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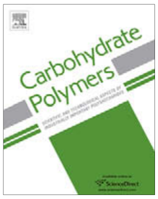

XRD studies of polyurethane elastomers based on chitin/1,4-butane diol blends

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ABSTRACT

Chitin based polyurethane elastomers (PUEs) were synthesized by step growth polymerization techniques using poly (ε-caprolactone) (PCL), 4, 4′- diphenylmethane diisocyanate (MDI) and blends of chitin and 1,4-butanne diol (BDO). The conventional spectroscopic characterization of the samples with FT-IR, ^{1}H NMR and ^{13}C NMR were in accordance with proposed PUEs structure. The crystalline behavior of the synthesized polymers were investigated by X-ray diffraction (XRD), differential scanning calorimetery (DSC), optical microscopic technique and loss tangent curves (tan δ peaks). Results showed that crystallinity of the synthesized PUEs samples was affected by varying the chitin contents used as chain extender. The contents of chitin favors the formation of more ordered structure, as higher peak intensities were obtained from the PU extended with chitin than 1,4-butane diol (BDO). X-ray diffraction experiments results correlates with optical microscopy findings. The higher ΔH value; 41.57 (J g^{-1}) was found in the samples extended with chitin than BDO (31.32 J g^{-1}).

1. Introduction

Segmented polyurethanes, consisting of hard and soft segments are known to have microphase separated structure, which brings them to be used in various ways such as adhesives, coatings, biomedical materials and elastomers (Barikani & Hepburn, 1986; Barikani & Hepburn, 1987). Polyurethane elastomers (PUEs) are possibly the most versatile class of polymers as they can be molded, injected, extruded and recycled (Zia, Bhatti, & Bhatti, 2007). Molecular characterization and morphological studies of polyurethane elastomers (PUEs) have been reported by many researchers. The effect of the diisocyanate structure (Rogulska, Podkoscielny, Kultys, Pikus, & Pozdzik, 2006) and chain extender (CE) length using α, ω- alkane diols on the crystallinity, surface morphology (Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008a) and thermo-mechanical properties (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008b) of PUEs have been investigated and well documented. Structural and surface characteristics of UV-irradiated polyurethane elastomers extended with α, ω- alkane diols has been also reported elsewhere (Zia, Barikani, Bhatti, Zuber, Bhatti, & Islam-ud-Din, 2008c). Detailed molecular characterization (Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008d), XRD studies varying diisocyanates structure (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008e), thermal (Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008f) and shape memory properties (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008) of chitin based polyurethane elastomers has also been previously discussed and reported.

Chitin, a β-(1→4)-linked polymer of 2-acetamido-2-deoxy-D-glucose (*N*-acetyl-D-glucosamine) is structurally similar to cellulose, but it is an amino polysaccharide having acetamide group at the C-2 positions in place of hydroxy group. Chitin itself is a crystalline polymer of *N*-acetyl-D-glucosamine (GlcNAc) monomers, its crystalline structure has been previously reported and well documented (Cardenas, Cabrera, Taboada, & Miranda, 2004; Zia et al., 2008e). The uses of X-ray absorption spectroscopy in the study of synthetic polymers have been comprehensively reviewed. Attempts have been made previously on X-ray studies on the composition of polyurethane elastomers and precipitated silica (Petrovic et al., 2004). Grazing incidence X-ray diffraction was also carried out to analyze the structure of polyurethane films as a function of X-ray penetration depth (Kim, Ryba, & Bai, 2003).

In this work, we have characterized a series polyurethane elastomers based on PCL and 4,4′-diphenylmethane diisocyanate (MDI), extended with different proportion of chitin and BDO. The effect of chitin contents on the crystallinity is currently being investigated and reported using differential scanning calorimetery (DSC), X-ray diffraction (XRD), optical microscopic techniques and loss tangent curves (tan δ peaks).

2. Experimental

2.1. Chemicals

4,4′-Diphenylmethane diisocyanate (MDI) and 1,4-Butane diol (BDO) were purchased from Sigma–Aldrich Chemical Co. (Saint

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Louis MO, USA). Polycaprolactone polyol, CAPA 225, (molecular weight 2000 from Solvay Chemicals Co. Cashur, England) and BDO were dried at 80 °C under vacuum for 24 h before use to ensure the air and water tracers that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 225 was confirmed by applying the procedure reported in ASTM D-4274C. All the other materials were used as received. All the reagents used in this work were of analytical grade.

Chitin was kindly supplied by Department of Polymeric Biomaterials, Iran Polymer and Petrochemical Institute Tehran, Iran. Chitin was purified according to already established methods in literature (Wang, Qin, & Bo, 1991). Its molecular weight was deduced following the established methods reported in the literature (Chen, Sun, Fan, & Zhang, 2002; Zia et al., 2008e).

2.2. Synthesis of PU

For this investigation a prepolymer was synthesized as predicted in our previous studies (Barikani & Hepburn, 1986; Barikani & Hepburn, 1987) by the step-growth polymerization of PCL and MDI, and extended with different proportions (Table 1) of chitin and BDO (Zia et al., 2008d).

2.3. Measurements

Infrared measurements were performed on a Bruker-IFS 48 Fourier Transform Infrared (FT-IR) Spectrometer (Ettlingen, Germany). The ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO-d_6) solution using a Bruker Advance 400 MHz Spectrometer. Chemical shifts (δ) were given in ppm with tetramethylsilane (TMS) as a standard. The X-ray diffractograms of the polymers were obtained in a Siemens D-5000 diffractometer with radiation Cu–Ka (λ = 15.4 nm, 40 kV and 30 mA) at 25 °C. The relative intensity was registered in a dispersion range (2θ) of 5–40°. A Jenavert optical microscope was used to observe the images of the final PU films. Differential scanning calorimetery (DSC) was recorded on a NETZSCH DSC 200 under a protective nitrogen gas atmosphere. Accurately weighed dry material was placed in an aluminum cup and hermetically sealed. The measurements were carried out from 25 to 350 °C under nitrogen at a scanning rate of 10 °C/min. The value of tan δ versus temperature was recorded using dynamic mechanical measurements 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 frequency of 1 Hz. The dimensions of samples were 30 × 10 × 1 mm.

3. Results and discussion

3.1. Molecular characterization

FT-IR spectra of MDI, PCL, NCO terminated polyurethane prepolymer, original chitin and polyurethane extended with chitin (CPU5) are shown in Fig. 1(a–e). FT-IR spectrum of MDI (Fig. 1a) showed very strong peak at 2255 cm^{-1} attributed to the isocyanate (—NCO) group attached to 4,4′-diphenylmethane diisocyanate. The FT-IR spectrum show sharp peaks at 1527 cm^{-1}, which is due to the C=C stretching of benzene ring. The observed peaks in the FT-IR spectrum of PCL (Fig. 1b) were assigned as: 3447 cm^{-1} (OH stretching vibration); 2949 cm^{-1} (asymmetric CH$_2$ stretching); 2865 cm^{-1} (symmetric CH$_2$ stretching); 1727 cm^{-1} (C=O stretching); 1293 cm^{-1} (C—O and C—C stretching in the crystalline phase); 1240 cm^{-1} (asymmetric COC stretching); 1190 cm^{-1} (OC—O stretching); 1170 cm^{-1} (symmetric COC stretching); 1157 cm^{-1} (C—O and C—C stretching in the amorphous phase). FT-IR spectrum of NCO terminated PU prepolymer has also been presented in Fig. 1(c). It is clearly observed that the signal for the OH groups disappeared and that of the intensity of NCO groups has reduced to some extent resulting that isocyanate group has entirely reacted and a signal for NH units appeared at 3298 cm^{-1} suggesting that PU prepolymer had been formed (Fig. 1c). The other observed peaks in the FT-IR spectrum of PU prepolymer were assigned as: 2931 cm^{-1} (CH symmetric stretching of CH$_2$); 2889 cm^{-1} (CH asymmetric stretching of CH$_2$ groups); 2255 cm^{-1} (isocyanate (—NCO) group); 1727 cm^{-1} (C=O stretching of soft segment of PCL). The changes in the intensity of the signal of the carbonyl groups (C=O) of the PCL at 1728 cm^{-1} indicates the chemical reac-

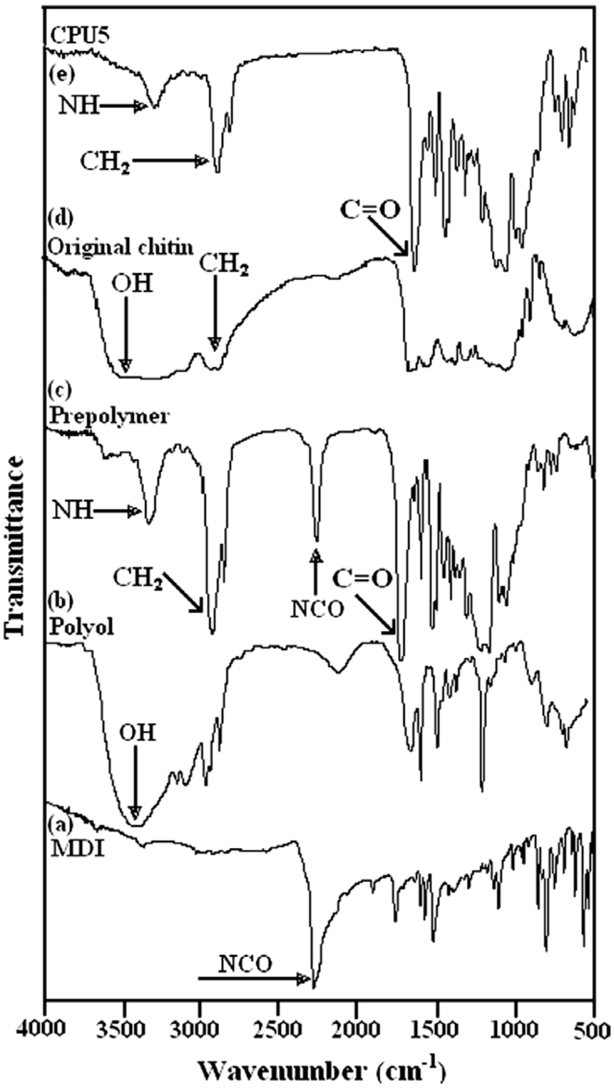

Fig. 1. FT-IR spectra of (a) MDI; (b) Polycaprolactone (c) NCO terminated prepolymer; (d) Original chitin; (e) NCO terminated prepolymer extended with chitin (CPU5).

Table 1
Sample code designation and different formulation of PUs.

S#	Sample code	Composition (chitin/BDO) % by mass	Molar ratio (whole number) of CAPA225/MDI/Chitin/1,4-BDO
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

tion of the diisocyanate with PCL. The chain extender chitin was added in the final step to end the polymerization reaction. FT-IR spectrum of chitin has been presented and discussed (Zia et al., 2008d). To provide clear information about the vibrational mode changes due to involvement of chitin to the polyurethane backbone during the polymerization reaction, FT-IR spectrum obtained from the cast film (CPU5) is shown in Fig. 1(e). In the FT-IR analysis obtained for the PU sample (CPU5), the disappearance of the NCO peak at 2255 cm^{-1} and the appearance of N–H peak at 3330 cm^{-1} confirmed the completion of polymerization reaction. The observed peaks in the spectrum imply that the reaction was completed and the predesigned PU was formed. FT-IR spectrum obtained support the proposed structure of the final polymer. The peaks assignment of the FT-IR spectrum of PU sample extended with chitin has been presented and discussed (Zia et al., 2008d).

^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (400 MHz, DMSO-d_6) spectra of final polyurethane samples were also in accordance with proposed structures (Zia et al., 2008d).

3.2. X-ray diffraction studies

Chitin has a highly ordered crystalline structure. Crystalline structure of chitin has been reported (Zia et al., 2008e). X-ray diffraction analysis was carried out in order to find the changes of the crystalline structure upon the substitution reaction with NCO terminated prepolymer. In segmented PUs, phase separation of soft segments (SS) and hard segment (HS) can take place depending upon their relative contents, structural regularity and thermodynamics incompatibility.

The X-ray diffraction studies showed that crystallinity much depends on the concentration of chitin in the polyurethane backbone, crystallinity increased as the concentration of chitin in to the final PU increased (Fig. 2). We can observe that the presence of chitin favor the formation of more ordered structure. The increase in chitin contents results to increase in the intensity of the peak localized at $2\theta = 21.5°$ confirming that soft segment tend to crystallize generating better defined peak. Previous studies (Kovacevic et al., 1990; Kovacevic et al., 1993) stated that the crystallinity of PU elastomers is provided by the soft segments. As the hard segments have a higher polarity than soft segments, they interact with each other faster than the soft segments, and thus, the part of the PUs structure due to the hard segments would be less crystalline than the one due to the soft segments, which are able to reorganize themselves until they reach a more stable disposition before interacting with each other, and hence, give a structure as crystalline as possible. Only when the hard segments are annealed, are they able to reorganize themselves before crystallizing, give crystallinity to the TPU structure. It is worth while mentioning that hard segment, when present at higher concentration, present diffraction peak in a range of $2\theta = 11.12°$. So that crystallinity in the under study project is due to soft segment and chitin itself. We can conclude that PU extended with 100% chitin and with combination of chitin/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 chitin 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 degree. It can be seen that the sample CPU1 has shown a lower diffraction peak height and broader upper half peak height area which indicates that this sample has smaller crystal particles resulting decrease in crystallinity. It is well known that greater the H-bonding higher will be the crystallinity. To support this it is stated that chitin itself is a crystalline polymer and higher intensity of crystallinity in the final PU is due to chitin itself. On the other hand chitin; a crystalline polymer of *N*-acetyl-D-glucosamine monomers, is capable of forming three dimensional ordered structures, because of the ability of the acetamide group to form hydrogen bonding. Moreover, the linked glucosamine rings on chitin had better miscibility with linked double rings 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 for 100% chitin–PU (CPU5) is more obvious than that of 100% BDO–PU (CPU1). It was also observed that the intensity peaks of polymers based on different chitin/BDO proportion (CPU2 to CPU4) are shifted to higher degree (towards right), indicating a slightly smaller inter domain spacing. This effect may be due to the denser packing of hard domains within the matrix. This behavior has been attributed to the chain-folding of the HS lamellar morphology.

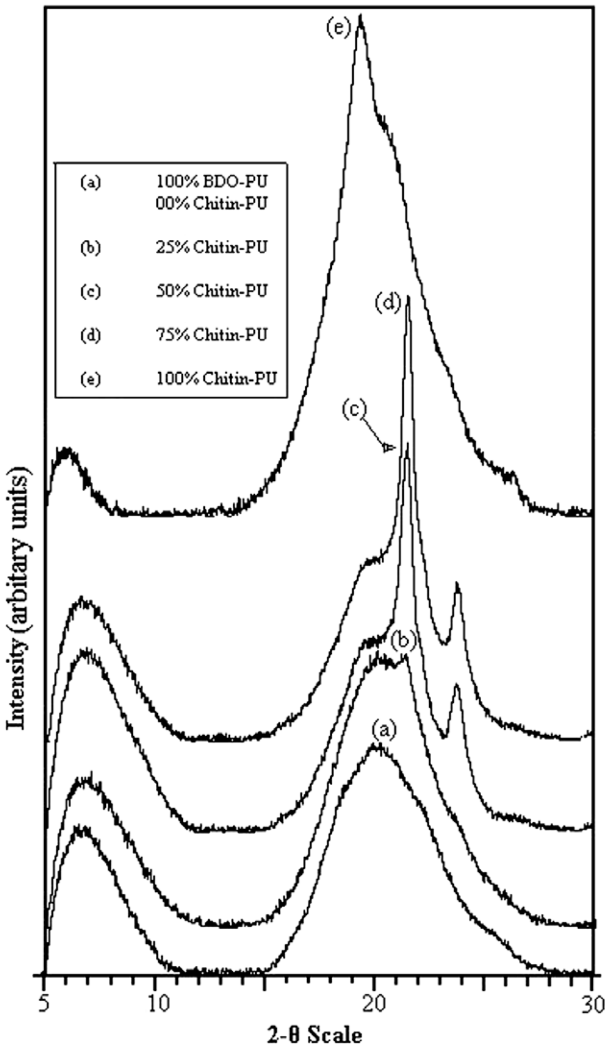

Fig. 2. X-ray diffractograms of (a) CPU1–0% chitin–PU; (b) CPU2–25% chitin–PU; (c) CPU3–50% chitin–PU; (d) CPU4–75% chitin–PU; (e) CPU5–100% chitin–PU.

3.3. Optical microscopy studies

Crystallinity of some polymers was clearly observed by optical microscopic studies (Fig. 3). X-ray diffraction experiments results correlates with optical microscopy findings. A crystalline polymer is distinguished from an amorphous polymer by the presence of sharp X-ray lines superimposed on an amorphous halo. Under an optical microscope, the presence of polycrystalline aggregates show as spherulites (Fig. 3). Spherulites are made up of small crys-

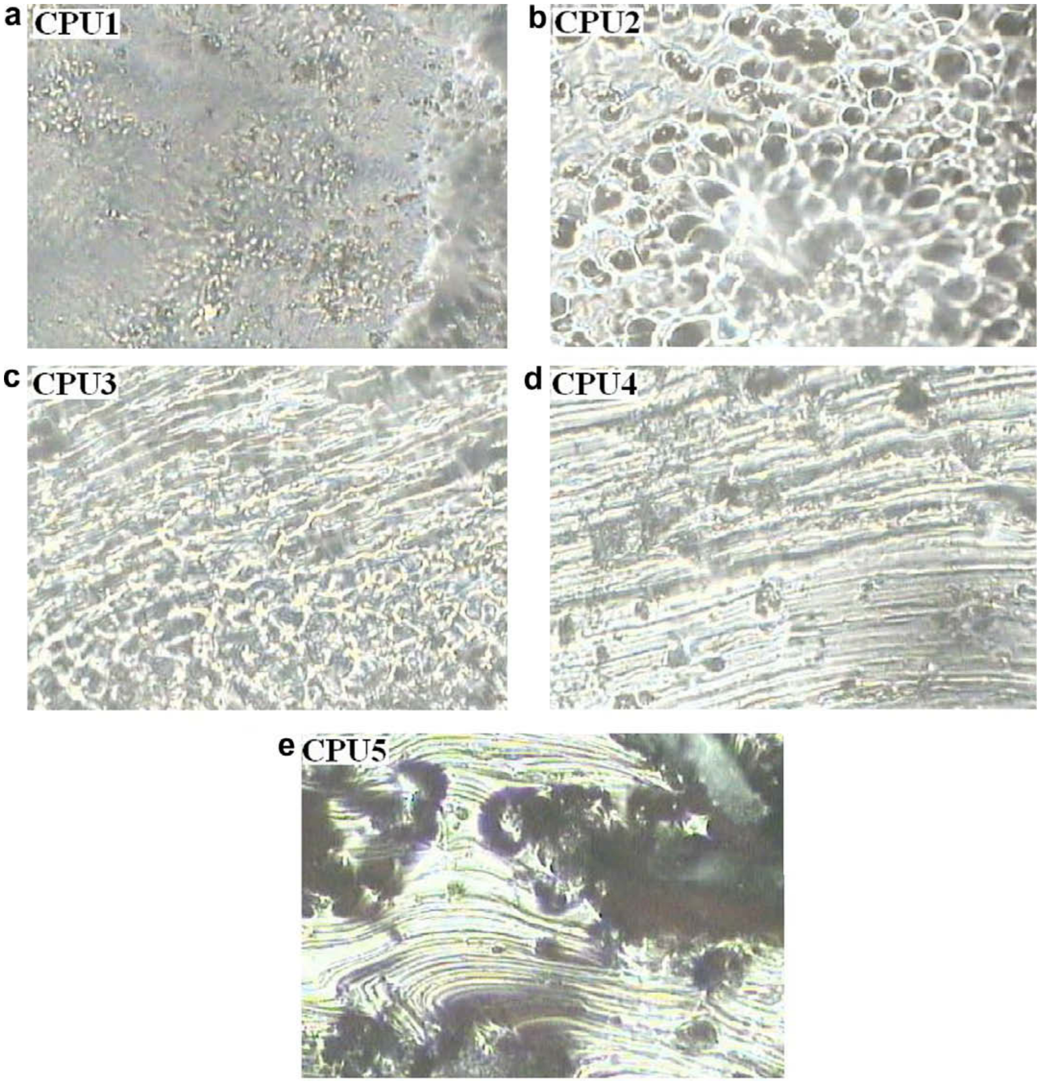

Fig. 3. Optical microscope pictures of sample films (a) CPU1–0% chitin–PU; (b) CPU2–25% chitin–PU; (c) CPU3–50% chitin–PU; (d) CPU4–75% chitin–PU; (e) CPU5–100% chitin–PU.

tallites and grow from a nucleus at their centre. They consist of narrow chain folded lamellae growing radially. Since the fibrous crystals are radial, the chains folded with the lamellae are circumferentially oriented. From the evaluation of the X-ray and optical microscopic studies, we can state that by the involvement of chitin in the PU formulation, we have improved crystallinity of the final polyurethane.

3.4. Thermal properties studies

DSC analysis data of all the PU samples is presented in Table 2. The value of peak enthalpy ΔH ($\mathrm{J\,g^{-1}}$ dry weight) are much consistent with the crystalline pattern of the PU samples. It is obvious from the X-ray diffraction studies that PU samples extended with chitin showed better crystalline pattern as compared to the PU extended with BDO. All the samples showed same trend in DSC analysis. Higher ΔH value was shown by the samples having much crystallinity. Generally chitin is biopolymer and high thermal energy is required for dissociation of its structure. The amount of peak enthalpy correlates with the compactness of supra-molecular chitin structure (Prashanth, Kittur, & Tharanathan, 2002). In other words, higher the peak enthalpy, the greater the crystallinity would be. ΔH for the samples extended with BDO (CPU1) showed lower values than the samples extended with chitin (CPU5). The higher ΔH value in sample CPU5 (41.57 ($\mathrm{J\,g^{-1}}$)) revealed that the crystallinity was greater than the crystallinity of the CPU1 (31.32 ($\mathrm{J\,g^{-1}}$)).

The data of altitude of tan δ peak (damping peak) is presented in Table 2. Investigation of loss tangent curves showed that the height of tan δ peak becomes smaller as the crystallinity of the PU samples increased. It has also been previously reported that the intensity of damping peak decreases with increasing degree of crystallinity. The intensity of the damping peak (tan δ) often is given by the equation (Myrayama, 1978)

$$\tan\delta = W_C(\tan\delta)_C + (1 - W_C)(\tan\delta)_a \tag{1}$$

where W_C is the degree of crystallinity, and the subscripts a and c refers to the contributions of the amorphous and pure crystalline phases, respectively. Since the loss tangent (tan δ), in general, is mostly due to the amorphous phase, the tan δ equation for the maximum in the tan δ peak simplifies to

$$\tan\delta \cong (1 - W_C)(\tan\delta)_a \tag{2}$$

This Eq. (2) shows the intensity of damping peak decreases with increasing degree of crystallinity and we have found same trend in this study.

Table 2
Thermal properties data of the samples.

Sample	ΔH (J g^{-1})[a]	Altitude of tan δ peak
CPU1	31.32[b]	1.05[b]
CPU2	33.82	0.91
CPU3	36.06	0.83
CPU4	38.92	0.70
CPU5	41.57[b]	0.62[b]

[a] Value of peak enthalpy (J g^{-1}) on dry weight basis.
[b] Results from previous study (Zia et al., 2008e).

4. Conclusion

Chitin based polyurethane elastomers (PUEs) were synthesized by step growth polymerization techniques using poly (ε-caprolactone) (PCL), 4,4′- diphenylmethane diisocyanate (MDI) and blends of chitin and BDO. The conventional spectroscopic characterization of the samples with FT-IR, ^{1}H NMR and ^{13}C NMR were in accordance with proposed PUEs structure. The crystalline behavior of the synthesized polymers were investigated using X-ray diffraction (XRD), differential scanning calorimetery (DSC), optical microscopic technique and loss tangent curves (tan δ peaks); and found that crystallinity increased with increase in chitin contents into the PU backbone. The contents of chitin favors the formation of more ordered structure, as higher peak intensities were obtained from the PU extended with chitin than 1,4-butane diol (BDO). X-ray diffraction experiments results correlates with optical microscopy findings.

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References

Barikani, M., & Hepburn, C. (1986). Isocyanurate crosslinking as a means of producing thermally stable polyurethane elastomers. *Cellular Polymers, 5*, 169–185.

Barikani, M., & Hepburn, C. (1987). The relative thermal stability of polyurethane elastomers: 3. Influence of chain extender structure. *Cellular Polymers, 6*, 47–67.

Barikani, M., Zia, K. M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008). Molecular engineering and properties of chitin based shape memory polyurethane elastomers. *Carbohydrate Polymers, 74*, 621–626.

Chen, B. Q., Sun, K., Fan, Y. Z., & Zhang, K. B. (2002). Intial rheoligical properties of chitin/dicholoacetic acid solutions. *The Journal of Functional Polymer, 15*, 311–314.

Cardenas, G., Cabrera, G., Taboada, E., & Miranda, S. P. (2004). Chitin characterization by SEM, FTIR, XRD and ^{13}C cross polarization/mass angle spinning NMR. *Journal of Applied Polymer Science, 93*, 1876–1885.

Kim, J., Ryba, E., & Bai, J. (2003). Grazing incidence X-ray diffraction studies on the structures of polyurethane films and their effects on adhesion to Al substrates. *Polymer, 44*, 6663–6674.

Kovacevic, V., Smit, I., Hace, D., Suceska, M., Mundri, I., & Bravar, M. (1993). Role of the polyurethane component in the adhesive composition on the hydrolytic stability of the adhesive. *International Journal of Adhesion and Adhesives, 13*, 126–136.

Kovacevic V, Kljajie-Malinovic LJ, Smit I, Bravar M, Agic A, Cerovecki Z. (1990). *AdhesiveComposition Systems in Degradative Conditions*, In: Allen KW (Ed.), Elsevier Appl Sci, Adhesion 14 London, pp. 126–160.

Myrayama, T. (1978). *Dynamic Mechanical Analysis of Polymeric Material.* Amsterdam: Elsevier. pp. 71–75.

Petrovic, Z. S., Cho, Y. J., Javni, I., Magonov, S., Yerina, N., Schaefer, D. W., et al. (2004). Effect of silica nanoparticles on morphology of segmented polyurethanes. *Polymer, 45*, 4285–4295.

Prashanth, K. V. H., Kittur, F. S., & Tharanathan, R. N. (2002). Solid state structure of chitosan prepared under different N-deacetylating conditions. *Carbohydrate Polymers, 50*, 27–33.

Rogulska, M., Podkoscielny, W., Kultys, A., Pikus, S., & Pozdzik, E. (2006). Studies on thermoplastic polyurethanes based on new diphenylethane-derivative diols. I. Synthesis and characterization of nonsegmented polyurethanes from HDI and MDI. *European Polymer Journal, 42*, 1786–1797.

Wang, W., Qin, W., & Bo, S. Q. (1991). Influence of the degree of deacetylation of Mark–Houwink equation parameters. *Makromoleculare Chemie-Rapid Communications, 12*, 559–561.

Zia, K. M., Bhatti, H. N., & Bhatti, I. A. (2007). Methods for polyurethane and polyurethane composites, recycling and recovery: A review. *Reactive and Functional Polymer, 67*, 675–692.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Bhatti, H. N. (2008a). Morphological studies of polyurethane elastomers extended with α ω-alkane diols. *Iranian Polymer Journal, 17*, 61–72.

Zia, K. M., Barikani, M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008b). Synthesis and thermo-mechanical characterization of polyurethane elastomers extended with α ω-alkane diols. *Journal of Applied Polymer Science, 109*, 1840–1849.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Islam-ud-Din (2008c). Surface characteristics of UV-irradiated polyurethane elastomers extended with α ω-alkane diols. *Applied Surface Science, 254*, 6754–6761.

Zia, K. M., Barikani, M., Zuber, M., Bhatti, I. A., & Sheikh, M. A. (2008d). Molecular engineering of chitin based polyurethane elastomers. *Carbohydrate Polymers, 74*, 149–158.

Zia, K. M., Bhatti, I. A., Barikani, M., Zuber, M., & Sheikh, M. A. (2008e). XRD studies of chitin based polyurethane elastomers. *International Journal of Biological Macromolecules, 43*, 136–141.

Zia, K. M., Barikani, M., Bhatti, I. A., Zuber, M., & Bhatti, H. N. (2008f). Synthesis and characterization of novel biodegradable thermally stable chitin based polyurethane elastomers. *Journal of Applied Polymer Science, 110*, 769–776.