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Molecular engineering of chitin based polyurethane elastomers

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ABSTRACT

Biodegradable polyurethane elastomers with potential for biomedical application as non-absorbable sutures with improved hydrophobic properties were synthesized by the reaction of poly(ε-caprolactone) (PCL) and 4,4′-diphenylmethane diisocyanate (MDI), extended with different mass ratio of chitin and 1,4-butane diol (BDO). Their molecular engineering and structural transition due to the changes of hydrogen bonding was confirmed by using FT-IR, ^{1}H NMR and ^{13}C NMR. Involvement of chitin was evidenced by the appearance of new signals in both ^{1}H NMR and ^{13}C NMR spectra, and very strong peak at 1724 cm^{-1} in FT-IR spectra. From the results, it was concluded that the reaction of the urethane group occurred mainly at C6—OH group of chitin in which strong intermolecular and intersheet hydrogen bonds are involved. Contact angle and surface tension measurement of the synthesized polyurethane as a function of chitin contents were investigated. Optimum hydrophobicity was obtained from elastomer extended with chitin in comparison to elastomers extended with BDO. The surface free energy was also affected by chemical composition of the final PU. Structure–property relationship for prepared elastomers showed that the main determining factors were hydrogen bonding, hydrophobicity and content of chitin in polyurethane backbone.

1. Introduction

Recently, natural polymers and their derivatives as renewable and biodegradable materials have attracted considerable attention because of the serious pollution problems caused by synthetic materials and shortage of resources (Barikani & Mohammadi, 2007; Chandra & Rustgi, 1998). Biodegradable polymers can be used in some medical applications such as surgical implants, artificial blood vessels, absorbable and non-absorbable sutures, drug delivery systems and dietary supplements, but their uses are still limited because of their high cost and/or their low performance (Aminabhavi, Balundgi, & Cassidy, 1990; Cao, Zhang, Huang, Yang, & Wang, 2003).

Segmented polyurethanes, consisting of hard and soft segments are known to have microphase separated structure, which makes them useful in some applications such as adhesives, coatings, biomedical materials and elastomers. Polyurethanes have a large number of commercial applications as they can be molded, injected, extruded and recycled (Zia, Bhatti, & Bhatti, 2007). Modification of the physical and chemical properties of these materials, through reaction or blending with other biodegradable and non-biodegradable polymers, is often necessary to meet the required performances (Iannace, Ambrosio, Huang, & Nicolais, 1994, 1995; Iannace, DeLuca, Nicolais, Carfagna, & Huang, 1990). The synthesis of biodegradable polyurethanes (PUs) is a relatively recent issue in PU chemistry. It is well-known that polyester based PUs are much more susceptible to biodegradation than PUs derived from polyether diols (Huang, 1989). Biodegradable urethanes were also synthesized by using polyester segments, such as lactic acid (Harkonen, Hiltunen, Malin, & Seppala, 1995; Owen, Masaoka, Kawamura, & Sakota, 1995) poly(3-hydroxybutyrate) (Hori, Suzuki, Okeda, Imai, & Sakaguchi, 1992) and polyethylene adipate (Sreenivasan, Jayabalan, & Rao, 1991). There is a correlation between flexibility and biodegradability. It is known that, the more flexible the PUs material, the more susceptible to biodegradation (Huang, Macri, Roby, & Benedict, 1981). A successful method of increasing biodegradability is to develop biopolymer based materials (Huang, Koenig, & Huang, 1993, chap. 6; Meister, Aranha, Wang, & Chen, 1993, chap. 5). 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 like soil, sewage and marine locations where bacteria are active (Alfani, Iannace, & Nicolais, 1998). As a biopolymer from natural sources, chitin and its derivatives with hydroxyl and acetamide groups have been considered as an alternative material in developing degradable elastomers because

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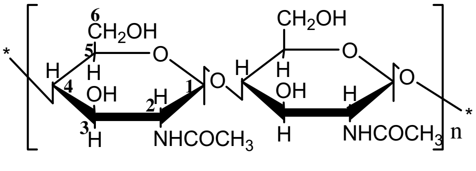
of their biodegradability, derivability, availability and low cost (Kurita, 2001; Rinaudo, 2006). However, the applications of pure chitin materials are limited because of poor solubility, so by itself cannot satisfactorily replace the functional and physical properties of non-degradable polymers (Jang, Kong, Jeong, Lee, & Nah, 2004; Zeng, Zhang, Wang, & Zhu, 2003).

Chitin ($(C_8H_{13}O_5N)n$) having cellulose like rigid structure, composed of 1,4-2-acetamido-2-deoxy-β-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 wall of the bacteria (Muzzarelli, 1997). Chitin is structurally similar to cellulose, but it is an amino polysaccharide having acetamide group at the C-2 positions in place of hydroxy group (Scheme 1). Chitin and its derivatives have been used as natural flocculants for wastewater treatment. However, the trend is toward producing high-value products for medical, pharmaceutical, biotechnological and cosmetic use (Kurita, Muzzarelli, Jeuniaux, & Gooday, 1986).

Materials made of chitin or modified chitin have the attractive advantages of being non-toxic, biodegradable and antibacterial and relatively good biocompatibility, which offer large unexplored commercial applications (Miyashita, Kobayashi, Kimura, Suzuki, & Nisho, 1997). For the last two decades, much attention has been paid to chitin to overcome restrictions of solubility and processibility (Chandra & Rustgi, 1998; Jang et al., 2004; Kurita, 2001; Kurita et al., 1986; Muzzarelli, 1997; Rinaudo, 2006).

Attempts have been made to synthesize biodegradable PU through structural modification of final PU structure via e.g., the incorporation of starch (Barikani & Mohammadi, 2007; Swamy & Siddaramaiah, 2003) and chitosan (Silva, Menezes, & Garcia, 2003; Yang, Yang, Lin, Wu, & Chen, 2007; Yu et al., 2006), but nothing has been reported on the synthesis and characterization of chitin based PU. In present work we have studied the molecular characterization of PU using chitin as a chain extender. In our previous study (Barikani & Mohammadi, 2007) corn starch was reacted with urethane prepolymer in order to modify starch and preparing new hydrophobic copolymers. Due to the unique and novel characteristics of chitin, this article reports on the synthesis and molecular characterization of novel biodegradable polyurethane elastomers based on chitin and BDO. In chitin there are two —OH groups located at C3—OH and C6—OH position of chitin and one acetamide group at C2-position. The hydroxyl and acetamide functionalities of this biopolymer allows chemical reactions with conventional diisocyanates or urethane prepolymer. In this study, it was shown that the —OH group at C6-position of chitin react with prepolymer to give final PU product. For this investigation a prepolymer was synthesized as predicted in our previous studies (Barikani & Hepburn, 1986, 1987) by the step-growth polymerization of PCL and MDI, and extended with different proportions of chitin and BDO. Molecular characterization of the synthesized samples has been provided using available spectroscopic techniques. After characterization the intended beneficial affects on the samples (MPU2–MPU5) hydrophilicity and morphology, as compared to when pure aliphatic diol (MPU1) is used as chain extenders were studied and discussed.



Scheme 1. Structure of chitin designated with carbon-position.

2. Experimental

2.1. Chemicals

Chitin ($\bar{M}_v = 6.067 \times 10^5$) was kindly supplied by the Iran Polymer and Petrochemical Institute (Tehran, I.R. Iran). Its molecular weight was deduced from the intrinsic viscosity, as described in the literature (Chen, Sun, Fan, Zhang, 2002). Chitin was purified according to already established methods (Wang, Qin, Bo, 1991). The material was immersed in 0.5 wt% aqueous potassium permanganate (Merck) solution for 1 h and washed with distilled water. The washed chitin was then immersed in 1 wt% aqueous oxalic acid (Merck) solution at 30 °C for 20 min. The resulting product was washed and dried. 4,4′-Diphenylmethane diisocyanate (MDI) and 1,4-butane diol (BDO) were purchased from Sigma–Aldrich Chemical Co. Polycaprolactone polyol, CAPA 225, (molecular weight 2000 from Introx Chemicals) and BDO were dried at 80 °C under vacuum for 24 h before use to ensure the removal of all air bubbles and water that may otherwise interfere with the isocyanate reactions. Molecular weight of CAPA 225 was confirmed by applying the procedure reported in ASTM D-4274C (ASTM Standards, 2004). MDI and all other materials were used as-received. All the reagents used in this work were of analytical grade.

2.2. Synthesis of PU based on BDO (MPU1)

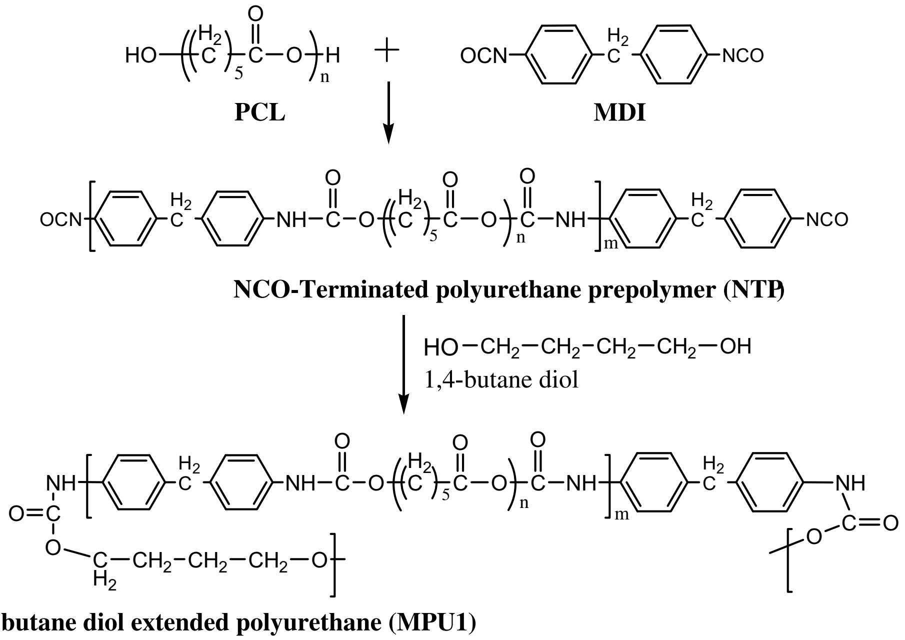
PCL (31.25 g) was placed into a four-necked reaction kettle equipped with mechanical stirrer, heating oil bath, reflux condenser, dropping funnel and N_2 inlet and outlet was placed. The temperature of the oil bath was increased to 60 °C. Then MDI (11.95 g) was added and the temperature was then increased to 100 °C. It took almost 1.0 h to obtain NCO terminated prepolymer. Conversion of the prepolymer into the final PU was carried out by stirring the prepolymer vigorously, and then adding a previously degassed chain extender, 1,4-butane diol (2.81 g). When 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. 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 one week at ambient temperature (25 °C) and 40% relative humidity before testing. A schematic illustration of the chemical route for synthesis of BDO based polyurethane (MPU1) is shown in Scheme 2.

2.3. Synthesis of PU based on mixture of chitin: BDO (MPU2–MPU4) and pure chitin (MPU5)

Prepolymer synthesis and film casting were carried out as described briefly in the synthesis of MPU1 (Section 2.2). Weighed amount of chitin according to molar ratio as predicted in Table 1 was dissolved in solvent (a mixture of *N*-methyl-2-pyrrolidine (NMP) and dimethyl sulfoxide (DMSO) with ratio 2:1) (Agboh & Qin, 1997; Austin 1984). For samples designated as MPU2–MPU4, the prepolymer was extended with different proportions of chitin/BDO (Scheme 3) while the sample designated as MPU5, was extended with 100% chitin (4.25 g). All other parameters, temperature condition remain same as described previously in the synthesis of MPU1.

2.4. Measurements

Infrared measurements were performed on a Bruker-IFS 48 Fourier Transform Infrared (FT-IR) Spectrometer (Ettlingen, Germany). The ^1H NMR and ^{13}C NMR spectra were recorded in deuterated dimethyl sulfoxide (DMSO)-d_6 solution using a Bruker Advance



Scheme 2. Chemical route for synthesis of 1,4-butane diol based polyurethane elastomers.

Table 1
Sample code designation and different formulation of PUs

Sr #	Sample code	Composition (chitin/BDO) % by mass	Molar ratio of CAPA225/MDI/Chitin/1,4BDO
01	MPU1	0/100	1:3:0:2
02	MPU2	25/75	1:3:0.5:1.5
03	MPU3	50/50	1:3:1:1
04	MPU4	75/25	1:3:1.5:0.5
05	MPU5	100/0	1:3:2:0

400 MHz Spectrometer. Chemical shifts (δ) were given in ppm with tetramethylsilane as a standard. A Kruss G10 contact angle measuring system was used for measurement of water droplet angle on the polymer film surface. Contact angles were measured using two test liquids (water and diidomethane) for more precise results. All the data presented were average of four measurements. Surface tension and their polar and dispersive portions were calculated applying two different methods (Owens–Wendt Method and Wu Method). NCO content of polyurethane prepolymers was determined according to procedure reported in ASTM D-2572 (ASTM Standards, 2004).

3. Results and discussion

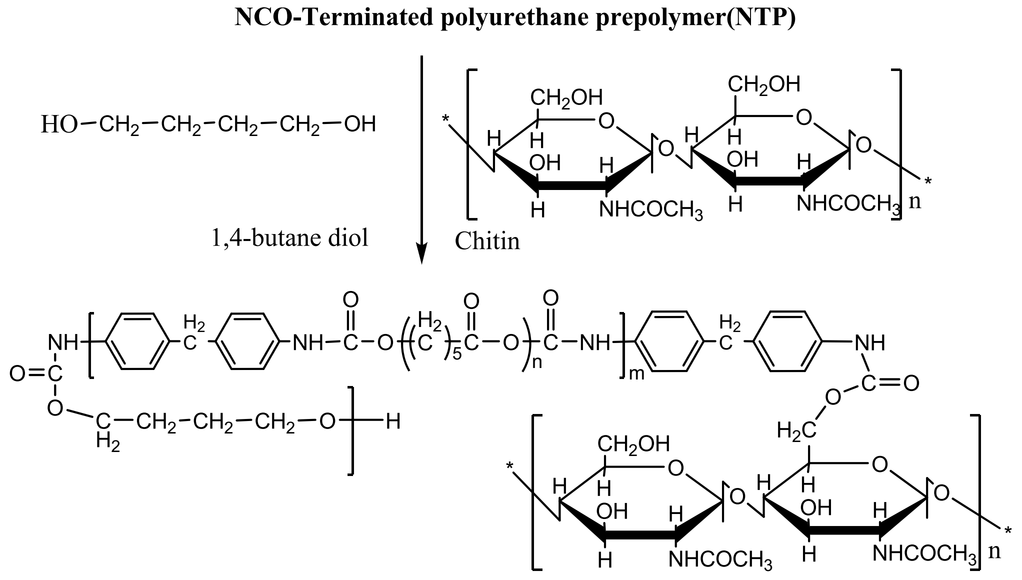
Synthesis of chitin based polyurethane was considered following the synthetic route as outlined in Schemes 2 and 3. The reaction of one equivalent of polyol with three equivalents of MDI leads to NCO terminated polyurethane prepolymers (NTP), which was subsequently extended with two equivalents of chain extender with different proportions of chitin/BDO. The final polyurethanes were characterized by conventional spectroscopic methods.

3.1. FT-IR studies

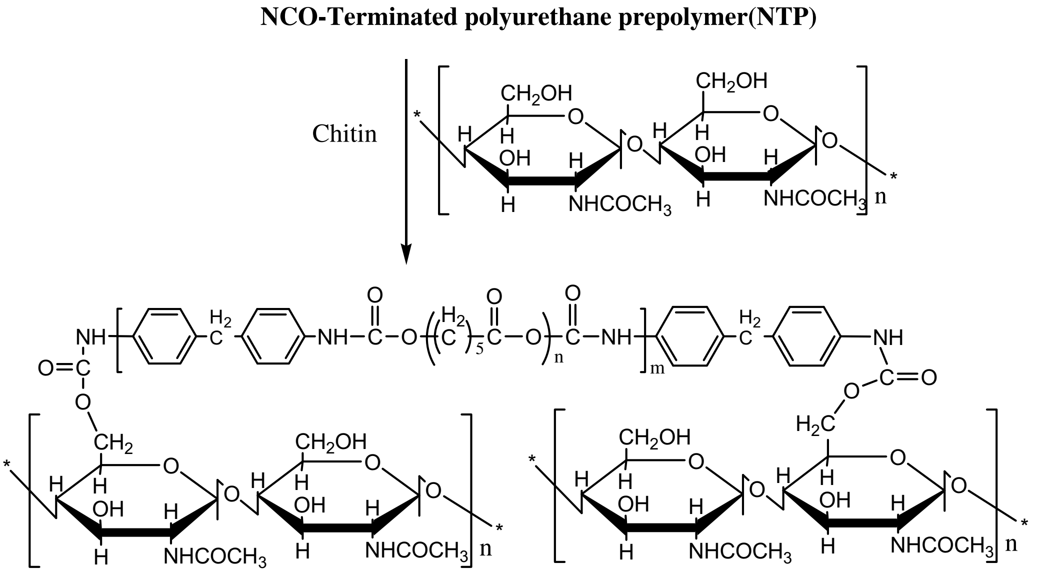
FT-IR spectra of the original chitin, polyurethane extended with 100% BDO (MPU1), mixture of chitin/BDO (MPU3) and 100% chitin (MPU5) are shown in Fig. 1(a–d). FT-IR spectra of original chitin (Fig. 1a) showed that broad OH stretching vibration band appeared at 3443 cm^{-1}. The NH symmetric and asymmetrical stretching vibration bands appeared at 3289 and 3105 cm^{-1}, respectively. The CH symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2931 and 2889 cm^{-1}, respectively. The spectral region of 686–1661 cm^{-1} is the information-rich region. The faint absorptions at 1661, 1626 are due to C=O bond and at 1563 cm^{-1} is due to NH deformations. The absorption bands at 1427, 1377 and 1307 cm^{-1} were attributed to CH_2 bending vibration, CH bending vibration and CH_2 wagging, respectively. The bands appearing at 1261 and 1204 cm^{-1} are due to NH bending vibration and OH in-plane bending. The absorption band appearing at 1158 cm^{-1} is due to the asymmetric in-plane ring deformation. The absorption bands appearing at 1046 and 1026 cm^{-1} are due to C—O and C—C stretching vibration. The two absorption bands at 950 and 896 cm^{-1} are due to C—O ring vibration and ring bending. The broad intense band at 1000–1220 cm^{-1} was attributed to the ring and bridge C—O—C vibrations of chitin-ether-type absorption. On the other hand, a weak shoulder at 710 cm^{-1} and well-resolved band at 686 cm^{-1} are assigned to the out-of-plane bending of NH (amide).

To provide clear information about the vibrational mode changes due to involvement of chitin in to the polyurethane backbone the FT-IR spectra of chitin were compared with polyurethane having different proportions of chitin. FT-IR spectra of polyurethane extended with 100%BDO (MPU1) is shown in Fig. 1b. FT-IR spectra of MPU1 showed characteristic bands of urethane groups at 3330 cm^{-1} (N—H stretching). The peaks located at 2947, and 2810 $cm^{-1}$are assignable to CH symmetric and asymmetric stretching vibrations of CH_2 groups. The peaks observed at 1728, 1642 and 1599, 1529 cm^{-1} are 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 correspond to the absorption of —NH, —CO, —CHN were observed at 3330, 1728 and 1464 cm^{-1} respectively, which indicated that the new synthesized product had —NHCOO groups.

FT-IR spectra of MPU3 (Fig. 1c) showed characteristic bands of urethane groups at 3335 cm^{-1} (N—H stretching); 2947 and 2810 cm^{-1} (CH symmetric and asymmetric stretching vibrations



(a) Chitin/1,4-butane diol based polyurethane (MPU2-4)



(b) Chitin based polyurethane (MPU5)

Scheme 3. Chemical route for synthesis of (a) chitin/1,4-butane diol (b) chitin based polyurethane elastomers.

of CH_2 groups). The spectral regions of 737–1727 cm^{-1} provided rich information and peaks observed in this region were assigned as: 1727, 1644 cm^{-1}(C=O bond); 1596, 1533 cm^{-1} (NH deformations); 1461 cm^{-1} (CH_2 bending vibration); 1413 cm^{-1} (CH bending vibration) and 1308 cm^{-1} (CH_2 wagging). Peaks located at 3335, 1727 and 1461 cm^{-1} provides evidence about the new synthesized product include —NHCOO groups. FT-IR spectra of MPU5 (Fig. 1d) showed a strong absorption peak of NH stretching vibration at 3339 cm^{-1}. The CH symmetric and asymmetric stretching vibrations of CH_2 groups were observed at 2935, and 2865 cm^{-1}, respectively. The other peaks were assigned as: 1726, 1645 cm^{-1} (C=O bond); 1597, 1534 cm^{-1} (NH deformations); 1460 cm^{-1} (CH_2 bending vibration); 1412 cm^{-1} (CH bending vibration); 1306 cm^{-1} (CH_2 wagging). The band at 1000–1221 cm^{-1} was attributed to the ring and bridge C—O—C vibrations. By extending prepolymer with different proportions of chitin/BDO, the FT-IR spectra showed a very strong, new peak at about 1728 cm^{-1} (MPU1-1728 cm^{-1}; MPU3-1727 cm^{-1} and MPU5-1725 cm^{-1}) which was assigned to C—O—C stretching of the soft segment of PCL. Another new peak was also observed at about 1460 cm^{-1} which was assignable to urethane —NH group. It was observed that the intensity of hydrogen-bonded NH increased as the chitin content increased, suggesting that the hydrogen bonds of chitin were broken and new hydrogen bonds between chitin and polyurethane prepolymer were formed. Moreover, the hydrogen-bonded NH stretching absorption band around 3330 cm^{-1} for the MPU1 shifted to higher wave numbers with increasing chitin content, indicating an enhancement of free NH group in the chitin based PU (MPU3, MPU5), which led to a reduction in interchain interaction between chitin and PU in MPU5. It was also observed that with

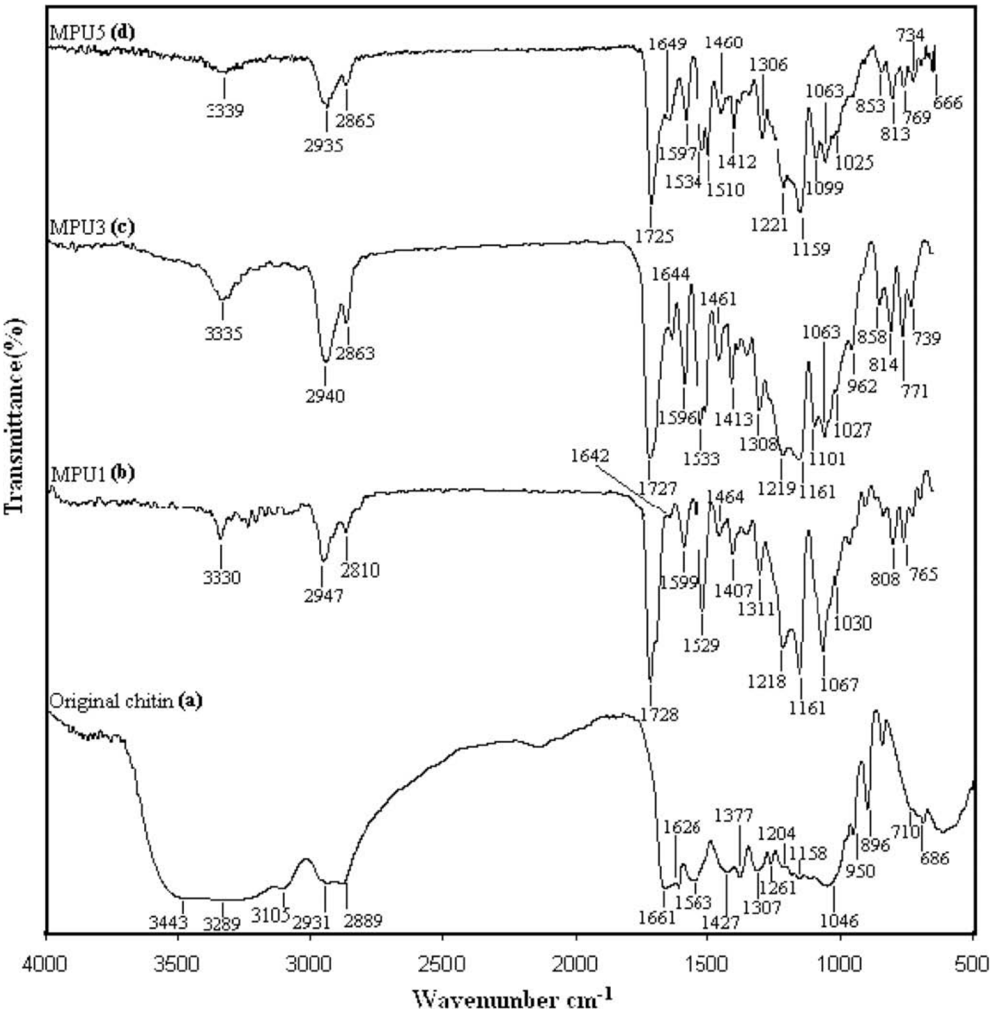


Fig. 1. (a–d) FT-IR spectra: (a) original chitin; (b) MPU1-BDO based polyurethane; (c) MPU3–chitin/BDO (50:50) based polyurethane; (d) MPU5–chitin based polyurethane.

increasing chitin content, the peak of urethane carbonyl groups at around 1728 cm^{-1} (MPU1-1728 cm^{-1}; MPU-1727 cm^{-1} and MPU5-1725 cm^{-1}) decreased and shifted to lower wavenumber while the band around (1642–1649 cm^{-1}) for hydrogen-bonded carbonyl of chitin increased and shifted to higher wave number. This implies that stronger interchain interactions between chitin and PU prepolymer, in chitin based PU than that in BDO based PU. From Fig. 1(a–d) it can be noticed that a broad band appeared at 3443 and 2950 cm^{-1} in original chitin has been disappeared in the final polyurethane extended with chitin. This provides the evidence that all of the chitin has been consumed and there is no free chitin in the final polyurethane sample.

The structural transition due to the changes of hydrogen bonding can be confirmed by FT-IR spectroscopic technique. As shown in Fig. 1a, the absorption band of C=O stretching at 1626 cm^{-1}, attributed to hydrogen bonding between the acetamide carbonyl group and C6—OH group, disappeared after reaction with NCO terminated prepolymer. This may explain the reaction of NCO terminated prepolymer has taken place at C6-position (C6—OH) of chitin. Moreover, the relative intensity of the C—O stretching band at 1067 cm^{-1} and the absorption band at 1030 cm^{-1} (related to primary alcohol), has been decreased in MPU3 and MPU5 by the involvement of chitin in to the final synthesized product. This also explains the reaction of NCO terminated prepolymer has taken place at C6-position (C6—OH) of chitin.

3.2. NMR studies

NMR spectra of polyurethane extended with 100% BDO (MPU1), mixture of chitin/BDO (MPU3) and 100% chitin (MPU5) are shown in Figs. 2–4. ^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (400 MHz, DMSO-d_6) spectra of final synthesized polyurethane samples (MPU1-5) were in accordance with proposed structures.

3.2.1. MPU1

^{1}H NMR spectra (Fig. 2a): 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).

^{13}C NMR spectra (Fig. 2b): 173.2, 173.1, 154.8 ppm (CO); 137.6, 135.9, (ArC); 129.2, 118.7 (ArCH); 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).

3.2.2. MPU3

^{1}H NMR spectra (Fig. 3a): 8.43 ppm (s, NH); 7.3–7.2 (m, 4H); 7.17–7.05 (m, 4H); 4.41 (s, 4H); 4.08–3.94 (broad, 3H); 3.92–3.73 (s, 3H); 3.38–3.25 (broad, 4H); 2.47 (DMSO); 2.25–2.21 (m, 6H); 1.51–1.49 (m, 3H); 1.27–1.24 (m, 2H).

^{13}CNMR spectra (Fig. 3b): 174.1, 173.2, 154.0, 152.9 ppm (CO); 138.1, 137.6 (ArC); 129.3, 118.7 (ArCH); 103.8 (C1-chitin); 78.3,

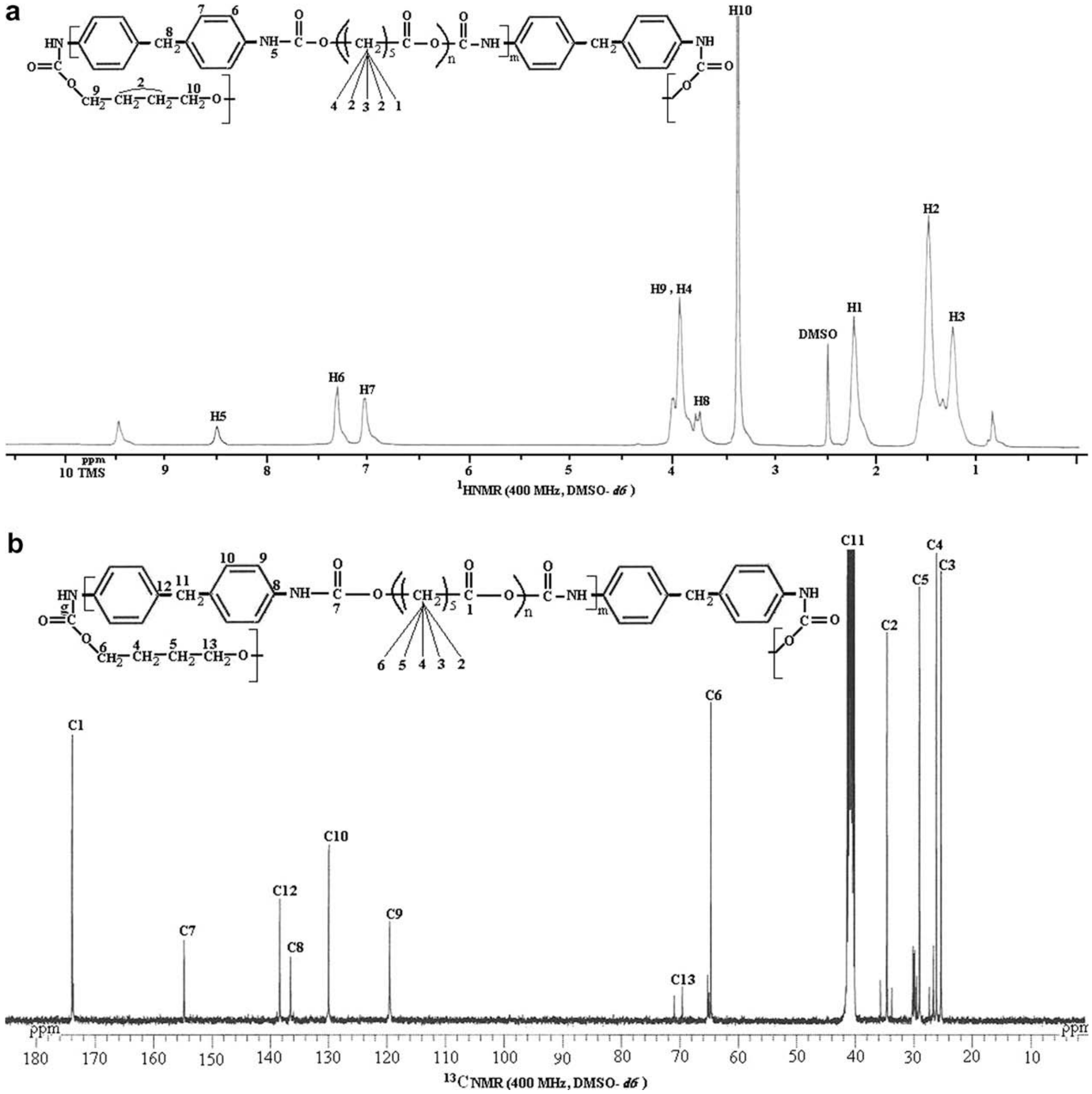


Fig. 2. (a) ^{1}H NMR (b) ^{13}C NMR spectra of BDO based polyurethane (MPU1).

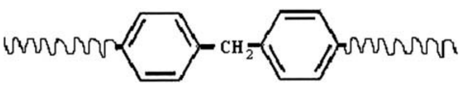
78.1(C4-chitin); 68.8 (C3- and C5-chitin); 64.4, 63.9, (C6-chitin); 55.5 (C2-chitin); 78.1, 64.3, 40.9, 40.6, 40.4, 40.2, 40.0, 39.8, 39.6, 39.3, 34.9, 33.8, 28.7, 28.3, 25.3, 24.5, 21.7 (CH_2).

3.2.3. *MPU5*

^{1}H NMR spectra (Fig. 4a): 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}CNMR spectra (Fig. 4b): 173.1, 173.0, 154.0, 152.9 ppm (CO); 138.1, 137.6, 135.8, 135.3 (ArC); 129.3, 118.7 (ArCH); 104.1 (C1-chitin); 77.5 (C4-chitin); 69.6 (C3 and C5-chitin); 63.3, 63.2, (C6-chitin); 56.6, 56.2 (C2-chitin); 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 (CH_2).

^{1}H NMR spectra obtained for MPU3 and MPU5 exhibited new peaks at 4.41 ppm (MPU3), 4.48 ppm (MPU5) which was assigned to the proton of C1, C3 and C6-position of chitin. ^{13}CNMR spectra obtained for the chitin based PU samples (MPU3–5), exhibited peaks at 23.0 and 174 ppm, which were attributed, respectively, to the $—CH_3$ (methyl) and C=O (carbonyl) group of chitin (Cardenas, Cabrera, Taboada, & Miranda 2004). Moreover, peaks located at about 56.2, 63.3, 69.6, 68.8, 77.5 and 104 ppm were attributed to C2, C6, C3, C5, C4 and C1 position of chitin, respectively (Nishio, Koide, Miyashita, Kimura, & Suzuki 1999; Kim, Ha & JuJo 2002), which provides evidence of involvement of chitin in final polyurethane structure (MPU3–5). There is no such peak in MPU1. In all the ^{13}CNMR spectra of final PU samples, it was observed that the peak at 40 ppm presents a progressive intensity increase. This result can be attributed to the overlapping of $—CH_2—$ signals with those due to aromatic chemical structure.



As earlier stated that in chitin there are two —OH groups located at C3—OH and C6—OH position of chitin and one acetamide group at C2-position. There is no significant indication for the reaction of

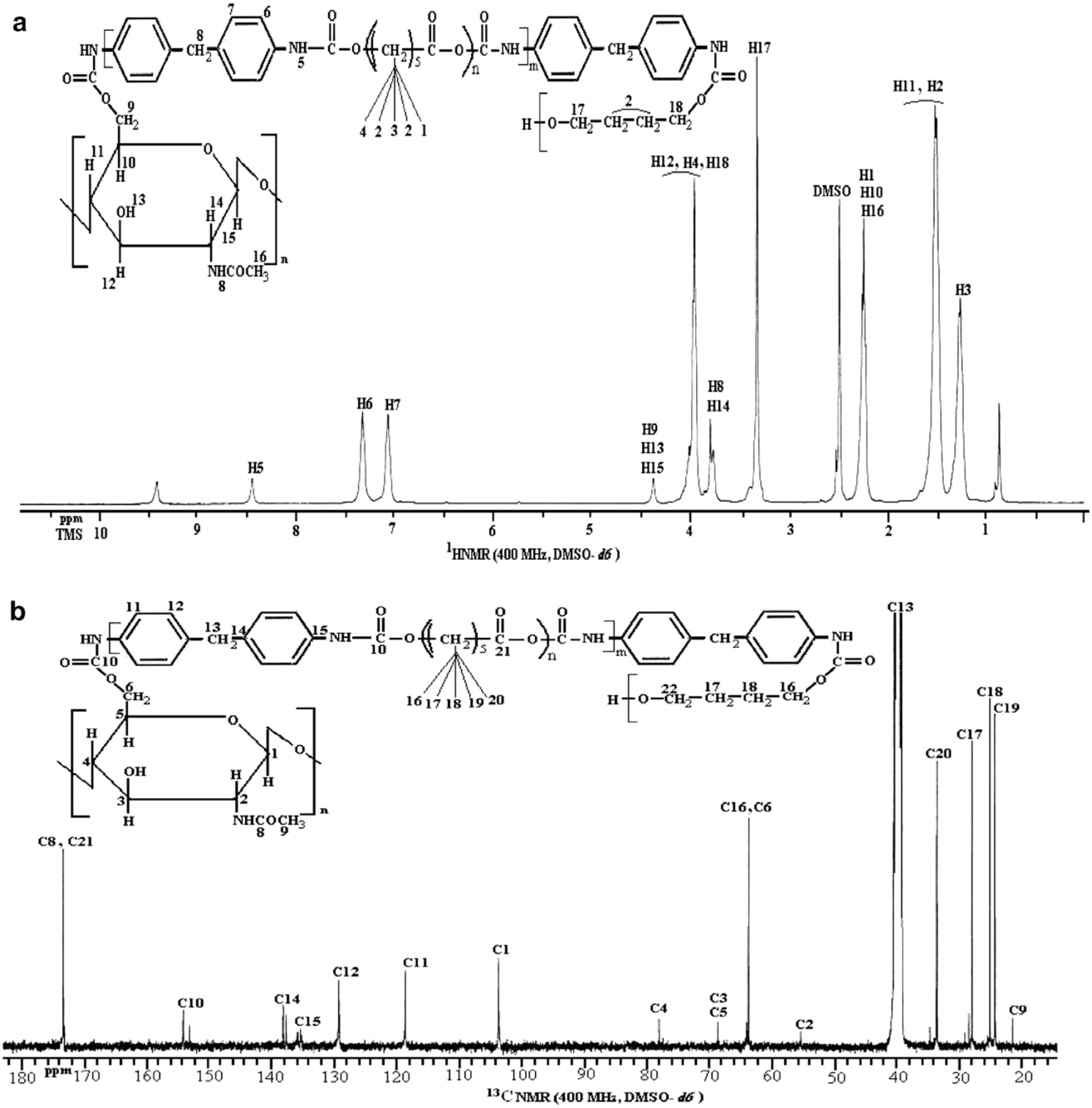


Fig. 3. (a) ^{1}H NMR (b) ^{13}C NMR spectra of chitin/BDO based polyurethane (MPU3).

amine group located at C2-position with that of NCO terminated prepolymer. It is worth to mention that the peak related to —NH located at C2-position is absent at the 2.8 ppm chemical shift (Fig. 4a) after exchanging this proton with deuterium when the sample was treated with D_2O. Therefore, it can be said that the reaction takes place mostly at hydroxyl groups in the chitin. These results are in agreement with a previous study (Park & Park, 2001). It may be assumed that the reaction occurs at C6—OH rather than C3—OH because of the high reactivity, the lack of intermolecular hydrogen bonds with neighbouring units, and the lack of steric hindrance against neighbouring acetamide group (Anthonsen & Sandford, 1989). This behaviour has also been predicted in FT-IR studies.

3.3. Measurements of contact angle and surface free energy

The surface morphology of biomaterials is very important for biomedical application. MPUs surface hydrophilicity, as characterized by static water contact angle, is shown in Fig. 5. In present study for validation of results, the contact angle was measured using two different test liquids (water and diiodomethane). The values of contact angle using both the test liquid increases as the concentration of chitin in the PU backbone vary from 0% to 100%. As it can be seen, there is a large difference between precursor PU (MPU1) and PU extended with 100% chitin (MPU5). This means hydrophilicity of the final PU film decreases by extending prepolymer with chitin. This phenomenon is due to fact that chitin itself is crystalline polysaccharide and its affinity with water is negligible. Therefore by increasing the percentage of chitin in the PU backbone, the hydrophobicity of the final PU increases. On the basis of investigation into their in vitro biocompatibility and non-toxicity made on the similar material, it can be suggested the final polyurethane material is useful for biomedical application as non-absorbable sutures (Zia, 2008). Surface tension and their polar and dispersive portions were

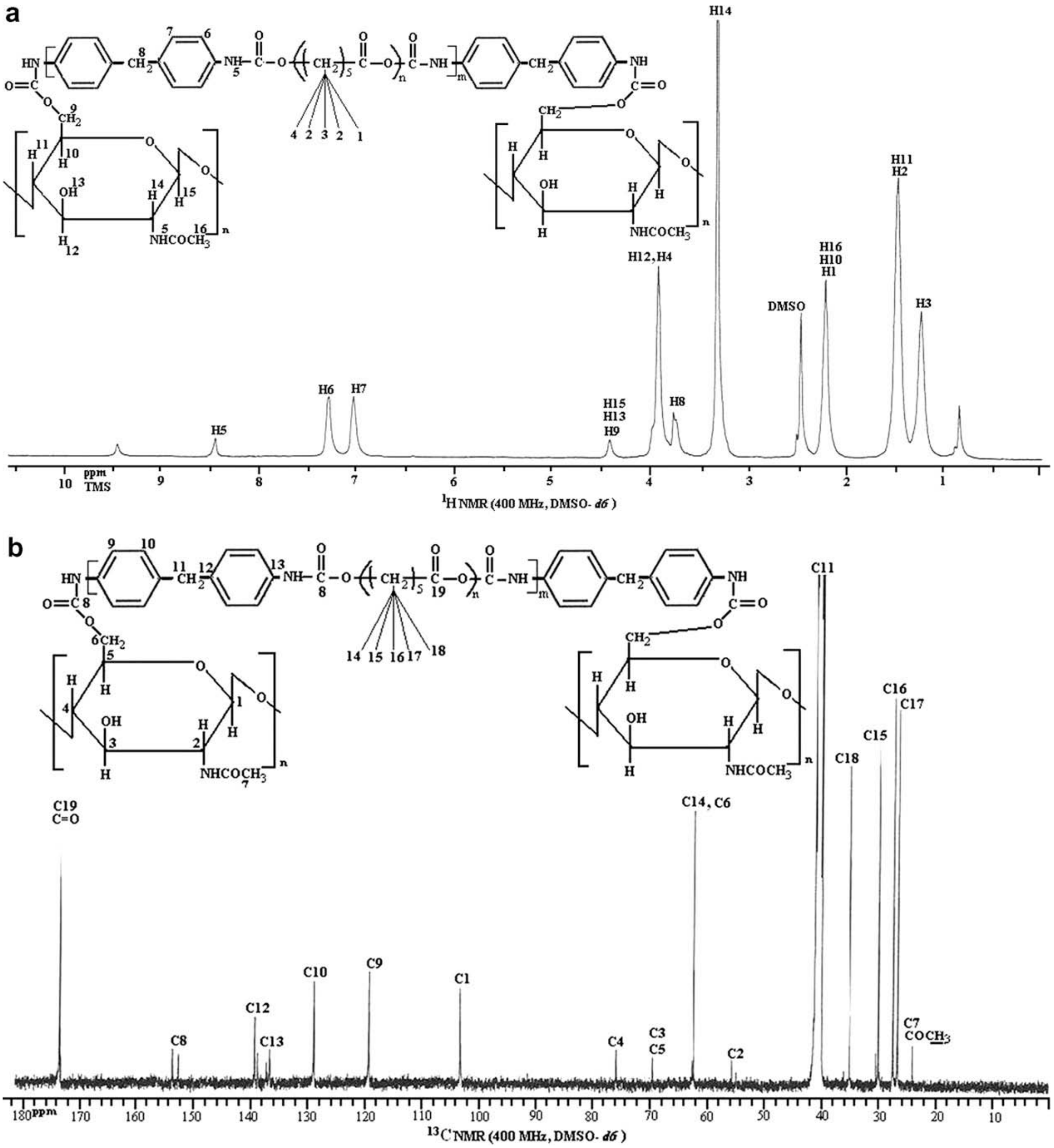


Fig. 4. (a) ^{1}H NMR (b) ^{13}C NMR spectra of chitin based polyurethane (MPU5).

calculated applying two different methods (Owens–Wendt Method & Wu Method) for accuracy of the results (Table 2). It was found that surface energy decreases as the chitin percentage in the final PU backbone increases. This behaviour was evidenced from the results of both applied method. It is known that increase in contact angle values leads to decrease in surface energy. In addition to this, with increasing chitin percentage, the polar component steadily decreases, whereas the dispersive part is hardly changed.

4. Conclusion

Chitin based biodegradable polyurethane network based on PCL and MDI, extended with different mass ratio of chitin and

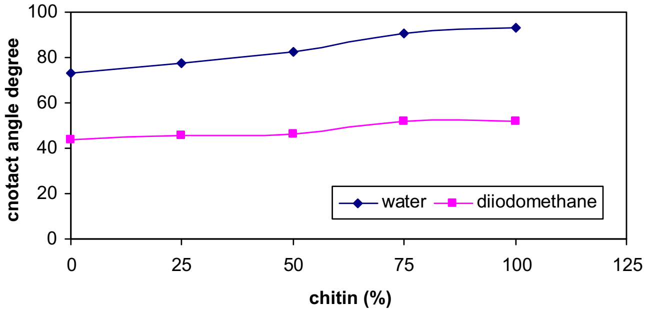


Fig. 5. Variation of contact angle with two different test liquid (a) water (b) diidomethane.

Table 2
Total surface energy calculated data with Owens–Wendt Method and Wu Method

S. No.	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	MPU1	39.14	8.73	47.86	38.40	11.78	50.19
2	MPU2	37.66	6.57	44.23	39.88	9.46	49.34
3	MPU3	39.30	4.34	43.64	42.42	2.86	45.28
4	MPU4	42.08	0.30	42.38	38.48	3.81	42.29
5	MPU5	36.67	3.20	39.88	40.27	0.81	41.08

BDO were synthesized. The conventional spectroscopic characterization of the samples with FT-IR, ^{1}H NMR and ^{13}C NMR were in accordance with proposed polyurethane structure. The structural transition due to the changes in hydrogen bonding was confirmed by using these techniques. Involvement of chitin was evidenced by the appearance of new signals in both ^{1}H NMR and ^{13}C NMR spectra, and very strong peak at 1724 cm^{-1} in FT-IR spectra. It was concluded from NMR as well as FT-IR analysis that the reaction of the urethane group occurred mainly at C6—OH group of chitin in which strong intermolecular and intersheet hydrogen bonds are involved. The interactions of chitin based polyurethane with water and diidomethane on the surface was clearly related to the mass ratio of chitin content. The surface free energy was affected by chemical composition of the final PU. It was suggested the final polyurethane material is useful for biomedical application as non-absorbable sutures. Finally it can be concluded that these polymers can be utilized in a number of potential applications, offering the unique properties of these two polymers i.e., polyurethane and chitin. Investigation of structure–property relationship for prepared elastomers showed that the main determining factors for observed properties were hydrogen bonding, hydrophobicity and content of chitin in the polyurethane backbone.

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