SYNTHESIS AND CHARACTERIZATION OF POLYURETHANE NANOCOMPOSITES FOR BIOMEDICAL APPLICATIONS

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In the present research programme, the polyurethane manufactured from castor oil by reacting with diisocyanates, is being tried as an alternative to the conventional industrial petro-based polyurethane to check environmental pollution. Polyurethane / montmorillonite nanocomposites were synthesized with organically modified layered-silicates (organoclays) by in situ polymerization. Morphology was studied by Scanning Electron Microscope. Clay dispersion of polyurethane-nanocomposites was investigated by X-ray diffraction analysis and transmission electron microscopy. The morphology and properties of polyurethane-nanocomposites greatly depend on the functional groups of the organic modifiers, synthesis procedure, and molecular weight of polyol because of the chemical reactions and physical interactions involved. FTIR studies indicated the specific changes in the composites. The thermogravimetric analysis of the composite materials has been followed using a computer analysis method, LOTUS package, for assigning the degradation mechanism. The nanocomposites showed great enhancement in tensile modulus, toughness and strength, as well as stiffness, as compared to the unfilled blend. Biomedical applications of these nanocomposites are under investigation.
INTRODUCTION

Nanocomposites are combinations of two or more materials present as separate phases where one of the phases has at least one dimension in the nanometer range (10^{-9} m). They are combined to form desired structures with certain desirable properties of each component. When compared to metals, nanocomposite parts can be easily made with a relatively affordable cost. The main technological advantages of such materials are low weight, high specific strength and stiffness, environmental resistance and long shelf-life. The low concentrations of clay to the composites are sufficient to modify the desired properties, as higher levels of clay can adversely increase the system viscosity and thereby lead to poor processibility (Kumar and Krishnamoorti, 2010; Sinha Ray and Okamoto, 2003).

Today, the high price of petroleum raw materials, scarcity of petroleum products, and stringent environmental rules and regulations are pressuring synthetic polymer scientists to use natural renewable resources as the feedstocks for the development of many industrially important polymers. Fortunately, many researchers are now using renewable natural resources as their feedstocks for the development of many polymers (Nanda et al., 2007a; Nanda et al., 2007b, Nanda et al., 2007c, Sasmal et al., 2007; Nayak et al., 2008). These feedstocks, especially vegetable oils, are well accepted by synthetic polymer chemists for social, economic and environmental reasons.

The unusual composition and chemistry of castor oil make it quite valuable for many applications, including the preparation of polyurethane. Approximately 90% of fatty acids in castor oil are ricinoleic acid. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, has a hydroxyl functional group at the twelfth carbon, this is a very uncommon property for a biological fatty acid and is the main driving point for the direct use of this oil as a hydroxyl-containing trifunctional monomer (A3). This oil is an excellent renewable source for chemical industry and particularly for polymer applications. Polyols, derived from castor oil, also are new polyurethane raw materials and with isocyanates they produce polyurethane that can compete in many aspects with ones derived from the petrochemical polyols. In this research, castor oil is selected to synthesize the polyurethane nanocomposites. The curing agent used is a polymeric aromatic isocyanate based on Toluene 2, 4-diisocyanate (TDI) (Nayak, 1999; Nayak, 2000; Swain et al., 2004; Bhunia et al., 1999).

Recent advancements in polymer technology has yielded a new class of biomaterials by incorporating phyllosilicates into polymer matrices out of which montmorillonite (MMT) has been widely used in many polymers. This MMT acts as a reinforcement agent to improve the mechanical properties of the polymers, or as a flame retardant additive to improve the thermal stability and flame retardancy of the polymers (Mravcakova et al., 2006; Samakande et al., 2007; Zhu et al., 2008; Hakan et al., 2008; Huang et al., 2001; Shah et al., 2004. Zheng et al., 2004; Meng and Hu, 2004; Ma et al., 2008; Koerner et al., 2005; Drummy et al., 2005; Chen-Yang et al., 2004; Cao et al., 2005; Harikrishnan et al., 2006; You et al., 2005; Tu et al., 2007 and Modesti et al., 2008).

Pristine MMT are intrinsically hydrophilic while most polymers are hydrophobic. To disperse MMTs in the polymer matrices, it is necessary to replace the hydrophilic inorganic cations (Na^+, Ca^{2+}, or K^+) residing in the gallery space of MMTs with more organophillic cations (Yang et al., 1999; Zhong et al., 2005; Chua and Lu, 2007; Yang et al., 2007).

In the present research program, a commercially available organoclay (Cloisite 30B) using methyl tallow bis (2-hydroxyethyl) quaternary ammonium chloride (MT2ETOH) has been used as the intercalating agent, which contains two OH groups in its molecule. As it is well known, hydroxyl groups (OH) can react with the isocyanate groups (`NCO) of Toluene 2, 4 `-disocyanate (TDI), so it is usually expected that the intercalating agents with OH groups can improve the interface interaction between organoclay fillers and PU matrix.

The purpose of this study is to investigate the influence of different organoclay loadings, their dispersion in
the PU matrix on various physico-chemical and the mechanical properties of the nanocomposites.

**MATERIALS AND METHODS**

**Materials**
Pure castor oil was purchased from local market. TDI was purchased from Bayer Group, Mondur MRS-4 (NCO index: 129; functionality: 2.4; viscosity at 25°C: 40 MPa). The organoclay, Cloisite 30 B was procured from Southern Clay Products, USA.

**Preparation of PU nanocomposites (PUNCs)**
TDI and castor oil were dehydrated under vacuum overnight at room temperature and 60°C, respectively. The clay was dehydrated in an oven at 100°C overnight before use. For PU nanocomposites, clay was first mixed with one castor oil by a high shear mixer for 3 min, and then mixed polyol and stirred for 6 hr under N₂ atmosphere. Polymerization was carried out at ambient condition. The prepared hybrid was then post-cured in an oven at 100°C for 4hr. Excess TDI (ca. 5 mol%; NCO/OH) was used to assure the complete reaction of polyol.

**Characterization**

**FT-IR Analysis**
A Vector-22 FT-IR spectrometer (Bruller Optics, Billerica, MA) with a resolution of 1cm⁻¹ from 4000 to 400 cm⁻¹ using KBr pellets was used to verify the completion of the resin curing reaction and the presence of free isocyanate groups (NCO) in cured nanocomposites.

**Thermogravimetric analysis**
The thermal degradation pattern of the pristine PU as well as the PU-C30B nanocomposites were determined by Thermogravimetric Analysis (TGA, Universal V4.5A, TA Instruments) under a nitrogen atmosphere. The samples were heated from room temperature to 600 °C at a rate of 10 °C/min.

The weight change of each sample was recorded as a function of temperature and the results were compared to pure clay. Given that the inorganic clay has much greater decomposition temperature than the organic polymer, the content of the clay inside the samples was estimated from the comparison of curves.

**XRD analysis**
The clay dispersion was determined by XRD on a Scintag XDS-2000 X-ray diffractometer equipped with an intrinsic germanium detector system using Cu-Kα radiation (l=1.5418 Å).

**SEM studies**
The cellular morphologies of the foamed samples in the rising direction were investigated by a Philips XL30 scanning electron microscope (SEM). Sample surface was sputter-coated with gold before observation.

**TEM studies**
Transmission electron microscopy (TEM) was also adopted to characterize the structure of the nanocomposites. The nanocomposites were sectioned into ultra-thin slices (<200 nm) at -70°C in liquid nitrogen atmosphere using a microtome, Leica EMFCS Ultracut (Leica Microsystems, Austria) and then mounted on 200 mesh copper grids. The sections were pre-conditioned for 24 hrs prior to TEM testing. TEM was performed on a JEOL (JEM-2100, JEOL Ltd., Tokyo, Japan) using an accelerating voltage of 200 kV with a resolution of 1.5 Å.

**Mechanical properties**
Tensile property was measured according to ASTM D 638 by a universal testing machine (LR 50K, Lloyd Instrument, UK) with a gauge length of 20 mm and a crosshead speed of 5 mm/min.

**RESULTS AND DISCUSSION**
FTIR spectra of PUs (and polyol-based polyurethanes) are well known to be sensitive to hard domain
organization and the urea and urethane hydrogen bonding (McCarthy et al., 1997; Wang and Cooper, 1983; Sung et al., 1980; Meuse et al., 1992; Coleman et al., 1997). Consequently, to understand the possible reactions that may occur among the reactants (TDI, PU and C30B), the FTIR spectra of C30B, TDI cured PU and TDI cured PU/C30B nanocomposites containing 2.5 wt% modified clay (SM-27) are recorded in Fig. 1. As seen in the Fig. the characteristic absorptions peaks of the PU are observed at 3306 cm\(^{-1}\) (N–H stretching frequency), 2925–2852 cm\(^{-1}\) (–CH\(_2\)– and –CH\(_3\) stretching frequencies), 1731 cm\(^{-1}\) (carbonyl urethane stretching), 1526 cm\(^{-1}\) (CHN vibration), 1223 cm\(^{-1}\) (coupled C–N and C–O stretching), and 1079 cm\(^{-1}\) (C–O stretching). Comparison of neat PU with the nanocomposite, i.e. SM-27 indicates that all the characteristic absorptions of PU remain unchanged in the PU/C30B nanocomposite.

But the urethane characteristic peaks at 1732 and 1526 cm\(^{-1}\) are enhanced due to the formation of more number of urethane linkages during the course of the curing reaction. Absence of peak at 2270 cm\(^{-1}\) (–NCO group) confirms that all the TDI have been used in the curing reaction. Besides, the characteristic absorption peaks of benzene ring of TDI are observed in the region of 900–675 cm\(^{-1}\) (C–H deformation). In case of the

![Figure 1: FT-IR spectra of Cloisite 30B; SM-22 (PU without clay) and SM-27 (PU with 2.5% clay)](image1)

![Figure 2: TGA Thermograms of PU/C30B nanocomposites; SM-22 PU/C30B 0%, SM-27 PU/C30B 5%](image2)
nanocomposite, it is evident that the characteristic absorption peaks at 522 cm\(^{-1}\) (Al–O–Si deformation) and 1047 cm\(^{-1}\) (Si–O in plane stretching) are observed in the nanocomposites (SM-27). Furthermore, the extra absorptions at 3700–3400 cm\(^{-1}\) (N–H stretching) and 1240 cm\(^{-1}\) (amide vibration) indicate the formation amide structure between C30B and the PU matrix. The FTIR spectra also reveals that the nanocomposite with Cloisite 30B has the characteristic peaks at 1731 cm\(^{-1}\) (carbonyl urethane stretching), 1526 cm\(^{-1}\) (C–NH– vibration), 1223 cm\(^{-1}\) (coupled C–N and C–O stretching), 1079 cm\(^{-1}\) (C–O stretching), 522 cm\(^{-1}\) (Al–O–Si deformation), and 1047 cm\(^{-1}\) (Si–O in plane stretching), indicating that the polymer chains have intercalated into the gallery of C30B (Zhang et al., 2003). Some polymer chain-ends with –NCO groups come closer to the vicinity of the clay galleries during nanocomposites preparation and react with –CH\(_2\)CH\(_2\)OH group of the quaternary ammonium ions to produce urethane linkage, –CO–NH–, leading to a fine dispersion of the clay particles, as seen in the TEM image.

**Thermogravimetric analysis**

The TGA thermogram provides a comparative illustration of the thermal properties of the neat PU and PU/C30B nanocomposite as in Fig. 2. A two-step degradation pattern with an enhanced thermal stability of the nanocomposite, i.e. SM-27 was observed when compared neat PU. For SM-27, the onset temperature of degradation (\(T_{\text{onset}}\), the onset point as 5 wt.% weight loss) is significantly enhanced to 260\(^\circ\)C when compared to 210\(^\circ\)C for SM-22 (Yano et al., 1993; Ward et al., 1991). This can be explained by the strong interaction between the polymer chains and the organoclay layers in the nanocomposite, hence preventing the decomposition. This increase in the thermal stability can be attributed to the high thermal stability of clay and to the interactions between the clay particles and the polymer matrix.

The SM-27 was almost stable up to 300\(^\circ\)C with a weight loss of ~7\% when compared to SM-22 where ~20\% weight loss was observed (Table 1). The clay layers acted as a superior insulator and as a mass-transport barrier to the volatile products generated during decomposition for increasing the thermal stability; also delayed the thermal degradation and enhanced the carbonaceous char formation (Song and Hu, 2003; Gilman et al., 2000; Gilman et al., 1998).

The polymers decomposed in two steps due to the soft and hard segments in the polyurethane, and weight loss due to polymer decomposition was observed at about 225–285 \(^\circ\)C. During the reaction, if any allophanate and biuret linkages are formed, they reopen quite readily on heating at relatively high temperatures as they are most thermolabile. However, the urethane linkages decompose only at quite high temperatures, whereas the aromatic moiety of the disocyanates decomposes at the highest temperature (Szycher, 1999) in this case. This increase in the number of urethane linkages is also reflected in the thermal stability of the polymer.
X-ray diffraction analysis

The results of X-ray diffraction analysis are presented in Fig. 3. Pure C30B displays a peak at $2\theta = 4.78^\circ$, which corresponds to $d_{001}$ basal spacing of 18.48 Å. In the case of 1 wt% PU/C30B composites, this peak shifts to $2\theta = 3.21^\circ$ which indicates a little expansion of the basal spacing due to low penetration of the PU chains within the gallery spaces. But with a clay loading of 2.5 wt%, not only the peak position was shifted to lower angles, but also a decrease in peak intensity was observed. This suggests that a partial exfoliation of C30B in PU matrix has taken place.

When the mixture was proceeded with a higher clay loading, i.e. 5 wt%, no significant change in the diffraction peak on was observed, which suggested that, before complete exfoliation could occur, the hydroxyl groups on the edge and surfaces of MMT platelets reacted with the isocyanate, thereby cross-linking the C30B aggregates in the PU matrix.

SEM Studies

The SEM images of the abraded surfaces of pristine PU and the nanocomposites of 2.5 wt% C30B are shown in Fig. 4. Progressive magnifications reveal that the abraded surface of the nanocomposite appears to be much smoother than that of the pristine PU. When compared to the neat PU, the surface of the nanocomposite exhibited a finer three dimensional texture. The cracks bifurcate, creating multiple fracture surfaces and causing greater energy dissipation. It indicates that the addition of both TPU and organoclay can increase the toughness of the nanocomposites markedly.

TEM Studies

Fig. 5 shows TEM micrographs of PU/C30B nanocomposites confirming that the 2.5% C30B nanoclay achieved exfoliation state in the polymer matrix. TEM images revealed that the layer of C30B disperses well in the PU-matrix suggesting that it is compatible with PU owing to the presence of hydroxyl groups. The black dots in the background of the micrographs are a typical nanostructure of the hard segment of the PU network (Dodiuk et al., 2006).

Higher magnification reveals stacked platelets with substantial layer separation indicating the existence of intercalated structure of C30B in the PU matrices in all the samples except SM-27 where partial

![Figure 4: SEM images of PU/C30B nanocomposites. (Left: PU/C30B 0%, Right: PU/C30B 2.5%)](image)

![Figure 5: TEM Micrograph of PUNCs with varying % of C30B; [a. 0 , b. 1 %, c. 2.5 %, d. 5%]](image)
exfoliation is seen. As seen from the TEM images, the overall distribution of MMT is random in all the samples but the size and distribution uniformity of the organoclay agglomerates varies with varying C30B content although some aggregation appears at 5 wt % of MMT (Fig. 5d).

The mechanism for the formation of the organoclay agglomerates with exfoliated structure can be explained as follows. According to previous studies (Cao et al., 2005; Tien and Wei, 2001) the hydroxyl groups on the edge and surfaces of MMT platelets are reactive with isocyanate. Therefore, it is possible that the C30B aggregates were cross-linked by polyurethane molecules before they were completely delaminated in the PU matrix by mechanical stirring.

**Mechanical properties**

The mechanical properties of the pristine PU and PU/C30B nanocomposites (PUNCs) are given in Table 3. The tensile strength of all the nanocomposites is higher than that of the pristine PU, indicating that the layered silicate has an enhanced function on the polymeric material. The layered silicate acts as high aspect ratio reinforcement, similar to fibres within a fibre-reinforced plastic, and therefore enhances the tensile strength of the PU (Song and Lu, 2003).

However, the tensile strength of SM-30 nanocomposites with 5 wt. % MMT loading has slightly decreased value, because of the silicate clays with huge surface area and high activity begin to aggregate along with the abundant MMT and result in a pre-dominant filler–filler interaction over the filler–polymer interaction (Cai et al., 2007; Tien and Wei, 2001). Also, Maiti et al., in 2006, reported the same trend of an increase in the tensile strength of ethylene–octene copolymer nanocomposites with clay loading where agglomerated particles acted as defects. The elongation at break of the nanocomposites is less than that of the pristine PU and decreases as clay content rises, indicating that the elasticity of PU/MMT nanocomposites decrease when the clay is added, especially the aggregation of MMT with high clay loading in PU matrix is very severe.

The higher improvement of tensile modulus in the PUNCs can be attributed to the better dispersion and intercalation/exfoliation of the nanoparticles, as shown in Fig. 3 and 5.

**REFERENCES**


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