Synthesis and mechanical properties of polyurethane/clay nanocomposites

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PU/OMMT (Polyurethane/Organically Modified Montmorillonite) nanocomposites were prepared by in situ polymerization Technique. The structure of prepared nanocomposites and dispersion state of filler was studied and characterized by XRD and TEM. An intercalation type of morphology was observed by TEM. The mechanical properties of these nanocomposites at different loading levels of OMMT were also investigated using the Universal testing machine. The tensile strength, elongation at break and hardness shore were enhanced with the increase in the loading level of OMMT as compared to pure polyurethane. The obtained properties may be used in MEMS applications like pressure diaphragm, where the mechanical properties on nanoscale are crucial.

1. Introduction

Polymer nanocomposites are developing a great deal of interest due to their unusual properties and some new novel properties developed in to them, which are not present in the neat polymers or the conventional composites. These unusual and new properties are derived by the addition of some nanoscale fillers into the matrix. The nanoscale filler means that the filler has at least one dimension in the nanometer range (<100 nm). Nanocomposite technology has been described as the next gtreat new frontier of materials scince because it involves the use of a small quantity of nano filler (< 5wt%) and enhances the mechanical, thermal, optical, electrical and barrier performance properties significantly [1]. various polymer have been studied for a long time to prepare polymer nanocomposites by using diffrent types of nanofillers. The inorganic layered nonofillers like graphite, clay minerals, transition metal dichalcogenides, metal phosphates, and layered doubly hydroxides are widely used in preparation of nanocomposites [2]. Among these the clay nanoplatelets belonging to semectic family are attracting attention due to their high aspect ratio (100-1500), high surface area to volume ratio (750m^2/gm) , abundantly present in nature, high cation exchange capacity and low cost [3]. Moreover in the structure of clay the atoms in the layers are held together by chemical bonds while the successive layers are held together by weak Vander wall forces. These weak physical forces can easily be broken when the large organic polymer molecules enter into the gallery. So the layered structure of clay provides a great potential for the large organic

molecules to be intercalated/exfoliated into them. The clays are consist of units called sheets or platelets. One platelet is made up of two silica tetrahedral layers and one central alumina or magnesia octahedral layers. The octahedral layer is sandwiched in between the two silicon tetrahedral layers. The inorganic cations like Na$^+$, K$^+$, Li$^+$ are naturally present in gallery which can be exchanged with some organic ammonium cations e.g. alkylammonium cations in order to modify the clay platelets so that they become hydrophobic to be compatible with polymers . Naturally the clay platelets are not present in nanometer range but they can be easily delaminated or exfoliated into nanometer platelets with a thickness of about one nm [4].

The clay nanoplatelets are generally supposed to enhance the mechanical performance of various polymers which find their applications in transport industries (automotive and aerospace). The research in are of polymer nanocomposites got a boost up after the pioneer work from Toyota motors in 1987 [5]. Toyota prepared Nylon-6/Clay (OMMT) nanocomposites and first commercial product of clay based polymer nanocomposites is the timing-belt cover in 1990. These Nylon-6/clay based nanocomposites prepared by Toyota had significant improvement in strength and modulus namely 40% in tensile strength, 60% in flexural strength, 68% in tensile modulus, 126% in flexural modulus, and heat distortion temperature was increased by 80°C as compare to pure Nylon [6]. There are numerous studies on dispersion and mechanical properties of polyurethane nanocomposites with clay particles. The present work addresses the enhancement in mechanical properties of

polyurethane with nanoclay. The polyurethane nanocomposites with OMMT have been prepared by using in situ polymerization technique and mechanical properties of resulting nanocomposites was studied. It is known that in-situ polymerization is an efficient method to improve the dispersion of OMMT in the polymer matrix [7]. Here the monomers are polymerized in the presence of filler and consequently the in-situ technique would confer strong interaction between the reinforcing filler and polymeric phase [8]. The resulting nanocomposites were characterized by XRD and TEM and their mechanical properties were studied by universal testing machine.

2. Experimental section

2.1 Materials

Cloisite 30B is supplied by Connell Bros. Company (India) Pvt. Ltd. The monomers Toluene, 2,4-Diisocyanate (TDI) with molecular weight 174.16 and Polypropylene glycol (PPG) with molecular weight 2000 were supplied by MP Biomedicals Fine Chemicals Division, India. The monomers were of analytical grade purity and were used as received. The chain extender 1,4-Butanediol (BDO) was supplied by same company.

2.2 Preparation of polyurethane OMMT nanocomposites by In-Situ polymerization

The PU/OMMT nanocomposites were prepared by using TDI:PPG:BDO in the mole ratio of 3:1:2. PPG and nanoclay were mixed and stirred for 12 h at 50°C to obtain PPG-OMMT suspension. This suspension was subjected to sonication for one hour to avoid the agglomeration of nanoclay particles. The viscosity of PPG maintains a uniform distribution of particles in the solution. TDI was poured in to this suspension with continuous stirring. During the mixing of TDI, the temperature was maintained at 70°C as it was an exothermic reaction. After mixing TDI, the resultant solution was heated at 85°C for 4 h with stirring. Subsequently, after cooling the reaction mixture to 40°C, BDO was added with vigorous stirring for 1 min. immediately after this, a small portion of solution was mixed with DMF for spin coating and TEM characterization. The resultant nanocomposite solution was poured into a defined shape mold for final curing. The nanocomposite material in the mold was heated at 160°C for 16 h to dry it completely.

2.3 Characterization

The X-ray diffraction (XRD) patterns of processed materials were recorded on PANalytical's XPERT-PRO Diffractometer system with Cu K-Alpha1 [Å]: 1.54060 and 2θ (2°- 30°). The dispersion state of prepared nanocomposites samples were studied by Transmission Electron Microscope (TEM). The samples were prepared by dispersing the film on glass/silicon substrates by spin coater. The mechanical properties of prepared nanocomposites samples were studied by universal testing machine.

3. Results and Discussion

3.1 XRD and TEM Analysis

The results of X ray diffraction are shown in Fig. 1 in the form of diffraction peaks for the Closite 30B and nanocomposite samples containing 0.5 and 1.5 wt% loading levels of clay the Closite 30B displayed the major diffraction peaks at 4.81^{o} corresponding to d-spacing (d_{001}) of 1.8329 nm. The nanocomposite containing 0.5 wt% of clay nanoparticles showed the shifting of diffraction peak towards the lower angle (2.205^{o}) indicating the d-spacing of 4.0039 nm.

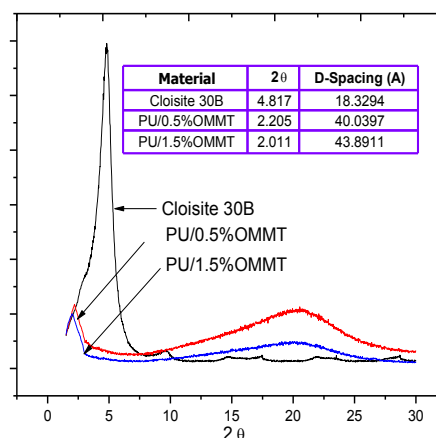| Material	2θ	D-Spacing (A)
Cloisite 30B	4.817	18.3294
PU/0.5%OMMT	2.205	40.0397
PU/1.5%OMMT	2.011	43.8911

Fig.1. X-ray Diffraction of pure Cloisite 30B, and prepared samples of polyurethane/clay nanocomposites.

Similarly the nanocomposite containing 1.5wt% of OMMT displayed the major defection peak at lower angle of 2.011^{o} indicating the d spacing of 4.389nm. so, this can be concluded that increase in d-spacing means that the polymer chains have diffused inside the gallery and intercalated type of nanocomposits are formed. The in-situ polymerization technique confers the strong interaction between clay platelets and the monomers, as polymerization takes place inside the gallery so expands it exponentially.
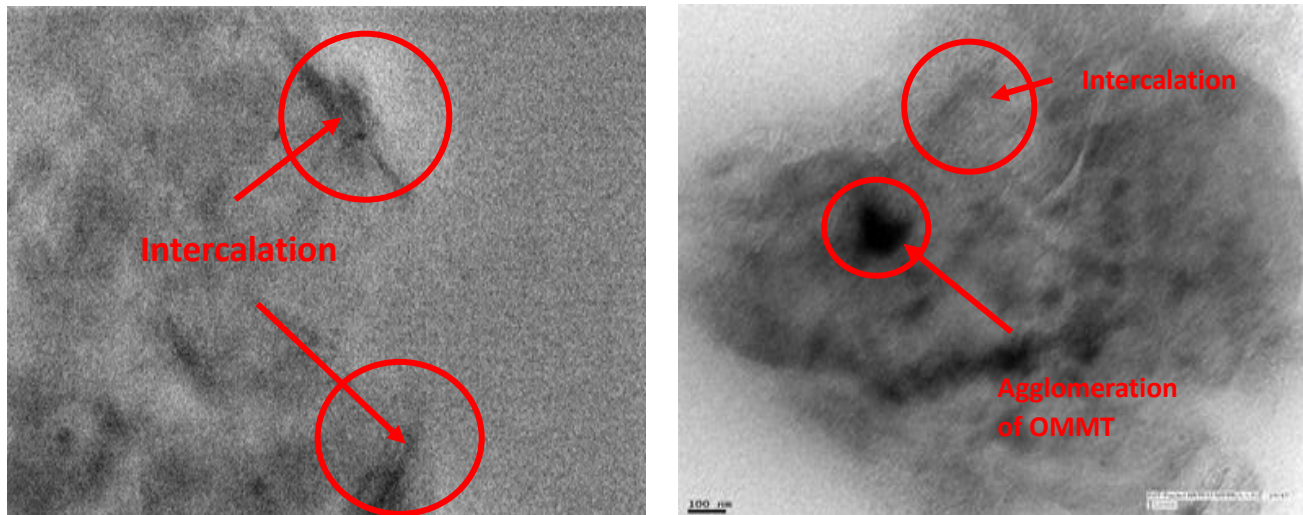
Fig. 2. TEM images of prepared samples of polyurethane/clay nanocomposites.

The morphology of prepared nanocomposites was further confirmed by TEM. The TEM images shown in Fig. 2 are clearly indicating the presence of clay platelets in the form of stacks or tactoids marked by arrows. Simultaneously the small quantity of clay platelets were agglomerated as the loading level was increased also shown in Fig. 2.

3.2 Mechanical properties

The mechanical properties of prepared nanocomposits were studied with a universal testing machine with the sample specifications shown in Fig. 3.
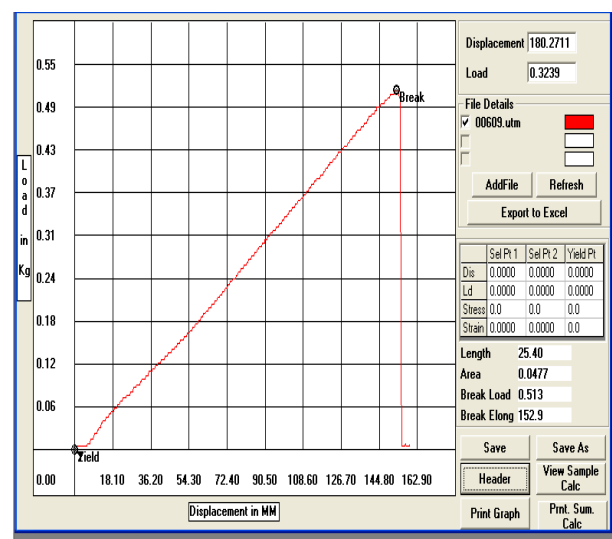

Fig. 3. Characterization of nanocomposite with universal testing machine.

The mechanical properties of pristine PU and PU/OMMT nanocomposite are shown in Figure 4. The tensile strength of composite samples is increased with the increase in % loading levels as compare to pristine PU because of good interfacial interaction between the OMMT layers and polymer matrix [9-11]. Due to high aspect ratio of layered silicate fillers similar to fibers within a fiber reinforced plastic, the tensile strength of PU enhanced. The elongation % is decreased with the different loading levels, however this downfall is very less as compare to pure PU and was maintained at a level close to that of pure PU [12].

Shore hardness is a measure of the resistance of a material to the penetration of a needle under a define spring force. The letter A is used for flexible type. The hardness shore A is also increased with the increase in % loading levels as compare to pristine PU [13]. At 0.5 wt% loading level of OMMT, the harness shore A was maintained at a level closed to that of pure PU. At 1.0 and 1.5 wt % of OMM, a slight increase in hardness has been observed.
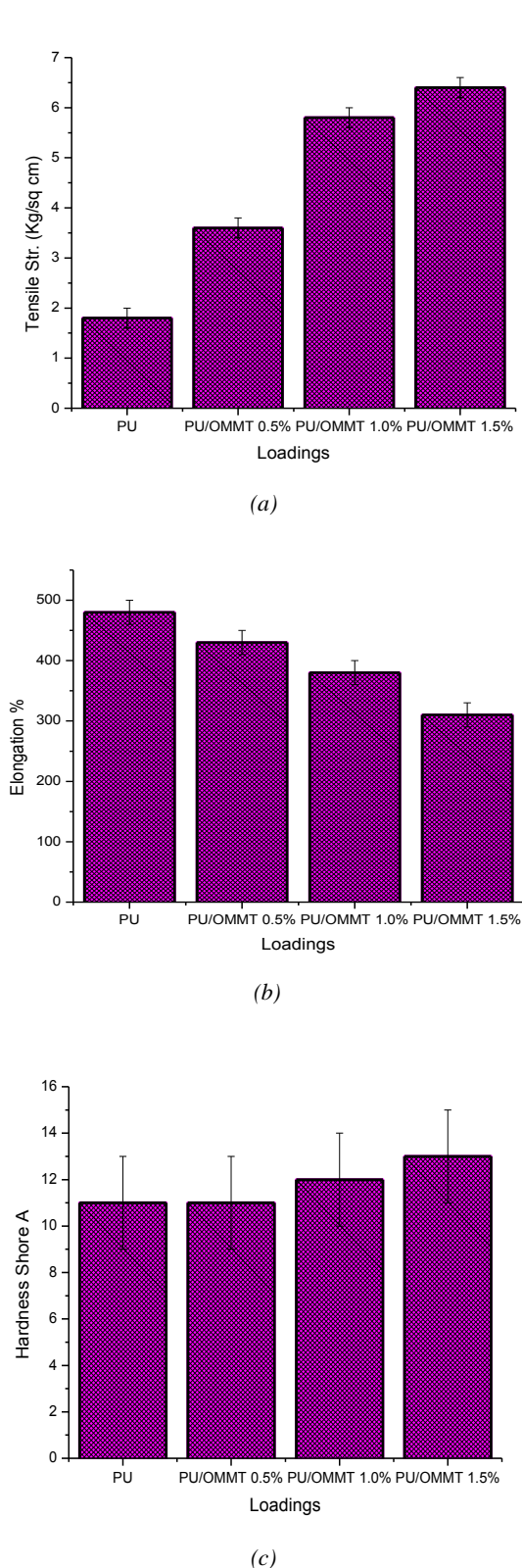
(a)

(b)

(c)

Fig. 4. Mechanical properties of PU/OMMT nanocomposites (a) tensile strength (b) elongation % (c) hardness shore A.
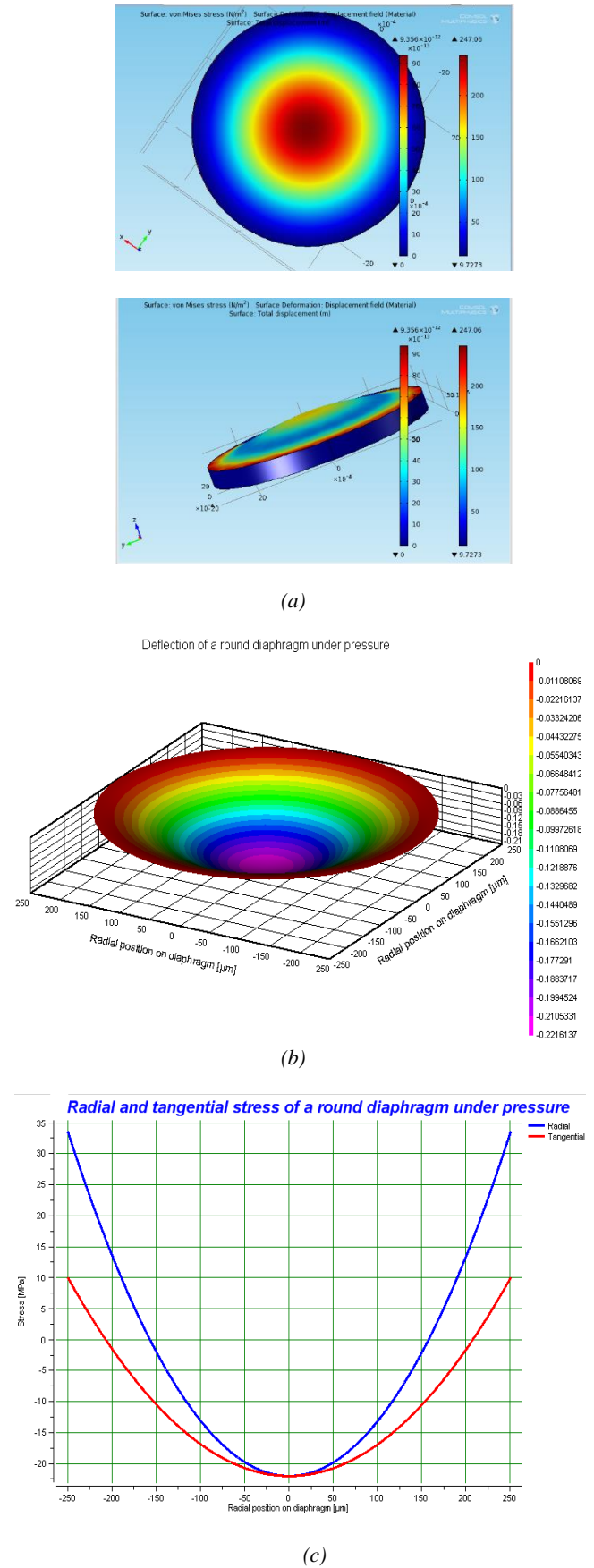

(a)

(b)

(c)

Fig. 5. PU/OMMT as pressure mems (a) comsol simulation snapshots (b) deflection of round diaphragm (c) radial and tangential characteristics.

Importing the obtained mechanical properties, we have simulated PU/OMMT for pressure MEMS application as shown in Fig. 5(a) and 5(b). We have prepared diaphragm on simulation platform [14]. The maximum possible deflection of this diaphragm is 30% of its thickness. The deflection y at radial distance r of a round diaphragm rigidly clamped, under a uniform pressure P, is given by:

$$y = \frac{3(1-v^2)P}{16Eh^3}(a^2 - r^2)^2 \qquad (1)$$

where h is thickness of diaphragm, E is the Yong's modules, v is the Poisson's ratio, a is the radius of diaphragm. The maximum deflection in Fig. 5(b), will occurs at the center of diaphragm where $r = 0$. The Poisson's ratio of nanocomposite is ≈ 0.5, the maximum deflection is given by:

$$y_o = \frac{0.14063Pa^4}{Eh^3} \qquad (2)$$

Radial and tangential characteristics with respect to radial position of diaphragm are shown in Fig. 5(c).

4. Conclusion

The PU/OMMT nanocomposite were prepared by using in situ polymerization. the structure and morphology of prepared nanocomposites were studied by XRD and TEM. Both techniques revealed the formation of an intercalated type of nanocomposites and some agglomerated clay platelets were also observed by TEM. The tensile strength of nanocomposite was increased as compare to pristine PU on increasing the loading level of clay. However the elongation % was decrease as compare to pure PU. The hardness shore A of these nanocomposites was also increased on increasing the loading level of clay but it was a fractional increase as compare to tensile strength. A pressure diaphragm is also simulated by using these properties as simulation parameters. In this MEMS the sensitivity of diaphragms is improved.

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