the samples designated as CPU2–CPU4, the prepolymer was extended with different proportions of chitin to BDO (Table I), whereas the sample designated as CPU5 (Fig. 2) was extended with 100% chitin (4.25 g). All other parameters and temperature conditions remained the same as described previously for the synthesis of CPU1.

### Measurements

Infrared measurements were performed on a Bruker-IFS 48 Fourier transform infrared (FTIR) spectrometer (Ettlingen, Germany). The <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>) solution with a Bruker Advance 400 MHz spectrometer (Ettlingen, Germany). Chemical shifts ( $\delta$ 's) are given in parts per million with tetramethylsilane (TMS) as a standard. Differential scanning calorimetry (DSC) was recorded on a Stanton Redcraft STA-780 instrument (London). Thermogravimetric analysis (TGA) was recorded on a Polymer Lab TGA-1500 instrument (London) under a N<sub>2</sub> atmosphere from room temperature to 650°C with a heating rate of 20°C/min. The dynamic mechanical thermal analysis (DMTA) measurements were performed on a UK Polymer Lab dynamic mechanical thermal analyzer (model MK-II) over a temperature range of –150 to 200°C at heating rate of 10°C/min and a frequency of 1 Hz. The dimensions of the samples were 30 × 10 × 1

mm<sup>3</sup>. Values of the loss tangent ( $\tan \delta$ ) and storage modulus ( $E'$ ) versus the temperature were recorded for each sample.

### Hydrolytic degradation studies

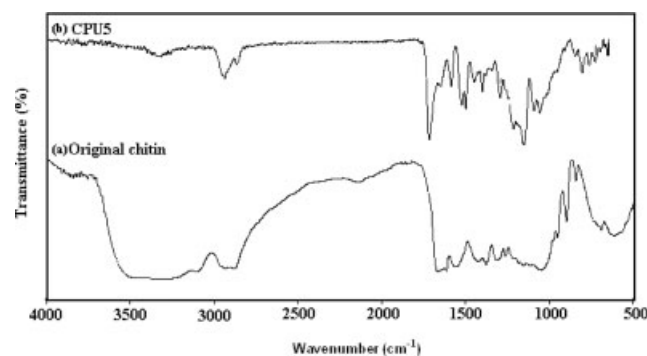
Although there are several approaches for assessing the biodegradability of polymers, it is worth mentioning that two main methods can be followed for biodegradability evaluation, including the measurement of the remaining polymer's molecular weight and the weight loss method. Hydrolytic degradation studies of the final PU samples were conducted with the weight loss (%) method in a phosphate buffer saline (PBS) solution of pH 7.4. Vacuum-dried samples were cut to the size 10 × 10 × 1 mm<sup>3</sup> and weighed to an accuracy of 0.1 mg. Each sample was placed into an individual vial containing 15 mL of PBS and incubated at 37°C. Four samples of each formulation were removed from buffer after 5, 10, 20, 30, 40, 50, and 60 days. The degradation media were refreshed every week. After the samples were washed with distilled water and dried *in vacuo* at room temperature for 3 days, they were reweighed to determine the weight loss percentage by subtraction of the film weight from the initial weight; the result was then multiplied by 100.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The main aim of this study was to prepare new biodegradable PU elastomers with improved thermal stability. So, the synthesis of the chitin-based PUs was considered according to the synthetic route as outlined in Figure 2. The reaction of 1 equiv of polyol with 3 equiv of MDI led to the NCO-terminated PU prepolymer, which was subsequently extended with 2 equiv of chain extender with different proportions of chitin to BDO to prepare the final PUs.

The FTIR spectra of the original chitin and PUs extended with 100% chitin (CPU5) are shown in



**Figure 3** FTIR spectra of the (a) original chitin and (b) PU extended with 100% chitin.

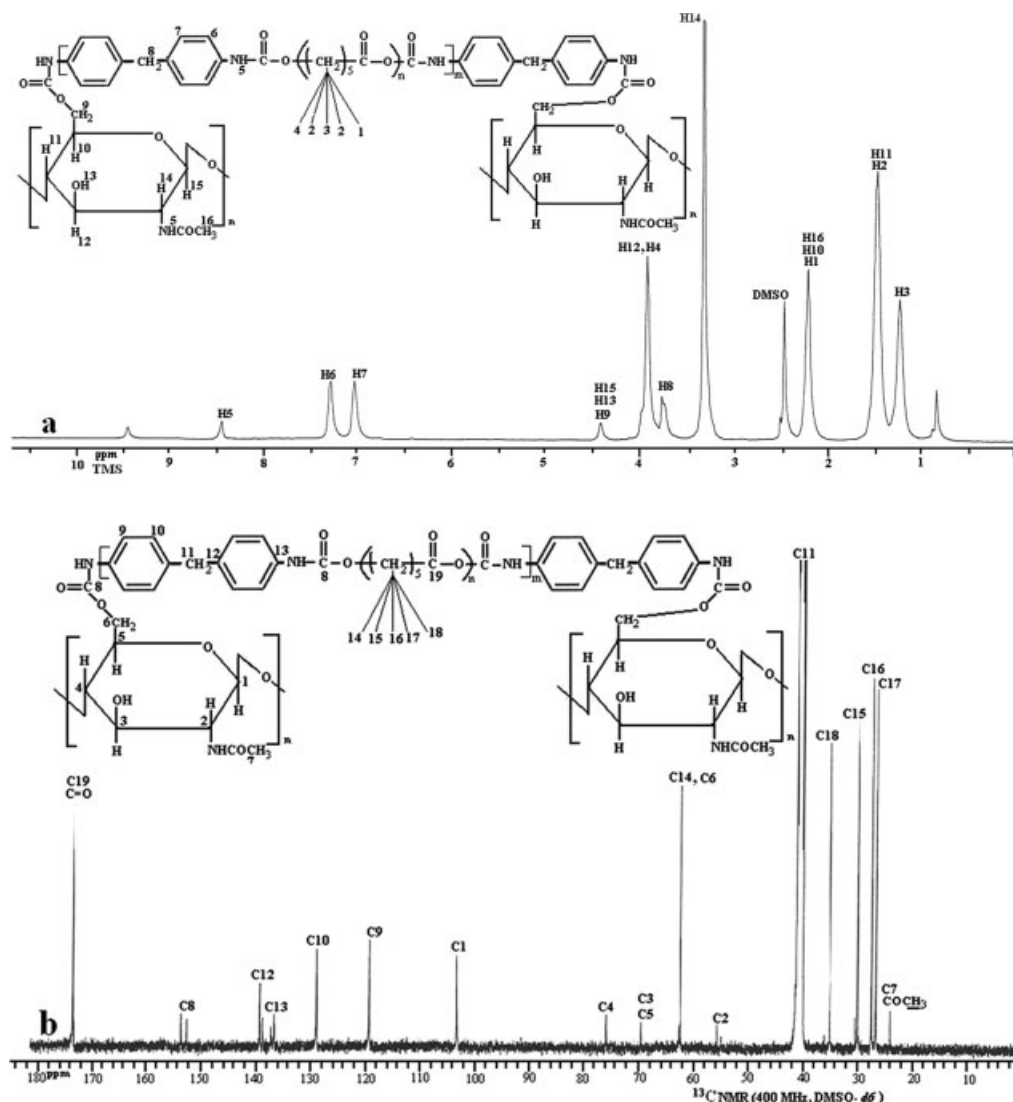


Figure 4 (a) <sup>1</sup>H-NMR and (b) <sup>13</sup>C-NMR spectra of the chitin-based PU (CPU5).

Figure 3(a,b). The FTIR spectra of the original chitin [Fig. 3(a)] showed that broad OH stretching vibration bands appeared at  $3443\text{ cm}^{-1}$ . The N—H symmetric and asymmetrical stretching vibration bands appeared at  $3289$  and  $3105\text{ cm}^{-1}$ , respectively. The C—H symmetric and asymmetric stretching vibrations of CH<sub>2</sub> groups were observed at  $2931$ , and  $2889\text{ cm}^{-1}$ , respectively. The faint absorptions at  $1661$ ,  $1626$ , and  $1563\text{ cm}^{-1}$  were due to C=O bond and N—H deformations. The absorption bands at  $1427$ ,  $1377$ , and  $1307\text{ cm}^{-1}$  were attributed to CH<sub>2</sub> bending vibrations, C—H bending vibrations, and CH<sub>2</sub> wagging, respectively. The absorption bands appearing at  $1046$  and  $1026\text{ cm}^{-1}$  were due to C=O and C—C stretching vibrations. The broad intense band at  $1000\text{--}1220\text{ cm}^{-1}$  was attributed to the ring and bridge C—O—C vibrations of chitin-ether-type absorption.

The FTIR spectra of CPU5 [Fig. 3(b)] showed a strong absorption peak of N—H stretching vibra-

tions at  $3339\text{ cm}^{-1}$ . The CH symmetric and asymmetric stretching vibrations of CH<sub>2</sub> groups were observed at  $2935$  and  $2865\text{ cm}^{-1}$ , respectively. The other peaks were assigned as follows:  $1726$ ,  $1645\text{ cm}^{-1}$  (C=O bond);  $1597$ ,  $1534\text{ cm}^{-1}$  (N—H deformations);  $1460\text{ cm}^{-1}$  (CH<sub>2</sub> bending vibrations);  $1412\text{ cm}^{-1}$  (C—H bending vibrations); and  $1306\text{ cm}^{-1}$  (CH<sub>2</sub> wagging). When the prepolymer was extended with different proportions of chitin to BDO, the FTIR spectra showed very strong, new peaks at about  $1728\text{ cm}^{-1}$ , which were assigned to the C=O stretching of the soft segment of PCL. Another new peak was also observed at about  $1460\text{ cm}^{-1}$ , which was assignable to the urethane —NH group. The intensity of the hydrogen-bonded —NH was observed to increase as the chitin content increased, which suggested that the hydrogen bonds of chitin were broken and new hydrogen bonds between the chitin and PU prepolymer were formed. Moreover, with



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

| Number | Sample code         | $T_{\text{onset}}$ (°C) | $T_{10}$ (°C) | $T_{20}$ (°C) | $T_{50}$ (°C) | $T_{\text{max}}$ (°C) | $T_g$ (°C) <sup>a</sup> | $\tan \delta$ <sup>b</sup> |
|--------|---------------------|-------------------------|---------------|---------------|---------------|-----------------------|-------------------------|----------------------------|
| 01     | Chitin <sup>c</sup> | 30.28                   | 225           | 285           | 335           | 642                   | —                       | —                          |
| 02     | CPU1                | 29.52                   | 305           | 320           | 350           | 603                   | -31.7                   | 0.59                       |
| 03     | CPU2                | 28.97                   | 320           | 345           | 375           | 601                   | -31.2                   | 0.48                       |
| 04     | CPU3                | 30.0                    | 330           | 370           | 410           | 601                   | -28.9                   | 0.55                       |
| 05     | CPU4                | 29.10                   | 345           | 375           | 410           | 601                   | -26.3                   | 0.72                       |
| 06     | CPU5                | 33.44                   | 369           | 400           | 440           | 596                   | -23.3                   | 0.84                       |

$T_{\text{onset}}$  = initial decomposition temperature;  $T_{10}$  = temperature of 10% weight loss (from TGA);  $T_{20}$  = temperature of 20% weight loss (from TGA);  $T_{50}$  = temperature of 50% weight loss (from TGA);  $T_{\text{max}}$  = maximum decomposition temperature (from TGA);  $T_g$  = glass-transition temperature.

<sup>a</sup> The central point of the maximum of the  $\tan \delta$  peak was used.

<sup>b</sup> Altitude of the  $\tan \delta$  peak.

<sup>c</sup> Original chitin sample.

increasing chitin content, the peak of the urethane carbonyl groups around  $1728 \text{ cm}^{-1}$  (CPU1,  $1728 \text{ cm}^{-1}$ ; CPU2,  $1727 \text{ cm}^{-1}$ ; CPU3,  $1727 \text{ cm}^{-1}$ ; CPU4,  $1726 \text{ cm}^{-1}$ ; and CPU5,  $1725 \text{ cm}^{-1}$ ) decreased and shifted to a lower wave number, whereas the band around ( $1642\text{--}1649 \text{ cm}^{-1}$ ) for the hydrogen-bonded carbonyl of chitin increased and shifted to a higher wave number. This implies stronger interchain interactions between the chitin and PU prepolymer in chitin-based PU than in BDO-based PU. As shown in Figure 3(a,b), the broad bands that appeared at  $3443$  and  $2950 \text{ cm}^{-1}$  in the original chitin disappeared in the final PU extended with chitin. This provided evidence that all of the chitin was consumed, and there was no free chitin in the final PU sample.

The NMR spectra of the PU extended with 100% chitin (CPU5) are shown in Figure 4. The  $^1\text{H-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ) and  $^{13}\text{C-NMR}$  (400 MHz,  $\text{DMSO-}d_6$ ) spectra of the final synthesized PU samples (CPU1–CPU5) were in accordance with proposed structures. In the NMR spectra, the signals observed were assigned as follows:

$^1\text{H-NMR}$  [Fig. 4(a)]: 8.44 (s, NH), 7.3–7.2 (m, 4H), 7.06–7.0 (m, 4H), 4.48 (s, 4H), 3.93–3.75 (broad, 3H), 3.64–3.52 (s, 3H), 3.34 (broad, 4H), 2.51–2.50 (s, 4H), 2.47 (DMSO), 2.34–2.22 (m, 6H), 1.48 (m, 3H), 1.24 (m, 2H).  $^{13}\text{C-NMR}$  [Fig. 4(b), ppm]: 173.1, 173.0, 154.0, 152.9 (C=O); 138.1, 137.6, 135.8, 135.3 (ArC); 129.3, 118.7 (ArCH); 104.1 (chitin C1); 77.5 (chitin C4); 69.6 (chitin C3 and C5); 63.3, 63.2, (chitin C6); 56.6, 56.2 (chitin C2); 75.5, 63.3, 40.8, 40.6, 40.4, 40.2, 39.9, 39.7, 39.5, 39.3, 34.9, 33.8, 28.7, 28.3, 25.3, 24.5, 21.7 ( $\text{CH}_2$ ).

The appearance of new peaks in the  $^1\text{H-NMR}$  spectra at 4.48 ppm (assigned to the protons in the C1, C3, and C6 positions of chitin) and in  $^{13}\text{C-NMR}$  spectra at 23.0 and 174 ppm (attributed to the methyl and carbonyl groups, respectively, of chitin)

provided evidence of the involvement of chitin in the final PU structure. Moreover, peaks located at about 56.2, 63.3, 69.6, 68.8, 77.5, and 104 ppm were attributed to protons in the C2, C6, C3, C5, C4, and C1 positions of chitin, respectively.<sup>25</sup>

### Thermal properties

The thermal stability of the prepared polymers and original chitin were evaluated by the TGA technique. The thermal decomposition of all of the PU samples was evaluated at different percentages of weight loss (i.e., 10, 20, and 50% and at the maximum), and the results are presented in Table II. The most valuable criterion for thermal stability, that is, at 10% weight loss, was found in the range  $305\text{--}369^\circ\text{C}$ . The temperature of the maximum decomposition rate was in the range  $596\text{--}603^\circ\text{C}$ . It was quite clear that samples extended with 100% chitin (CPU5) were more thermally stable than the samples extended with 100% BDO (CPU1). This was due to the higher thermal stability of the chitin polymeric structure in comparison to BDO molecular structure because the molecular chain of chitin is composed of *N*-acetyl-D-glucosamine monomers (Fig. 1).<sup>26</sup> The linked glucosamine rings on chitin had better miscibility with linked double rings in the hard segment of PU and could establish the formation of H bonds between the soft segment and NH group in the hard segment. Therefore, the intensity of crystallinity and the shift in the thermogravimetric values for 100% chitin–PU (CPU5) were more obvious than for 100% BDO–PU (CPU1). This behavior may also imply that chitin; a crystalline polymer of *N*-acetyl-D-glucosamine monomers, does not melt but degrades at elevated temperatures<sup>27</sup> and can play a role in the enhancement of thermal properties. The investigation of the data shown in Table II showed that for samples CPU2–CPU4, the thermal stability increased

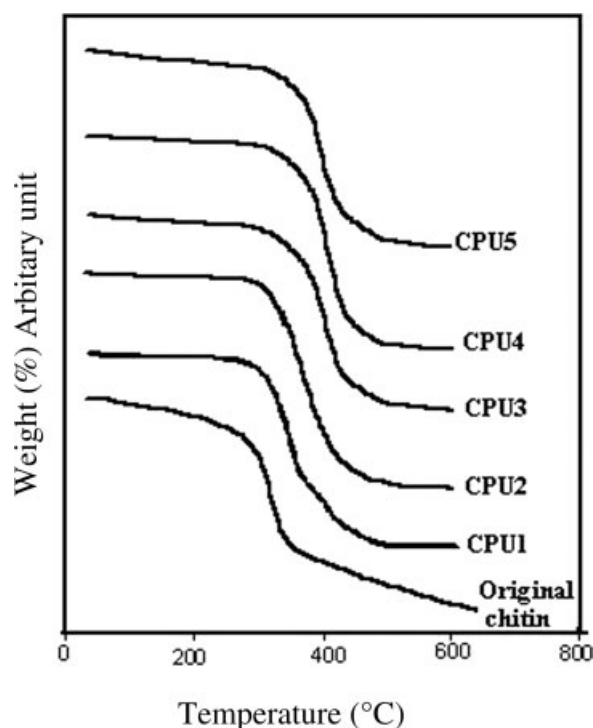


Figure 5 TGA thermograms of PU.

with increasing chitin content in the mixture. TGA data of the original chitin are also reported (Table II), and they were much lower than those of the final PU product, but the stability was at a maximum (642°C) at maximum weight loss among all of other PU samples with different levels of chitin. The TGA thermograms are shown in Figure 5.

DSC measurements were used to characterize the effect of chitin concentration on the structure of the PU samples. As an example, the DSC thermograms of the PUs extended with different ratios of chitin to BDO are shown in Figure 6. As shown in Figure 6, it was clear that all of the PU samples degraded partially at temperatures above 300°C, and this degradation temperature was confirmed by the TGA data (Table II). Sample CPU1 showed melting behavior, and all the remaining samples (CPU2–CPU5) did not show this. This behavior implied that the addition of chitin in the formulation resulted in an increase in the physically effective crosslink density. It is well known that crosslinked materials do not show any melting behavior. As the crosslink density of CPU5 was highest, it exercised a higher tolerance against thermal degradation. Reegen and Frisch<sup>28</sup> established the fact that PU with a high crosslinking density has good thermal stability. The peak observed at a temperature of about 356°C disappeared as the chitin contents increased in the PU backbone. We concluded that chitin had a considerable effect on the thermal degradation of PU and that increasing the chitin content caused a decrease in the thermal degradation, as is obvious from Figure 6.

The viscoelastic properties of prepared samples were studied by means of DMTA. DMTA allows different types of transitions and relaxations to be detected and related to the structure and morphology of the samples.  $E'$  and  $\tan \delta$  as a function of temperature are shown in Figures 7 and 8, respectively; the data of the thermal transition are also collected in Table II. As is obvious from Figure 7, an increase in the chitin content resulted in a change in the thermal transition behavior of the final PU. From the DMTA curves, samples CPU3–CPU5 showed just one thermal transition. This behavior implied that an increase in the chitin content in the PU backbone resulted in an increase in hydrogen bonding, which acted as physical crosslinking; therefore, these samples only showed one thermal transition, that is, the glass transition. From these results, we successfully concluded that the thermal history of these polymers was very much dependent on the chitin contents in the polymer composition. We also found that PU extended with 100% chitin had an obviously higher plateau modulus and wider plateau temperature range than all of the other samples. This suggested that molecular rigidity of CPU5 was higher than that of all the other samples, which could have played a significant role in the determination of the physical properties. In comparison with CPU1, CPU5 showed a much higher plateau modulus with a wider plateau temperature range than CPU1. This suggested that the strength and heat resistance of CPU5 increased with the incorporation of chitin in the PU backbone. It would be possible to use this material in a wide range of temperatures without

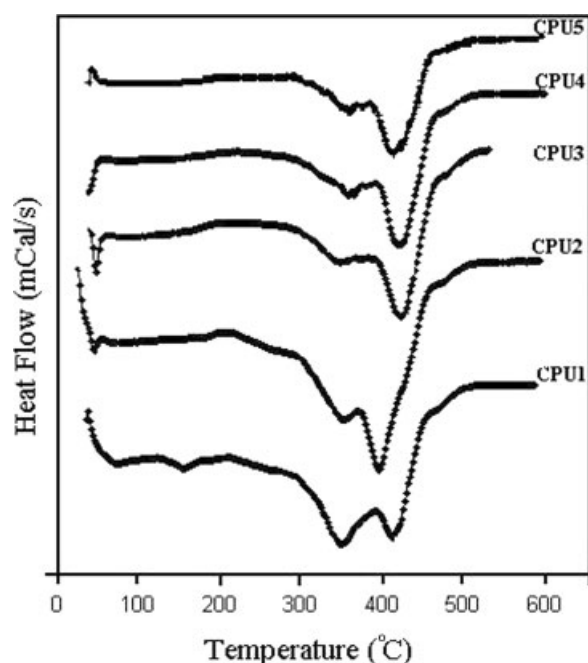


Figure 6 DSC measurements of PU.

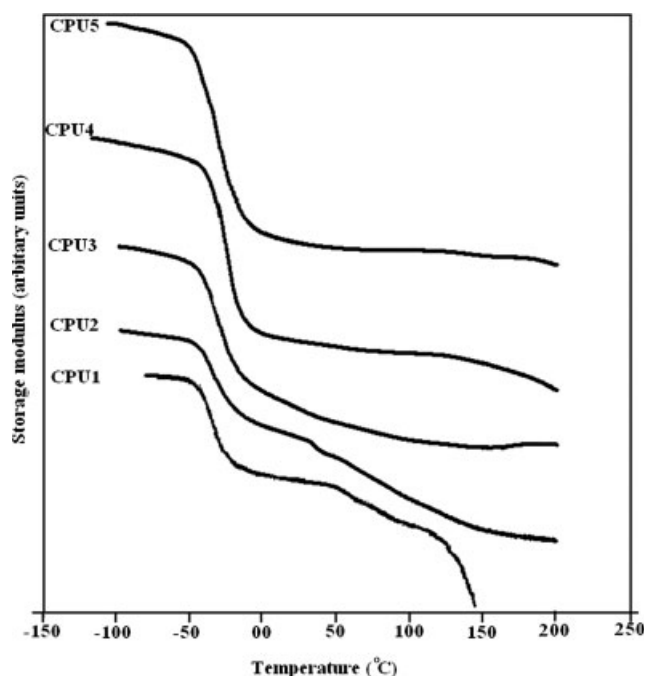


Figure 7  $E'$  versus the temperature of the PU samples.

sacrificing the properties. This behavior implies that the modulus in the plateau region is proportional to either the crosslink density or the chain length between crosslinks.<sup>29</sup> Below the glass-transition temperature, all of the samples had almost the same  $E'$ . Once the glass-transition temperature was reached, the modulus began to decrease rapidly. The modulus for sample CPU1 with no crosslinking and low crystallinity decreased at a faster rate than that of sample CPU5 with a higher crosslink density and crystallinity. At high temperatures, the modulus continued to diverge for samples CPU2–CPU5, as shown in Figure 7. We concluded that with increasing the chitin content in the PU formulation, the stiffness of the samples increased, and this behavior was strongly supported by the DMTA study.

Investigation of the  $\tan \delta$  curves (Fig. 8) showed that in the  $\tan \delta$  peaks (damping peaks) for all of the samples, the glass transition occurred within a broader temperature range. With increasing chitin components in the formulation, a slight increase in the broader temperature range was found in samples CPU4 and CPU5. This broadening was attributed to an increase in the distribution of molecular weights between crosslinks or an increase in the heterogeneity of the network structure. It was also found that with an increase in the mass ratio of chitin, the damping peak associated with the glass-transition temperature slightly shifted to a lower temperature (Fig. 8; Table II). Moreover, the amplitude of the  $\tan \delta$  peak became larger as the contribution of chitin content increased. This phenomenon was attributed to the increase in the crystallinity of the samples in

accordance with chitin content increases. It is known that chitin is a highly crystalline polymer and is capable of forming a three-dimensional ordered structure because of the ability of the acetamide group to form hydrogen bonding. An increase in chitin content results in an increase in crystallinity, and crystalline materials exercise a higher tolerance against thermal degradation. This phenomenon may also be attributed to a decrease in the degree of freedom for the segmental mobility of the polymer as the chitin contents increase as a result of an increase in the physically effective crosslink density. As is also shown in Figures 7 and 8, the sample CPU1 showed melting characteristics, whereas all of the other samples did not show any evident melting. This phenomenon was attributed to the linearity of CPU1 and the crosslink densities of all of the other samples.

### Hydrolytic degradation

The hydrolytic degradation of the PU samples was examined in PBS solution at 37°C by the calculation of the change of sample weight as a function of time (Fig. 9). The degradation rate of samples CPU1–CPU5 corresponded to the water absorption ability, with a faster degradation found in the more absorbent polymers. The hydrolysis rate of PU extended with pure chitin (CPU5) was greater than that of PU extended with pure BDO and increased with chitin contents. The slower degradation rate of CPU1 than CPU5 was presumably due to the absence of the chitin structure. As Figure 9 indicates, the weight loss due to hydrolytic degradation increased as the amount of chitin increased. A possible explanation is that the presence of more chitin accelerated the degradation reaction

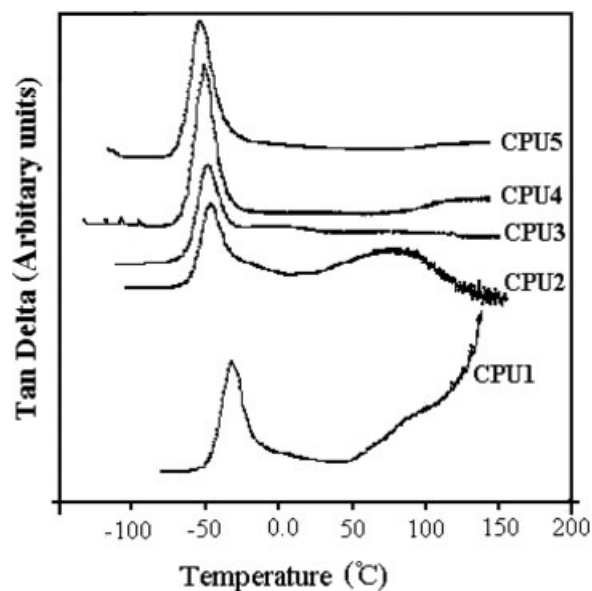
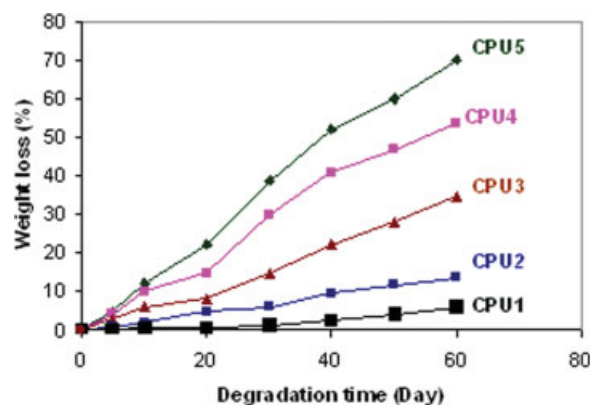


Figure 8  $\tan \delta$  versus the temperature of the PU samples.





**Figure 9** Degradation profiles of CPU1–CPU5 versus the time. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

through an increase in the number of effective collisions. A close inspection of the Figure 9 curves showed that the rate of hydrolysis increased with time, which may have resulted from the increased hydrophilicity of the networks through the generation of hydrophilic hydroxyl and amine groups at the surface during the degradation process.

### CONCLUSIONS

Chitin-based, biodegradable, thermally stable PU elastomers based on PCL and MDI and extended with different mass ratios of chitin to BDO were synthesized. Conventional spectroscopic characterization of the samples with FTIR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$  spectroscopy were in accordance with the proposed PU structures. From the whole thermal analysis, the thermal stability was found to increase with increasing chitin content. TGA data and DSC curves showed that the thermal stability increased with increasing chitin content in the mixture. The DMTA curves of CPU5 showed a much higher plateau modulus with a wider plateau temperature range, and it would be possible to use this material in a wide range of temperatures without sacrificing the properties. The molecular rigidity, strength, and heat resistance increased with the incorporation of chitin in the PU backbone, which makes this biopolymer a potential candidate for heat-resistant elastomers for biomedical and industrial applications. We concluded that with increasing chitin content in the PU formulation, the stiffness of the samples increased, and this behavior was strongly supported by DMTA study. Investigation of the  $\tan \delta$  curves showed that the glass transition occurred within a broader temperature range, the  $\tan \delta$  peak associated with the glass-transition temperature slightly shifted to higher temperatures, and the amplitude of the  $\tan \delta$  peak

became larger as the contribution of chitin was increased. The degradation rate increased with increasing chitin content in the PU formulation. The wide range of material properties that were achieved through relatively minor modifications in chemistry makes these degradable polymers applicable for biomedical and industrial applications. Finally, we concluded that these polymers had good thermal properties for further processing, and we can reasonably claim that they can be used in a number of potential applications and can offer the unique properties of these two polymers, that is, PU and chitin.

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