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XRD pattern of chitin based polyurethane bio-nanocomposites

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ABSTRACT

Chitin based polyurethane bio-nanocomposites (PUBNC) were prepared by emulsion polymerization. The existence of the intercalated clay by polyurethane (PU) in the hybrid was confirmed using X-ray diffraction (XRD), dynamic mechanical measurements and optical microscope (OM) techniques. The values of enthalpies changes (ΔH) associated with different bentonite nanoclay contents are much consistent with the crystalline pattern of the synthesized PUBNC samples. These results revealed that pure silicate disappear in PU/bentonite nanoclay hybrid and a set of new peaks appears corresponding to the basal spacing of PU/bentonite clay bio-nanocomposites. The values of tan δ versus temperature recorded using dynamic mechanical measurements were also in accord with crystalline pattern of the PUBNC samples.

1. Introduction

The traditional non-biodegradable polymers, which are produced from fossil fuels, have considerably disturbed and damaged the ecosystem of nature. Polylactide and polysaccharides are most promising candidates because they are made or come from naturally abundant products and are readily biodegradable (Ruiz-Hitzky, 2003). However, in order to render biopolymers able to compete with stronger and more ductile commodity polymers such as polyethylene or polypropylene, there is still a need to improve their properties including thermal stability, mechanical and barrier properties (Kawasumi, 2004; Wang et al., 2004). At this point it is noteworthy to point out that polymer-layer silicate nanocomposite (PLSNs) technology has already proven to be a good way to improve these properties significantly (Maiti, Nam, Okamoto, Hasegawa, & Usuki, 2002; Ray, Maiti, Okamoto, Yamada, & Ueda, 2002). Although much attention has been paid to polymer/clay nanocomposites, relatively little attention has been paid to biopolymer/clay nanocomposites. These are the cases of polylactide/clay nanocomposites (Paul et al., 2003), cotton/clay nanocomposites (White, 2004), poly(butylenes succinate)/clay nanocomposites (Ray et al., 2003) and plant oils/clay nanocomposites (Lu, Hong, & Wool, 2004).

In the most of the cited studies bentonite clay has been incorporated in the polymer hybrid to improve some targeted properties. Bentonite clays with composition [(Na, Ca) (Al, Mg, Fe) (Na, Ca) (Al, Mg, Fe)$_6$ (Si$_4$O$_{10}$)$_3$(OH)$_6$] are ordinarily composed largely of minerals of the montmorillonite group; is a 2:1 type aluminosilicate. Its crystalline structure presents an alumina octahedral between two tetrahedral layers of silica (Grim, 1968). The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. The imbalance of the negative charges at the surface is compensated by exchangeable cations, typically Na^+ and Ca^{2+}. The parallel layers in these structures are linked together by weak electrostatic forces (Parker, 1988). Intercalation of the clays via exchange of cations located in their interlayer space with large organic or inorganic cations is an effective way to modify them in order to obtain applicable material (Patterson & Murray, 1983).

Chitin and chitosan, next to cellulose, are the second most plentiful natural biopolymers. Due to their many properties, such as biocompatibility, biodegradability, antibacterial properties and non-toxicity, they have been extensively investigated for several decades for molecular separation, food packaging film, artificial skin, bone substitutes, water engineering and so on (Kumar, 2000). Chitin has also been used widely as an adsorbent for transition metal ions and organic species because the one acetamide (–NHCOCH$_3$) group at C-2 position and the two (02 hydroxy (–OH) groups at C-3 (C3–OH) and C-6 (C6–OH) positions on chitin chains can serve as the coordination and reaction sites. It has been reported in the established literature that hydroxy (–OH) group at C6–OH of chitin has reacted with isocyanate (–NCO) terminated polyurethane prepolymer rather than C3–OH (Zia, Barikani, Zuber, Bhatti, & Sheikh, 2008a). The reason of this reaction has been attributed because of the high reactivity, the lack of intermolecular

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hydrogen bonds with neighbouring units, and the lack of steric hindrance against neighbouring acetamide group (Anthonsen & Sandford, 1989). Because of the polyfunctionality of chitin, this biopolymer can be intercalated in Na^+-montmorillonite through cationic exchange phenomena.

There are only a limited number of reports about the enhancement of properties of biopolymer using PLSNs technology (Ruiz-Hitzky, 2003; Wang, Chen, & Ton, 2006). Wang and his co-workers had a preliminary study about chitosan clay nanocomposites and reported a markedly improved tensile property but inferior thermal property of composites to that of pure chitosan (Wang et al., 2006). Ruiz-Hitzky synthesized functional chitosan/montmorillonite nanocomposites, which can effectively act as active phase for an electrochemical sensor in the detection of different anions (Ruiz-Hitzky, 2003). Taking these antecedents into account, the aim of the present study is to prepare high-performance chitin based PU nanocomposite by incorporating bentonite clay at the nanometre scale through intercalation. The effects of bentonite clay contents on the morphology, crystalline pattern and thermal stability of the chitin based polyurethane bio-nanocomposites (PUBNC) have been investigated.

2. Experimental

2.1. Materials

Chitin was supplied by Department of Polymeric Biomaterials, Iran Polymer and Petrochemical Institute Tehran, Iran. Chitin was purified according to the established methods (Wang, Qin, & Bo, 1991). Delite® HPS bentonite (inorganic MMT with highest cation exchange capacity (CEC) i.e., 74 meq/100 g) was provided by Laviosa Chemica Mineraria (LCM) SpA Italy. Bentonite clay, 4,4′-diphenylmethane diisocyanate (MDI) and polycaprolactone polyol, CAPA 231 (3000 g/mol^{-1}) were used in this study.

2.2. Synthesis of polyurethane bio-nanocomposites

The appropriate amount of clay (Table 1) was thoroughly mixed with the solvent i.e., dimethyl sulfoxide (DMSO), and then polyol was mixed to the clay solvent mixture with continuous stirring about 1 h at 90 °C. Clay based PU prepolymer was formed following the addition of MDI and lasting the reaction at the same temperature for about another 1 h. The polymerization was completed by adding the chitin at last step as chain extender/crosslinker. It is worthwhile mentioning that the solvent was used for the dispersion of bentonite clay in all the samples even into the sample where clay was not used, for the purpose to make a comparative study.

2.3. Characterization

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°. 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 $30 \times 10 \times 1$ mm. Observation of optical microscopy (OM) was performed on thin sections using a Jenavert optical microscope.

3. Results and discussion

3.1. Nanostructure and morphological pattern

The clay dispersion within chitin has been characterized by both XRD and optical microscopy (OM), which is the most frequently, used and approachable methods to study the structure of nanocomposites. Depending on the relative distribution/dispersion of the stacks of clay platelets, three types of PLSN can be described (Alexandre & Dubois, 2000; Ray & Okamoto, 2003) intercalated PLSNs, where polymer chains are intercalated into the silicate layers resulting in a well ordered mutilayer morphology built up with alternating polymer and inorganic layers; flocculated PLSNs, where intercalated stacked silicate layers are sometime flocculated due to the hydroxylated edge–edge interactions, and exfoliated/delaminated PLSNs, where the silicate layers are completely homogenously dispersed in the polymer matrix. There are one acetamide ($-NHCOCH_3$) group at C-2 position and two (02 hydroxy (–OH)) groups at C-3 (C3–OH) and C-6 (C6–OH) positions on chitin chains which can serve as the coordination and reaction sites (Zia et al., 2008a). Because of the polyfunctionality of chitin, it is suggested that this biopolymer can easily intercalate in Na^+-montmorillonite into the inter layers by means of cationic exchange. The clay dispersion within chitin has been characterized by both XRD and optical microscopy (OM). The XRD patterns of pristine bentonite clay, MDI and chitin have been presented in Fig. 1. XRD plots of pristine bentonite clays (Fig. 1a) show the presence of montmorillonite (M) as a major phase. Other minor phases are kaolinite (K), quartz (Q), illite (I) and illite montmorillonite (IM). The XRD pattern of the bentonite clays shows a reflection peak at about $2\theta = 7.2°$, corresponding to a basal spacing of 1.25 nm. The XRD pattern of MDI (Fig. 1b) shows the characteristic crystalline peaks at around $2\theta = 11.7°$, 15.3°, 18.2°, 22.4° and 27.8°. The peaks around 11.7° and 22.4° are might be due to crystal (1) and crystal (2) in MDI, respectively. The crystalline structure of chitin has been reported by many researchers (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008b). Fig. 1(c) presents the XRD patterns of the original chitin. The chitin structure contains extended polymer

Table 1
Formulation of different PU bio-nanocomposites (molar ratio (as whole) of CAPA231/MDI/chitin; 1.0:3.0:2.0).

Sample code	Polyol (CAPA231[a]) (0.0156 mol)	Diisocyanate (MDI[b]) (0.047 mol)	Chain extender (chitin) (0.0313 mol)	Bentonite clay % by mass
PUBNC-1[c]	PCL[d]; (46.88 g)	MDI; (11.95 g)	Chitin; (4.25 g)	0.0
PUBNC-2	PCL; (46.88 g)	MDI; (11.95 g)	Chitin; (4.25 g)	1.0
PUBNC-3	PCL; (46.88 g)	MDI; (11.95 g)	Chitin; (4.25 g)	2.0
PUBNC-4	PCL; (46.88 g)	MDI; (11.95 g)	Chitin; (4.25 g)	4.0
PUBNC-5	PCL; (46.88 g)	MDI; (11.95 g)	Chitin; (4.25 g)	8.0

[a] Trade name of the used polyol (molecular weight 3000 g/mol).
[b] 4,4′-Diphenylmethane diisocyanate.
[c] Polyurethane bio-nanocomposites.
[d] Polycaprolactone polyol.

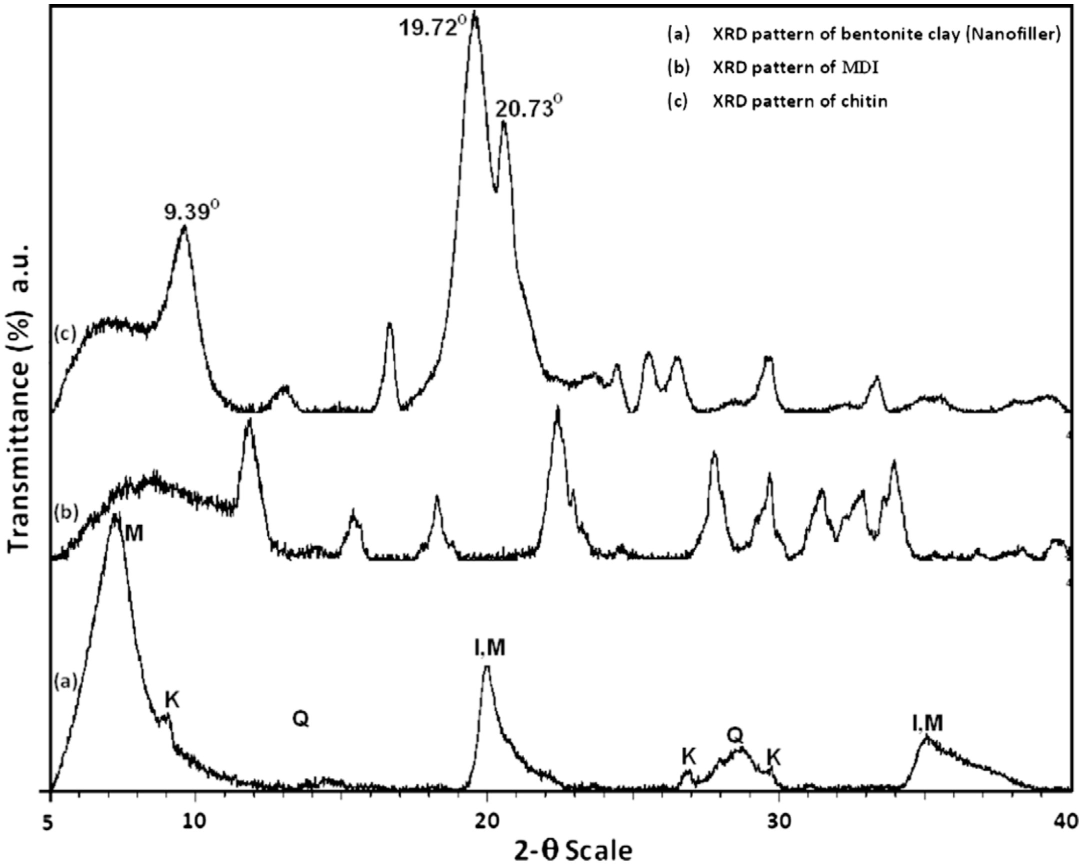

Fig. 1. XRD pattern of raw material used in the preparation of chitin based PU bio-nanocomposites, (a) bentonite clay, (b) MDI and (c) chitin.

chains indicating an anti-parallel arrangement of the chitin chain with strong intermolecular hydrogen bonding (Wada & Saito, 2001). The crystalline reflections were observed in the 2θ range of 5–30° (Fig. 1c). The observed patterns of the crystalline peaks in the 2θ range were indexed as 9.39°, 19.72° and 20.73° for the lower angle for chitin. As shown in Fig. 1(c) exhibited a broad signal centered at 2θ = 19.72°, which is attributed to the *N*-glucosamine (GlcN) sequences. Similarly, the intensity of the broad signal centered at 2θ = 9.39° due to *N*-acetyl-D-glucosamine (GlcNAc) sequences (Jayakumar & Tamura, 2008).

3.2. X-ray diffraction studies of the chitin bases PU bio-nanocomposites

Fig. 2(a–e) shows a series of XRD for PU/nanoclay bio-nanocomposites with different compositions (Table 1). Compared with bentonite clay, the diffraction peaks corresponding to the immaculate silicate disappear in PU/nanoclay hybrids, while a set of new peaks appears corresponding to the basal spacing of PU/clay nanocomposites. After incorporating bentonite clay within chitin based PU, the basal plane of bentonite clay at 2θ = 7.2° disappears (Fig. 1a), substituted by a new weakened broad peak at around 2θ = 5–7° (Fig. 2a). The movement of the basal reflection of bentonite clay to lower angle indicates the formation of an intercalated nanostructure, while the peak broadening and intensity decreases most likely indicate the disordered intercalated or exfoliated structure.

Fig. 2(a–e) illustrates the XRD patterns of chitin based PU bio-nanocomposites (PUBNC) with different bentonite nanoclay concentrations (varying 0–8.0 mass % bentonite nanoclay). The sample PUBNC-1 exhibits only one weak crystalline peak at 2θ = 6.5° indicating the formation of an amorphous structure (Fig. 2a). The X-ray diffraction pattern of the chitin based PU bentonite clay nanocomposite showed that the addition of 1.0 mass % of bentonite clay did not affect the crystallographic nature of PU (Fig. 2b). Comparing Fig. 2a with Fig. 2b, clearly shows that the sample PUBNC-2 with nanoclay contents (Fig. 2b) did not shows significant change in the crystalline pattern in comparison with that of sample PUBNC-1 without nanoclay (Fig. 2a). The lower crystallinity of PUBNC-1 is ascribed to the presence of solvent residue (as for comparative study solvent was used as dispersant in all the studied samples), which may hinder the formation of inter- and intramolecular hydrogen bonds PUBNC-1 and result in less packing. It has been previously reported in the literature that same applied concentration of chitin has significantly change the crystalinity of the studied samples (Zia, Bhatti, Barikani, Zuber, & Sheikh, 2008c). It is clear from the present results that solvent has hindered the formation of more ordered pattern. In contrast to chitin, the addition of bentonite nanoclay has changed the crystalline pattern, the intensity of the crystalline peaks going to increase with increase in bentonite nanoclay contents, as supported by the XRD patterns (Fig. 2), where the sample PUBNC-5 still keep the characteristic peaks of chitin. This complexity of clay morphologies among matrices and the different crystallinities of chitin and PUBNC samples will definitely affect the thermal and mechanical properties of the final products.

It is difficult, however, to draw definitive conclusions on the microstructure of the nanocomposites from XRD patterns exhibiting diffraction patterns, as the relatively featureless diffraction pattern of the exfoliated structure may have been covered up by the diffraction peak of the intercalated structure (Vaia, Jandt, Kramer, & Giannelis, 1996). Therefore optical microscopy (OM) is necessary

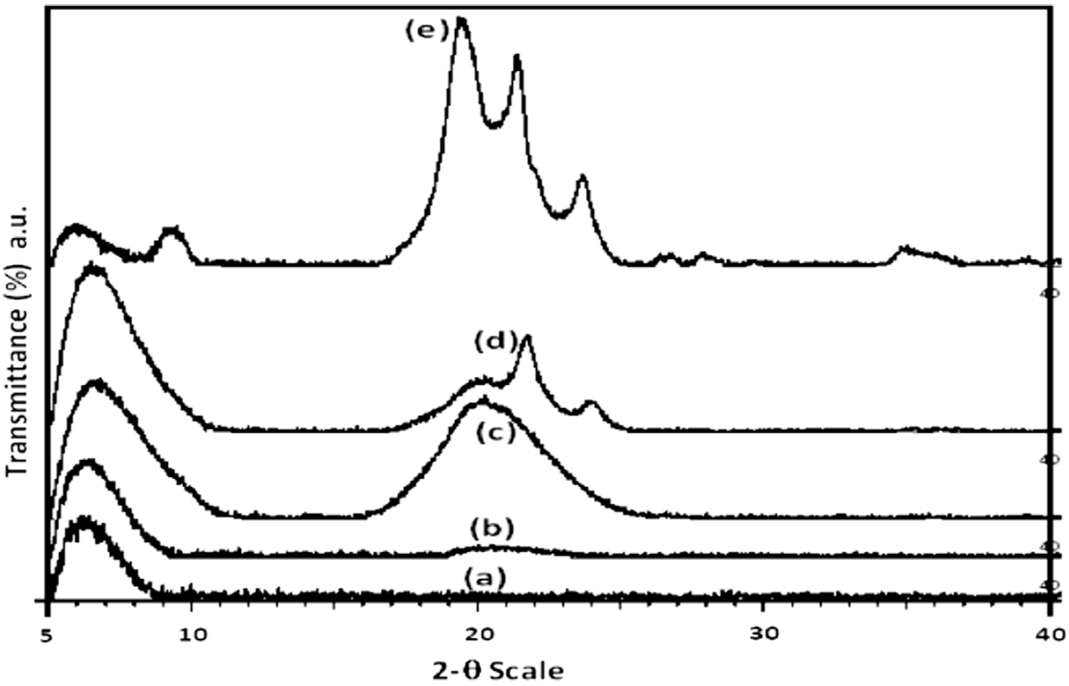

Fig. 2. XRD pattern of chitin based PU bio-nanocomposites varying bentonite nanoclay contents, (a) PUBNC-1; without bentonite nanoclay, (b) PUBNC-2; 1.0% bentonite nanoclay, (c) PUBNC-3; 2.0% bentonite nanoclay, (d) PUBNC-4; 4.0% bentonite nanoclay and (e) PUBNC-5; 8.0% bentonite nanoclay.

to determine the nature of the nanocomposites and to provide additional information that will be helpful in the interpretation of the XRD results. Optical microscopy photographs showed that some single silicate layers and ordered intercalated assemble layers of bentonite are well dispersed in PUBNC matrix (Zia, 2008), which revealed that most of bentonite layers are arranged in the direction parallel to the casting film, which is responsible for the improved barrier properties and thermal stability of the PUBNC. Based on the above OM and XRD results, the direct-cast PU/bentonite sample is apparently a nanocomposite with intercalated structure and disorderedly exfoliated structure of bentonite.

3.3. Thermal properties studies

Thermal stability is an important property for which the nanocomposite morphology plays a vital role. The PU/bentonite clay nanocomposites were analyzed by differential scanning calorimetry (DSC). Thermal behavior of PU/bentonite clay nanocomposites containing different amounts of bentonite is presented in Table 2. It is obvious from the X-ray diffraction studies that PUBNC samples intercalated with higher contents of bentonite clay showed better crystalline pattern as compared to the PUBNC intercalated with least contents. All the samples showed alike trend in DSC analysis. Higher ΔH value was shown by the samples having much crystallinity. A possible explanation for such an improvement could be the creation of a three-dimensional network of interconnected long silicate layers strengthening the material through mechanical percolation. In addition, dynamic mechanical analysis (Table 2) reveals a very marked improvement of the damping peak intensity. It can be seen that the intensity of the tan δ peak is going to decrease as the crystallinity of the PUBNC samples increased (Table 2). It has also been previously reported that the intensity of damping peak decreases with increasing degree of crystallinity (Myrayama, 1978). Therefore it can be concluded that increase in nanoclay contents definitely improve the crystalline pattern of the synthesized chitin based polyurethane bio-nanocomposites samples.

Table 2
Heat enthalpies and altitude of tan δ peak value of the chitin based PU bio-nanocomposites.

Sample code	Bentonite clay % by mass	ΔH (Jg^{-1})[a]	Altitude of tan δ peak
PUBNC[b]1	0.0	37.67	0.28
PUBNC-2	1.0	34.91	0.36
PUBNC-3	2.0	32.78	0.46
PUBNC-4	4.0	29.56	0.57
PUBNC-5	8.0	27.05	0.63

[a] Value of peak enthalpy (Jg^{-1}) on dry weight basis.
[b] Polyurethane bio-nanocomposites.

4. Conclusion

Chitin based polyurethane bio-nanocomposites were prepared by emulsion polymerization and characterized using XRD, dynamic mechanical measurement and optical microscopy. The results confirmed the formation of well dispersed ordered intercalated assemble layers of bentonite in PU matrix. Furthermore the mechanism of morphology formation is quite different from that of traditional polymer solution organic–inorganic nanocomposites. The results revealed that pure silicate disappear in PU/bentonite nanoclay hybrid and a set of new peaks appears corresponding to the basal spacing of PU/bentonite clay bio-nanocomposites. It has been observed that the values of ΔH associated with different bentonite nanoclay contents were much consistent with the crystalline pattern of the synthesized PUBNC samples. The values of tan δ versus temperature recorded using dynamic mechanical measurements were also in accord with crystalline pattern of the PUBNC samples.

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