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XRD studies of UV-irradiated chitin based polyurethane elastomers

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ABSTRACT

Chitin based polyurethane (PU) elastomers constituted on 4,4́-diphenylmethane diisocyanate (MDI), poly(ε-caprolactone) (PCL) and extended with blends of chitin/1,4-butane diol were synthesized via two step polymerization technique. The synthesized samples were irradiated for 50, 100 and 200 h in an UV exposure chamber as such the spectral distribution of the light is good match for terrestrial solar radiation. The crystalline behavior of the irradiated PU samples were investigated by X-ray diffraction (XRD), differential scanning calorimetery (DSC) and dynamic mechanical thermal analysis (DMTA) techniques. The effect of irradiation time and chitin contents on crystallinity were studied and investigated. The maximum decrease in the crystalline behavior of samples after irradiation observed by XRD, DSC and tan δ peaks were found for the PU samples extended with lower contents of chitin (chitin/BDO; 0/100). In comparison with irradiation times the 200 h irradiation showed maximum change in the crystalline behavior.

1. Introduction

Polymer pyrolysis is the chemical process of thermolytic degradation by chain scission (randomly along the chain backbone). These fragments can recombine to give different pyrolytic products. Pyrolysis is necessary for gasification and combustion of natural and synthetic macromolecules and is thus a common and important chemical reaction (Zia, Bhatti, & Bhatti, 2007). The thermal degradation of polymers especially polyurethane has been the centers of thermal analysis studies for many years (Gao, Kaneko, Amasaki, & Nakada, 2003). Segmented polyurethanes, consisting of hard and soft segments are known to have microphase separated structure, which make them useful in various ways such as adhesives, coatings, biomedical materials and elastomers (Barikani & Hepburn, 1986; Barikani & Hepburn, 1987). Molecular characterization and morphological studies of polyurethane elastomers (PUEs) have been reported by many researchers. The effect of the diisocyanate structure and chain extender (CE) length using α,ω-alkane diols on the crystallinity, surface morphology and thermo-mechanical properties of PUEs have been investigated and well documented (Rogulska, Podkoscielny, Kultys, Pikus, & Pozdzik, 2006; Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008b; Zia, Barikani, Zuber, Bhatti, & Bhatti, 2008a). Detailed molecular characterization, thermal and shape memory properties of chitin based polyurethane elastomers has been previously discussed and reported (Barikani, Zia, Bhatti, Zuber, & Bhatti, 2008; Zia, Barikani, Bhatti, Zuber, & Bhatti, 2008d; Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008c). XRD studies of polyurethane elastomers based on chitin/BDO blends and varying diisocyanates structure have also been documented elsewhere (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008e; Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008f).

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 hydroxyl group. Chitin itself is a crystalline polymer of *N*-acetyl-D-glucosamine (GlcNAc) monomer, its crystalline structure has been previously reported and well documented (Cardenas, Cabrera, Taboada, & Miranda, 2004; Zia et al., 2008e; Zia et al., 2008f). 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). Structural and surface characteristics of UV-irradiated polyurethane elastomers extended with α,ω-alkane diols has been also reported elsewhere (Zia, Barikani, Zuber, Bhatti, & Islam-ud-Din, 2008g). No reference is still available on the study of the effect of different exposure time of UV-radiation on morphological behavior of polyurethane elastomers extended with blends of chitin/BDO. It is

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known that PUEs undergo significant structural changes on exposure to UV-irradiation which causes deterioration in their crystalline pattern. In this work, we have irradiated a series of polyurethane elastomers based on PCL and 4,4′-diphenylmethane diisocyanate (MDI), extended with different proportion of chitin and BDO by ultraviolet (UV) radiations. The effect of chitin contents and UV-irradiation time on the crystallinity is currently being investigated and reported using X-ray diffraction (XRD), differential scanning calorimetery (DSC) and dynamic mechanical thermal analysis (DMTA) techniques.

2. Experimental

2.1. Chemicals

4,4′-Diphenylmethane diisocyanate (MDI) and 1,4-Butane diol (BDO) were procured from Sigma–Aldrich Chemical Co. (St. 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 provided by Department of Polymeric Biomaterials, Iran Polymer and Petrochemical Institute Tehran, Iran. Chitin was purified according to already established methods in the 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., 2008f).

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 of chitin and BDO (Table 1) The polymerization was completed to get the final product according to the method reported elsewhere (Zia et al., 2008c).

2.3. UV exposure

Irradiation of PUEs was carried out in an UV exposure chamber fitted with five 80 W medium pressure mercury vapor lamps (Latina Tendeng Cor., China) constructed with borosilicate glass envelopes which filter all wavelength below 300 nm. These conditions provided the spectral distribution of the light that is good match for terrestrial solar radiation. Irradiation was performed with sample to lamp distance of 20 cm at ambient relative humidity. Samples were irradiated for the time of 50, 100 and 200 h.

Table 1
Sample code designation and different formulation of PUs.

S#	Sample code	Composition (chitin/BDO[a])% by mass	Molar ratio (whole number) of CAPA225[b] /MDI[c] /Chitin/BDO[a]
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

[a] 1,4-Butane diol.
[b] Polycaprolactone polyol (molecular weight; 2000 g mol^{-1}).
[c] 4,4′-Diphenylmethane diisocyanate.

2.4. Measurements

The X-ray diffractograms of the polymers were obtained in a Siemens D-5000 diffractometer with radiation Cu K$_\alpha$ (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°. 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 atmosphere 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

FTIR spectra of original chitin, polyurethane extended with BDO, polyurethane extended with chitin and polyurethane extended with blends of chitin/BDO have been presented in our previous study (Zia et al., 2008c). The detailed peaks assignments have also been discussed elsewhere (Zia et al., 2008c). ^{1}H NMR (400 MHz, DMSO-d6) and ^{13}C NMR (400 MHz, DMSO-d6) spectra of final synthesized polyurethane samples were also in accordance with proposed structures (Zia et al., 2008c).

3.2. X-ray diffraction studies

Chitin has a highly ordered crystalline structure. Crystalline structure of chitin has been extensively studied and recently reviewed (Zia et al., 2008f). It has been previously observed through X-ray diffraction studies that crystallinity of chitin based PU increases as the contents of chitin in to the final PU increase (Zia et al., 2008f). Previous studies stated that the crystallinity of PU elastomers is dependent on the soft segments (Kovacevic et al., 1990; Kovacevic et al., 1993). So the observed crystalline behavior of the polymers is due to soft segment and chitin itself. These results were verified through the hypothesis that the presence of chitin results to increase in phase segregation and as consequence the soft segment mobility. This increase in mobility would be responsible for an increase in the degree of chain orientation.

The thermal degradation of chitin gave acetamide in addition to acetic acid, water and other minor degradation products. Acetamide is considered to be a volatile degradation product. Monomeric and oligomeric anhydro-sugars are primary degradation products of chitin for example, 2-acetamido-glucose with terminal anhydro sugar unit. Upon UV-irradiation, 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 (Fig. 1). It can also be observed that intensity of the crystalline peak is going to decrease with increase in irradiation time (50–200 h). This sample has shown the worst crystalline pattern at 200 h irradiation. The intensity of the crystalline peaks is going to increase as the concentration of chitin increased (Fig. 1). It can be observed that UV-irradiation has much effect on the crystalline pattern of the irradiated samples either we have extended the PU prepolymer with 100% BDO, blends of BDO/chitin or 100% chitin. There is continuous decrease in the crystalline pattern of all the irradiated samples with increase in irradiation time. In comparison of the blends of chain extender used, we can observe that degradation and crystalline

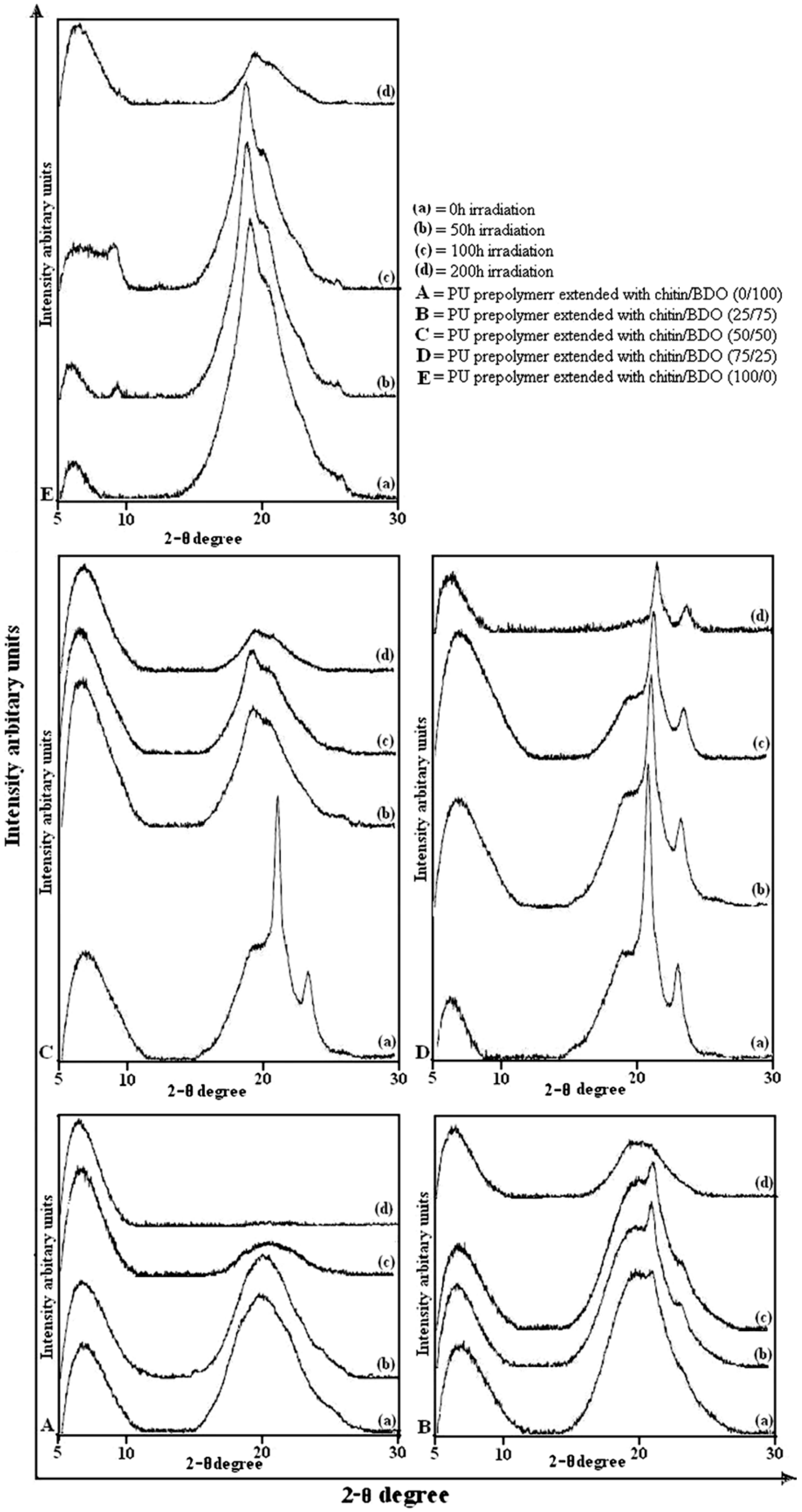

Fig. 1. X-ray diffractograms of polyurethane (PU) samples at 0 h (a) 50 h (b) 100 h (c) and 200 h (d) UV-irradiation; PU sample extended with (A) chitin/BDO (0/100); (B) chitin/BDO (25/75); (C) chitin/BDO (50/50); (D) chitin/BDO (75/25); (E) chitin/BDO (100/0).

pattern are less effected in the PU samples extended with higher contents of chitin (Fig. 1). 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 crys-

Table 2
Thermal properties data of the samples obtained before and after UV-irradiation.

Sample	Exposure time (h)	ΔH (J g^{-1})[a]	Altitude of tan δ peak
CPU1	00[a]	31.32[b]	1.05[b]
–	50	28.56	1.13
–	100	14.23	1.29
–	200	5.11	Nd[c]
CPU2	00[a]	33.82[b]	0.91[b]
–	50	29.38	1.03
–	100	23.47	1.11
–	200	14.61	1.25
CPU3	00[a]	36.06[b]	0.83[b]
–	50	32.44	0.94
–	100	25.67	1.04
–	200	15.09	1.19
CPU4	00[a]	38.92[b]	0.70[b]
–	50	35.91	0.88
–	100	31.28	0.97
–	200	22.69	1.06
CPU5	00[a]	41.57[b]	0.62[b]
–	50	37.52	0.71
–	100	33.27	0.85
–	200	23.51	1.05

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

talline polymer of *N*-acetyl-D-glucosamine monomers, is capable of forming three dimensional ordered structures. Therefore, intensity of crystallinity for 100% chitin-PU (CPU5) is more obvious at 200 h UV-irradiation than that of 100% BDO–PU (CPU1).

3.3. Thermal properties studies

Significant changes in the degree of order of the chitin structure caused by thermal degradation. Increase or decrease in the degree of crystallinity of chitin would cause decrease or increase in the rate of deacetylation which ultimately effect polyurethane structure corresponding to crystallinity which chitin have in its backbone. DSC analysis data of all the PU samples at different exposure times is presented in Table 2. The values of enthalpies changes (ΔH; J g^{-1} dry weight) associated with different irradiation treatments are much consistent with the crystalline pattern of the PU samples. It is obvious from the X-ray diffraction studies that (Fig. 1) PU samples extended with chitin showed better crystalline pattern as compared to the PU extended with BDO even after 200 h irradiation. Higher ΔH value was shown by the samples having much crystallinity and ΔH values of the samples decreased with increase in irradiation time. The effect of UV-irradiation on the thermal behavior can be best studied comparing irradiated and non-irradiated samples. We can observe that ΔH value show gradual decrease with increase in irradiation time. Generally, chitin is biopolymer and high thermal energy is required for dissociation of its structure. It has been observed that the amount of peak enthalpy (ΔH) correlates with the compactness of supramolecular chitin structure (Prashanth, Kittur, & Tharanathan, 2002). In other words, higher the peak enthalpy (ΔH), the greater the crystallinity would be. The enthalpy changes (ΔH) for the samples extended with BDO (CPU1) showed lowest values at different irradiation time than the samples extended with chitin (CPU5). The higher ΔH value in sample CPU5 at different irradiation time revealed that its crystallinity was higher than the crystallinity of the CPU1.

The comparative data of altitude of tan δ peaks (damping peaks) of all the studied samples is presented in Table 2. Investigation of loss tangent curves showed that the intensity of tan δ peak becomes higher as the irradiation time of the PU samples increased. Maximum height in δ peak was observed in the sample extended with BDO (CPU1) at 200 h irradiation time. The height of the δ peak decreased with increase in chitin contents in to PU backbone. On the other hand the height of the δ peak increased with increase in irradiation time. It has been previously reported in the literature that content of chitin favors the formation of more ordered structure (Zia et al., 2008e), the presence of chitin persist the attack of UV-radiation. It has also been previously reported that the intensity of damping peak decreases with increasing degree of crystallinity (Myrayama, 1978). The aforesaid discussed results are in accord with previous findings as reported by Myrayama (1978).

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 1,4-butane diol (BDO). The crystalline behavior of the irradiated and non-irradiated polymer samples were investigated using X-ray diffraction (XRD), differential scanning calorimetery (DSC) and dynamic mechanical thermal analysis (DMTA); and found that crystallinity decreased with increase in irradiation time. The contents of chitin persist the attack of UV-radiation, as higher peak intensities were obtained from the PU samples extended with chitin than the samples extended with 1,4-butane diol (BDO) even at 200 h irradiation.

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