

Mechanical and Crystalline Behavior of Polymeric Nanocomposites in Presence of Natural Clay

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ABSTRACT

Fabrication of nanocomposites from immiscible polymer blend system has been represented in this work. A new type of natural clay named Halloysite Nanotubes (HNTs) are modified by Polyethyleneimine (PEI) and these PEI grafted HNTs are incorporated into the immiscible blend system during melt mixing process to prepare halloysite based nanocomposites. Fourier Transform Infrared Spectroscopy (FTIR) study confirms the formation of PEI grafted HNTs. The nanocomposites are characterized by SEM for morphological study and, the dispersion manners of nanoclays by Transmission Electron Microscopy (TEM). Storage modulus is studied by Dynamic Mechanical Thermal Analysis (DMTA) instrument. The tensile measurement explored better tensile property of nanocomposites as compared to the virgin blend. XRD is performed to determine the crystalline behavior of the nanocomposites as well as for blend. The above investigations reveal that the HNTs act as reinforcing as well as nucleating agent in the blend system.

Keywords: Nanocomposite; Mechanical; Crystallinity; Halloysite; Polyethyleneimine

1. Introduction

Naturally occurring tubular halloysite clay has attracted considerable interest of the researches due to its multi-purpose features. This nanomaterial may be utilized as nanofiller for polymers. Reinforcement of thermoplastic matrices with HNTs has been studied extensively by different research groups. HNTs are used in polymeric nanocomposites to develop the mechanical strength, thermal stability, crystalline behavior etc of the polymers. Generally, layered halloysite are obtained in two polymorphs: the hydrated form with 10 Å basal distances and the anhydrous one with 7 Å basal distances. Halloysite comprised of Al and Si at 1:1 ratio with molecular formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, where “n” equals to 2 and 0, corresponding hydrated and dehydrated HNTs [1,2]. Kaolin has almost similar chemical composition to HNTs but presence of interlayer water in HNTs makes it distinguishable from kaolin. Weakly bonded intercalated water can be readily removed irreversibly. Halloysite has high aspect ratio (L/D ratio). Its length and diameter varies from 500 - 1000 nm and 15 - 100 nm respectively. Artificially, HNTs have not been synthesized yet. At the internal surface it contains gibbsite octahedral Al-OH groups, and the outer surface contains SiO_4 tetrahedra. This difference results in acid-base properties for both

surfaces. At pH range 2 - 8, outer surface gets negatively charged and inner lumen gets positively charged [3,4]. Grafting of HNTs can be done via covalent or non covalent approaches [5]. Polypropylene (PP) is widely used polymer worldwide due to its easy processibility and relatively low cost. It has good mechanical and physical properties, but its inferior properties (e.g. impact strength, low UV resistance, brittle at lower temperatures etc.) restrict its engineering applications. Many researchers have paid their attention on properties of PP/HNT composite [6-9]. Polyoxymethylene (POM), is also called acetal or polyacetal or polyformaldehyde etc. It consists of C-O backbone in main polymer chain [10]. This engineering thermoplastic have good toughness, excellent fatigue and creep resistance, high resistance to oxidative degradation and susceptible to UV degradation [11]. Polyethyleneimine (PEI), is a cationic hydrophilic polymer with amine groups [12]. Grafting of PEI had been done in case of carbon nanotubes (CNTs) [13]. It can also be used as a surface modifier for halloysites.

In the present work we have chosen PP and POM because both the polymers have comparable melting point leading to almost similar processing temperature [7,10]. In order to have the reasonable properties we have melt blended those polymers by melt mixing process in internal melt mixer. To gain better properties, raw HNTs have been incorporated and nanocomposite prepared. Misci-

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bility of this blend is not favorable so to overcome it, surface treatment of HNTs were done with PEI, and PEI grafted HNTs (gHNTs) are then melt mixed with the blend system and hence modified nanocomposites fabricated. We are mainly focusing on the mechanical property and crystallinity of nanocomposites after addition of raw HNTs/gHNTs.

2. Experimental

2.1. Materials

The PP of grade H030SG purchased from Reliance industries limited (India) and POM of the grade H2320 004 was received from BASF (Germany). HNTs were obtained from Sigma-Aldrich (Germany) as nanopowder and 50 wt% aqueous solution of PEI ($M_n = 70,000$) from Aldrich, USA.

2.2. Surface Treatment of HNTs

At first 500 mg of HNTs were taken in 200 ml distilled water and the suspension was dispersed in an ultrasonicator for 20 min at room temperature. The solution pH was then adjusted to 8 - 9 by adding NaOH solution. 2 ml PEI solution was added to it and the whole solution was heated at 60°C under constant stirring for 24 h. Then the reaction mixture was centrifuged for 20 minutes at an rpm of 4000. After centrifugation, the obtained particulates were washed with distilled water. The obtained product were kept overnight for drying in vacuum at 80°C and named as PEI grafted HNTs (gHNTs). **Scheme 1** shows the schematic representation of the reaction.

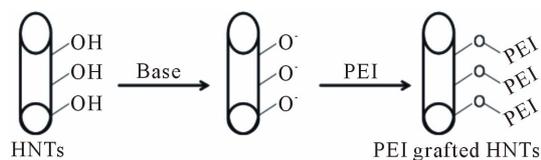
2.3. Preparation of Blend and Nanocomposites

At first one batch of PP/POM at 80/20 w/w pure blend was prepared (coded as S) by melt mixing process using internal melt mixer at 190°C and 40 rpm. Then unmodified nanocomposites (S-HNT) and modified nanocomposite (S-gHNT) were prepared via same way by incorporating raw HNTs and gHNTs. In the entire cases 80/20 w/w PP/POM ratio was maintained and HNTs/gHNTs were taken only 1 wt% in each case for respective nanocomposite fabrication.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy (FTIR) Study

FTIR of the HNTs/gHNTs and nanocomposite were performed using a Tensor 27 (Bruker, Germany) FTIR equipment. FTIR graphs are shown in **Figure 1**, of which (a) for raw HNTs (b) for gHNTs and (c) for S-HNT nanocomposite. In this figure peaks come at 3692 and 3620 cm^{-1} in all of the three cases (a) - (c) due to OH



Scheme 1. Schematic representation of the surface treatment of HNTs.

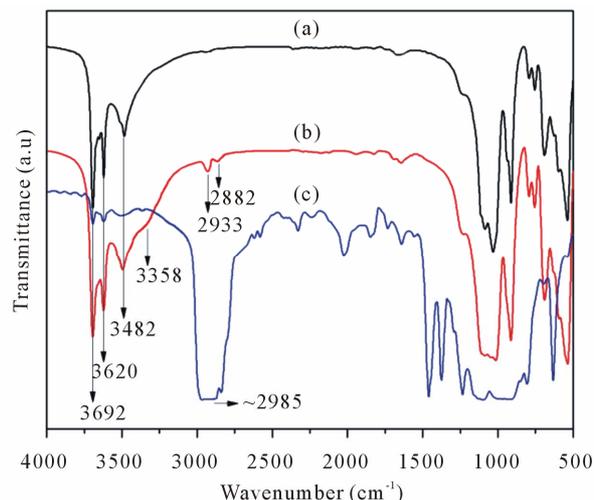


Figure 1. FTIR graphs of (a) raw HNTs; (b) PEI grafted HNTs (gHNTs); and (c) HNTs filled nanocomposite (S-HNT).

groups of HNTs, but peak intensities were not same for all three, which indicates OH groups were engaged in interaction between the modifier as well as blend matrices to different extent. Interlayer H_2O peak of HNTs was observed at around 3482 cm^{-1} . Beside these, gHNTs acquired some additional peaks e.g. 3358 cm^{-1} which belongs to N-H stretching; 2933 and 2882 cm^{-1} attributed to C-H asymmetric and symmetric stretching respectively. Peaks due to N-H and C-H bonds were present in case of PEI grafted HNTs but it was totally absent in case of raw HNTs. This IR result gives such a hint that PEI attached with HNTs. It was believed that negatively charged OH groups of HNTs had a noncovalent physical interaction with the H of NH_2 group of PEI. But it was very difficult to differentiate that peak because the peak raised due to the interlayer water molecules of HNTs (3482 cm^{-1}) might suppress the peak accession due to the interaction between HNTs and PEI. So from the above results it can be said that PEI was grafted on the surface of the HNTs [14]. Peak at around 2985 cm^{-1} at (c) for S-HNT nanocomposite was due to C-H stretching vibration. Due to similarity with S-HNT curve, S-gHNT nanocomposite curve was not entrained in this figure.

3.2. XRD Analysis

XRD of the pure blend and nanocomposites were done

with X-ray diffractometer (Rigaku XRD, Ultima-III, Japan). It was operated at 40 kV and 100 mA with nickel-filtered $\text{CuK}\alpha$ line ($\lambda = 0.15404$ nm). **Figure 2** shows the XRD curves. It can be said that after addition of raw HNTs % of crystallinity (χ_c) increases but further increase on addition of gHNTs. Prashantha *et al.* [7] reported on increase in crystallinity with incorporation of modified HNTs. As per the previous researchers, addition of very low percentage (1 wt%) of HNTs do not make any significant changes on peak positions [8]. The highest intense peak (near at 23°) and peak at its extreme right (near at 34°) appeared due to presence of POM [15]; and other peaks were due to PP [8]. It was clear that HNTs behaved as nucleating agent and enhanced the crystallinity of the nanocomposites. The percent of crystallinity was calculated by using the Scherer's equation.

Percent of crystallinity,

$$\chi_c = (I_c / I_a + I_c) \times 100 \quad (1)$$

where I_a and I_c are the integrated intensity of the amorphous and crystalline region respectively.

3.3. Scanning Electron Microscopy (SEM) Analysis

The surface morphology of our prepared samples was analyzed by JEOL SEM (JSM-5900 LV) with an accelerating voltage of 20 kV. For conductivity, the fractured surfaces of the samples were coated with thin layer of gold.

SEM images of pure blend, composites and raw HNTs are shown in **Figures 3(a)-(e)**. The micrograph states about the immiscibility of those two polymers. Certain changes were found in those micrographs, **Figure 3(a)** represents the pure blend where POM got dispersed in PP matrix. Similar trend was also found in case of S-HNT and S-gHNT nanocomposite (**Figures 3(c)** and **(d)**), as the corresponding polymer ratio was constant.

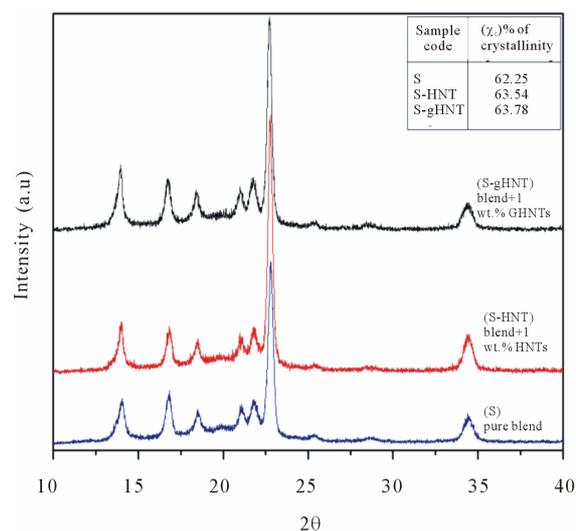


Figure 2. XRD curves of pure blend, HNTs filled nanocomposite and gHNTs filled nanocomposite (percent of crystallinity shown inset).

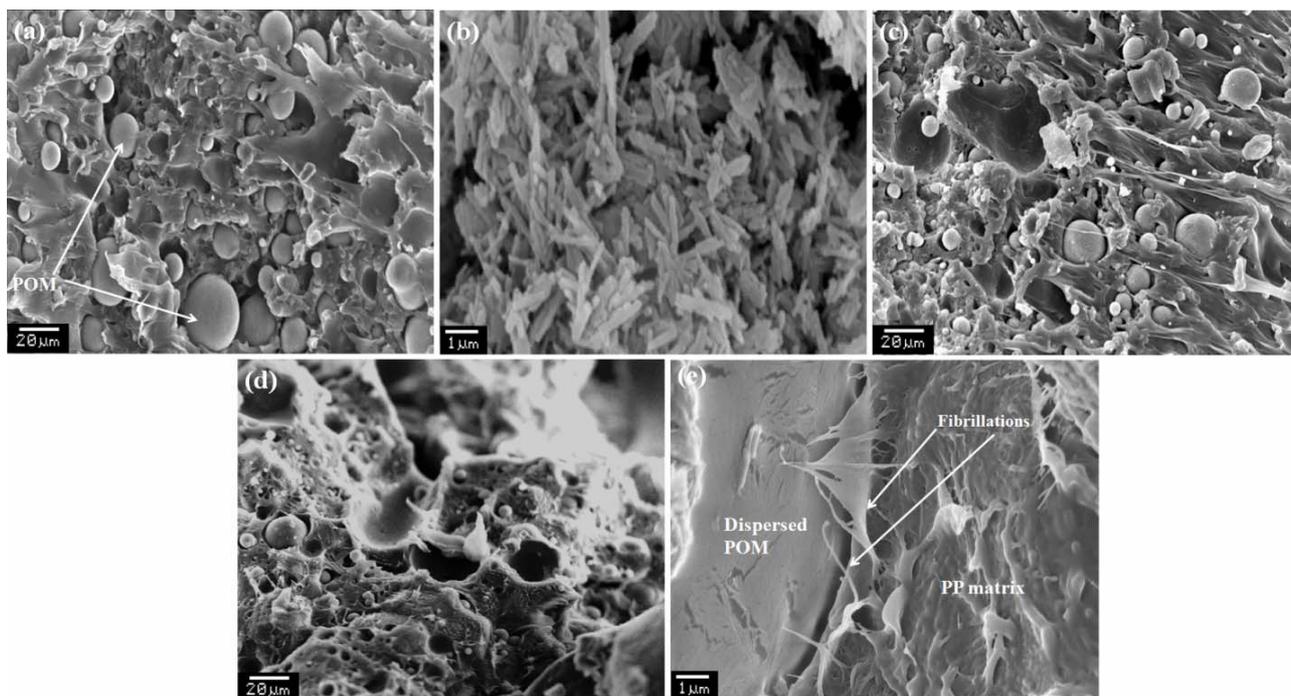


Figure 3. SEM micrograph of (a) Pure polymer blend of PP/POM 80/20 w/w (b) Raw HNTs (c) 1 wt% raw HNTs loaded nanocomposite (d) 1 wt% gHNTs loaded nanocomposite and (e) High magnified micrograph of 1 wt% gHNTs loaded nanocomposite.

After addition of raw HNTs few fibrillation was found in the micrograph 3c. G. V. Vinogradov *et al.* showed the fibrillation of POM [16]. Also after incorporation of gHNTs, droplet sizes of POM reduced in S-gHNT nanocomposite which imply about the compatibility of gHNTs. Micrograph 3e of S-gHNT was taken at high magnification to have better idea about the morphology. This micrograph stated the grafted HNTs were remaining in between two polymer phases.

3.4. Transmission Electron Microscopy (TEM) Analysis

TEM analyses of our samples were carried out by using JEOL TEM (JEM-2100) at 200 kV. Nanocomposites were cryogenically ultramicrotomed and taking the thickness of about 300 nm, the powdered samples were dispersed ultrasonically before the TEM analysis. In **Figure 4**, TEM micrographs along with one EDAX are shown. **Figure 4(a)** was for raw HNTs, **Figure 4(b)** for PEI grafted HNTs. From **Figure 4(b)** micrograph it can be seen that PEI was coated on the surface of HNTs. **Figure 4(c)** was the TEM-EDAX for PEI grafted HNTs. EDAX values gestured that nitrogen assimilation occurred during the surface treatment of HNTs by PEI.

Around more than 4% nitrogen inclusion occurred. This value was also in support of the FTIR results, *i.e.* grafting by PEI modifier on HNTs surface. **Figures 4(d)** and **(e)** represents the S-HNT and S-gHNT nanocomposites respectively. It can be said from those micrographs that agglomeration of raw HNTs were present in S-HNT nanocomposite but this agglomeration disappears for gHNTs in S-gHNT nanocomposite. This indicates the dispersion of gHNTs were better as compared to the raw HNTs of their respective nanocomposites.

3.5. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA study was carried out by TA Instrument (DMA 2980) at single cantilever bending mode vibration. The storage modulus (E') was recorded at 1 Hz frequency at temperature range -80°C to 140°C at the heating rate of $5^{\circ}\text{C}/\text{min}$. Experiment was conducted under purging of nitrogen.

Data on viscoelastic property of our prepared samples are recorded and plotted, which are shown in **Figure 5**. Graph stated that virgin blend had lowest storage modulus and gHNTs filled nanocomposite had the highest one. Reason behind this could be the dispersion of HNTs and gHNTs. We noticed that (from TEM micrograph) raw

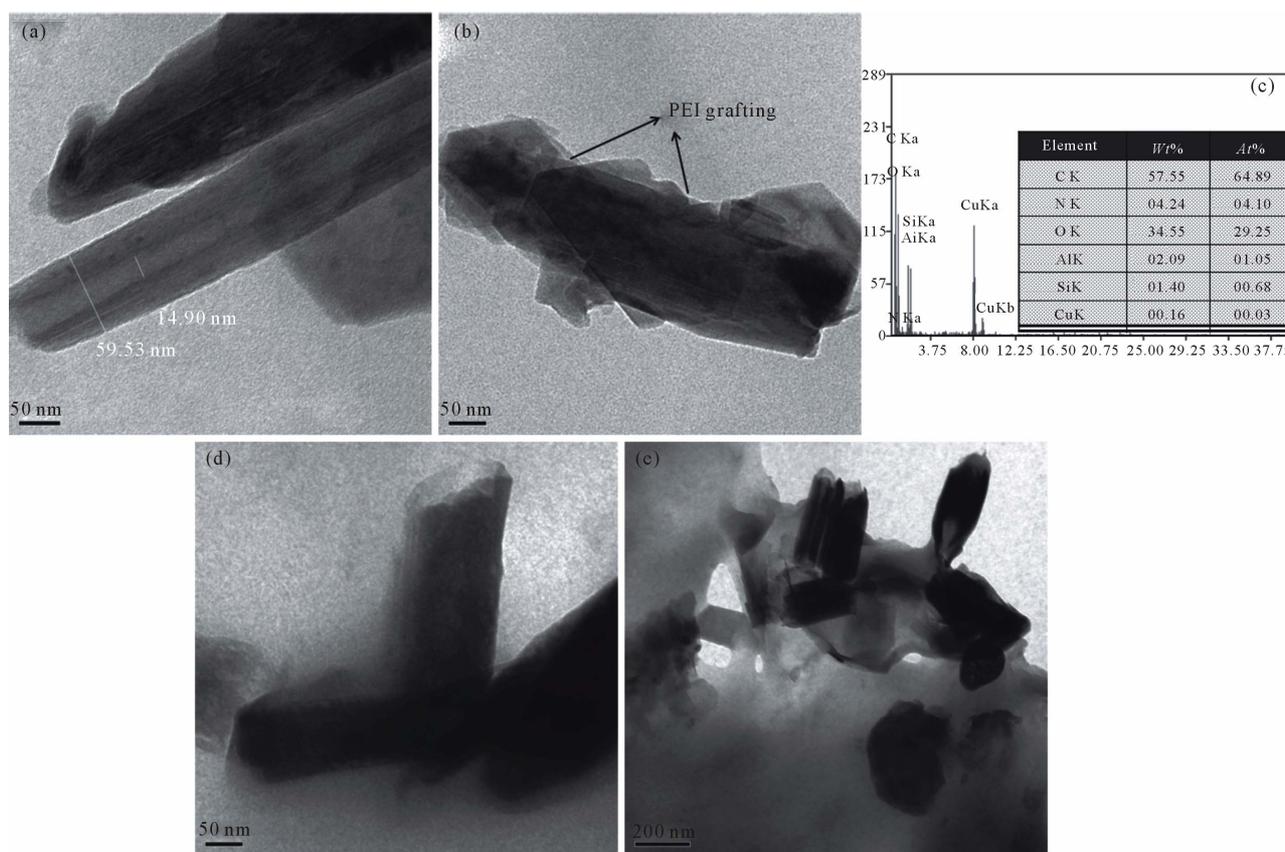


Figure 4. TEM micrograph of (a) raw HNTs (b) PEI grafted HNTs (c) TEM-EDAX of PEI grafted HNTs (d) raw HNTs filled nanocomposite and (e) gHNTs filled nanocomposite.

HNTs dispersion was poorer in comparison with gHNTs. Higher the agglomerations lower the surface area and vice versa, so better dispersion gives enough surface area for load transfer to the halloysite. As dispersion of fillers is a vital factor for the physical performances of the nanocomposites, S-gHNT showed the highest storage modulus value among the others.

3.6. Mechanical Properties

Tensile test of the specimens were performed by Hounsfield HS 10 KS (universal testing machine) tensile testing machine maintaining ASTM standard D638, with cross-head speed of 1 mm/min at room temperature (25°C). Micro hardness of the specimens were performed using UHL VMHT (VH001), maintaining the load 25 gf (gram force) and time 12 s. Tensile strength and hardness values are summarized in **Table 1**.

Gradual increase in tensile strength as well as hardness had been observed. In fact filler distribution helps to improve mechanical properties. Consequently nanocomposites can sustain maximum load. Load transfer was best for S-gHNT nanocomposite thus it showed the highest values in respective fields.

4. Conclusion

Virgin blend and nanocomposites were fabricated via

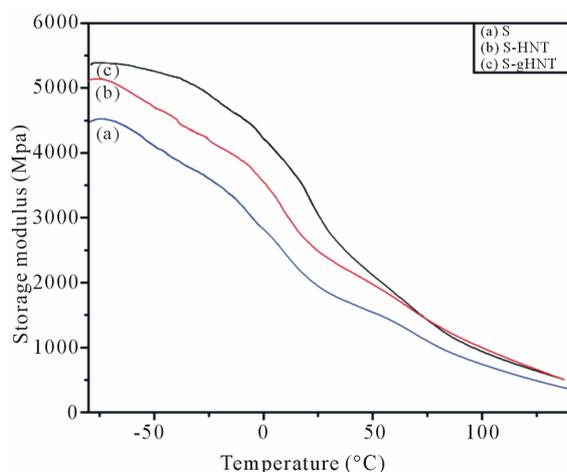


Figure 5. Storage modulus of (a) pure blend (b) raw HNTs filled nanocomposites and (c) gHNTs filled nanocomposite.

Table 1. Tensile strength and hardness value of blend and nanocomposites.

Sample Code	Tensile Strength (MPa)	Hardness Value
S	32.4	18.05
S-HNT	35.3	18.40
S-gHNT	36.9	19.09

melt mixing technique. Mechanical properties and crystallinity of these nanocomposites were investigated. HNTs acted as nucleating agent and therefore % of crystallinity increases. It was shown that, HNTs after surface treatment uniformly dispersed in blend matrices and remains mainly in between two phases. Better dispersion of gHNTs improves the ultimate performance of the nanocomposite.

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