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## Halloysite Nanotubes-Polymer Nano composites:A New Class of Multifaceted Materials

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### ABSTRACT

This Research on polymeric materials was widely focused on the development of polymer nano composites with various nano fillers during the last decades. In this context, the present lecture gives an overview on recent developments on halloy site nano tubes reinforced nano composites, including the processing, characterization and potential applications in industry. The naturally derived nano tubular halloysites represent a distinctive class of nanofiller for industrially significant polymers. Usage of such natural nanotubes not only enhances the material properties but also improves the sustainability and environmental impact of the manufactured products. Additionally, HNTs are biocompatible, and find various applications in biomedical field. In the present work, environmentally friendly HNTs were introduced into various thermoplastics such as polypropylene, polyamide-66, bio based polyamide 11 and thermoplastic starch matrices to generate novel nano composite materials through an advantageous melt-processing method. The effects of HNTs content on the structural, optical, thermal, mechanical, viscoelastic and dielectric properties were investigated. The incorporation of HNTs generates notable performance enhancements through reinforcement effects, highly efficient nucleation activity. In particular, compared to other nano fillers such as nano clays and carbon nanotubes, excellent mechanical properties have been observed (and especially a unique combination of strength, rigidity and ductility). A focus will also be made on the tuning of structural and mechanical properties of the thermoplastic starch through residence time, addition of different combinations of plasticizers and HNTs content. Finally, strategy of preparing conducting composite via the addition of polyaniline functionalized halloy site nano tubes into polymer matrix are presented in order to enhance the application of halloy site nano tubes. Such HNTs filled nano composites can provide an effective balance between performance, cost effectiveness and easy processing, and should be of great interest in the area of multifunctional polymer nano composite materials.

### Introduction

Polymer nanocomposites are new class of materials that are filled with nanofillers, and which usually exhibit exceptionally superior thermomechanical performance and physical properties at very lower filler loadings compared to conventional polymer composites [1]. Improvements in mechanical properties, such as stiffness and toughness, electrical, dimensional stability, barrier and thermal properties as well as fire retardant enhancements, with respect to the bulk polymer, are usually observed. The interfacial interactions and degree of dispersion state of fillers in polymer matrix is important in determining the final performance of polymer nanocomposites [2].

manuscripts Halloysite nanotubes have recently become the subject of research attention as a new type of additive for enhancing the mechanical, thermal and fire-retardant performance of polymers [3] Halloysite is mainly composed of aluminosilicate and has a predominantly hollow tubular structure with the chemical composition  $Al_2(OH)_4Si_2O_5(2H_2O)$ . It is a weathering product of volcanic rocks of rhyolitic up to granitic composition and occurs in great deposits. Common halloysites can be found in form of fine, tubular structures with a length of 300~1500 nm in length and inner diameter and outer diameters being 15-100 nm and 40-120 nm, respectively.

Even if the usage of a silica based, natural occurring nanotube as reinforcing material for polymers is still new, HNTs are considered as the ideal materials for preparing polymer

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composites due to the fact that HNTs are rigid materials and that unique crystal structure of HNTs resembles that of CNTs in terms of aspect ratio. Comparing with other nanoparticles such as fumed silica, montmorillonite, and carbon nanotubes, HNTs are more easily dispersed in polymer matrix by shearing due to their rod-like geometry and limited intertubular contact area. Chemically, HNTs are recognized for their relatively lower hydroxyl density on the HNTs outer surfaces compared with fumed silica and other layered silicates such as montmorillonite [4]. Halloysite nanotubes (HNTs) are readily obtainable, are much cheaper than other nanofillers such as carbon nanotubes (CNTs) and biocompatible. In addition, investigation shows that only traces of heavy metals were detected, much lower than standards of the restriction of harmful substances of the European Union. Consequently it can be concluded that HNTs are a type of 'green', unique and promising reinforcing material for thermoplastics [3]. Novel thermo-mechanical and chemical properties of HNTs have provided opportunity as low-cost and effective nanofillers for polymer matrix and hence have been incorporated into various polymers. Previous studies from our laboratory [4-5] indicate that incorporation of HNTs improves the thermomechanical properties of the nanocomposites. Unlike, other nanofillers such as CNTs and MMT, HNTs provides strength increase without loss of ductility. Importantly, HNTs are biocompatible materials and their usage in drug delivery, bioreactors and genes delivery applications is well established in the literature [3]. In this paper we present the overall benefits of using environmentally friendly HNTs as fillers into various thermoplastics such as polypropylene (PP), polyamide-66 (PA66), biobased polyamide 11 (PA11) and thermoplastic starch (TPS) matrices to generate novel nanocomposite materials through an advantageous melt-processing method. The effects of HNTs content on the structural, optical, thermal, mechanical, viscoelastic and dielectric properties were investigated.

## Experimental

### Processing of Nanocomposites

The nanocomposites of PP/HNT, PA-66/HNT PA-11/HNT and TPS/HNT filled with 2, 4 and 6 wt% HNTs were prepared by melt-compounding using twin screw extruder (Rheocord System 40, HaakeBuchler Product, Germany). The temperatures setting for PP/HNTs nanocomposites from the hopper to die were 180/190/200/210 °C and at a screw speed of 50 rpm. While for PA-66 and PA-11 nanocomposites was set from the hopper to the die was 225/230/235/240 °C. And for TPS nanocomposites was from 110 to 120°C. Approximately 2 kilograms of each formulation were produced using similar processing conditions. During melt-extrusion ventilation was kept on to remove trapped air in the compounds. Nanocomposites bearing 2, 4 and 6 wt% fillers in the polymer matrix were fabricated. Unfilled polymer pellets were also processed under the same conditions as a reference material. After pelletizing, the nanocomposites and neat polymer granules were dried for 5 hours under vacuum at 80°C before injection-moulding. Standard test specimens for tensile and dynamic mechanical analysis were moulded using an electric injection-moulding machine (KM80-160E, KraussMaffei, Germany). For rheological, dielectric and uv-visible measurements, the nanocomposite were prepared by compression-moulding using an hydraulic press (Dolouets, France). All the materials were

stored at 25 °C and 50% relative humidity (RH) for one week before testing nanocomposites.

### Characterization of Nanocomposites

Morphology of the Nanocomposites surfaces were observed by scanning electron microscopy (SEM) (S-4300SE/N, Hitachi, Japan). Melting and crystallization studies were carried out using a Perkin-Elmer (Pyris 1, USA) differential scanning calorimeter (DSC) under nitrogen atmosphere. The viscoelastic behaviour was studied in tension by dynamic mechanical analysis (DMA+150, Metravib, France). The mechanical properties were evaluated from injection-moulded specimens. Tensile properties such as strength, modulus and elongation at break were measured using a tensile machine (Model 1185, Instron, USA) at a crosshead rate of 10 mm.min<sup>-1</sup> at 25°C and 50 % RH according to ISO 527 standard.

### Results and discussion

The Scanning electron microscopy (SEM) and transmission electron microscopic (TEM) analysis were conducted on cryofractured nanocomposite samples in order to investigate the nanotube dispersion and interfacial features in nanocomposites. It was observed that, all nanocomposites showed a uniform dispersion of HNTs with individual nanotubes in polymer matrix is observed. Figure 1a shows typical SEM micrograph of 6 wt.% HNTs filled nanocomposites. The nanotube distribution appears to be uniform across the specimen. This observation is further supported by TEM micrographs (Figure 1b), which confirm that melt-compounding grants fairly homogeneous dispersion of the HNTs within the polymer matrix with occasionally micron-sized aggregates scattered within a matrix of neat polypropylene. Overall microscopy analysis indicate that halloysite nanotubes are distributed and dispersed quite homogeneously throughout the PP matrix with a good adhesion between nanotubes and PP.

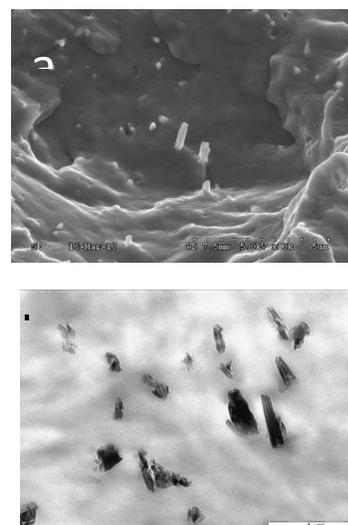


Figure 1: (a) Scanning electron microscopic image (b) and Transmission electron microscopic image of 6 wt.% nanotube filled PP/HNTs nanocomposites

In order to further analyse the viscoelastic properties, dynamic mechanical analyses (DMA) were performed on the

prepared nanocomposites materials. The variation in the storage modulus in tension ( $E'$ ) and the loss factor ( $\tan\delta$ ) with respect to temperature were recorded for neat polymers and their nanocomposites. As expected the storage modulus ( $E'$ ) increases with increasing halloysites content (Figure 2a, which is caused by the restrictions of the segmented motion of the polymer chains. The incorporation of halloysites into polymers matrix remarkably enhances stiffness and load bearing capability of the material.

For instance,  $\tan\delta$  peak the neat PA6 (or  $\alpha$  peak), commonly referred to the glass transition temperature ( $T_g$ ) (Figure 2b), was observed at around 51°C. It is believed to be related to the breakage of hydrogen bonding between PA-6 chain which induces long range segmental chain movement in the amorphous area. All the nanocomposites showed  $T_g$  values higher than neat PA-6, at 53, 57 and 58 °C for 2, 4 and 6 wt.%halloysites filled nanocomposites respectively. This result reflect the restriction of the motion of polymer chains induced by the nanofillers [5] and indicate effective interfacial interaction between the HNT and the PA-6 matrix, which is consistent with the reported literature [6].

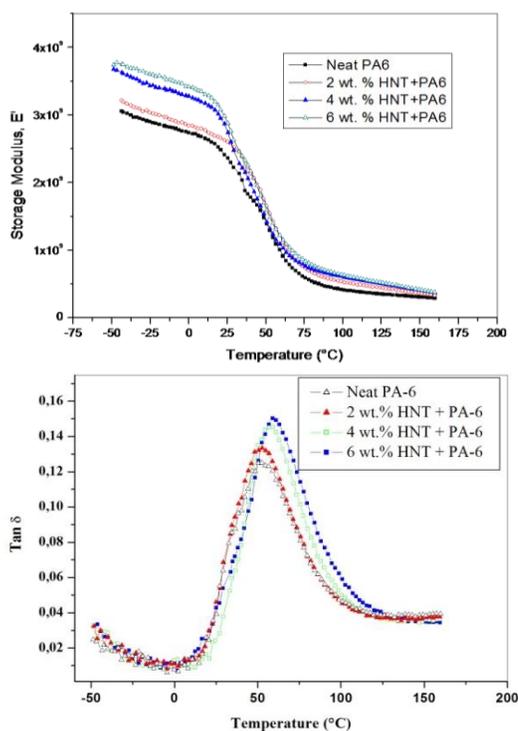


Figure 2

Dielectric characterization can provide information on the molecular dynamics of polymer systems monitoring the relaxation processes. Moreover, the dielectric properties of nanohybrids are of technological interest because they represent the capability to store/dissipate energy under the application of an electric field. It is determined by the ability of a material to polarize in response to the applied field. The real permittivity ( $\epsilon'$ ) of the neat PA-11 was compared to those of the PA-11/HNT nanocomposites in the electric field with a frequency range of 102–106 Hz (Figure 3).  $\epsilon'$  increases when the HNT concentration grows in the entire studied composition range. This is due to the

polar characteristics of HNTs and thus increases the number of charge carriers in the PA-11 matrix. Also,  $\epsilon'$  of all the samples decreases with increasing frequency. This may be ascribed to the fact that the interfacial dipoles do not have enough time to orient themselves in the applied field direction. Therefore, with increase in frequency, the interfacial polarization decreases resulting in the decrease in dielectric constant [7]. The increase in dielectric constant over all the frequency range, which can be attributed to the homogenous dispersion of halloysites in the PA-11 matrix and the PA-11/HNT compatibility, is consistent with our previous reports on carbon nanotubes filled polypropylene nanocomposites [7].

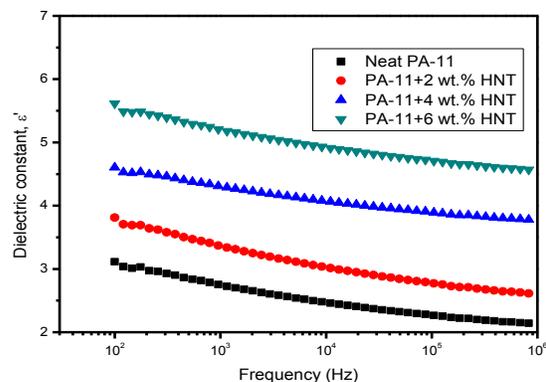


Figure 3 Frequency dependence of real permittivity ( $\epsilon'$ ) for neat PA-11 and PA-11/HNT nanocomposites.

The crystallization behaviour of thermoplastic and their nanocomposites and the role of the silicate nanotubes has been studied using DSC. Figure 4 represents the typical crystallization cooling curves for PA 6 and its nanocomposites obtained by DSC. It is clear from the figure 4 that, the incorporation of halloysite nanotubes into PA 6 matrix increases the crystallization temperature ( $T_c$ ) from 165 to 187° C. This implies that HNTs acts as a nucleating agents for PA 6 crystallization. However, the  $T_c$  of all nanocomposites remains unchanged irrespective of the halloysite content in the PA 6 matrix.

The crystallization parameters obtained for PA 6 and its halloysites filled nanocomposites are calculated using Figure 4. The addition of halloysites into the PA 6 matrix has led to increase in degree of crystallinity ( $X_c$ ) from 21.74% upto 26.61% after the addition of halloysites and the percentage crystallinity increases with increase in the halloysite content in the PA 6 matrix. Which further confirms that, effective nucleating effect of halloysites, facilitating formation of more crystalline PA 6 phase. Afore mentioned higher crystalline properties of the nanocomposites may also contribute to the enhancement in the mechanical properties of the nanocomposites.

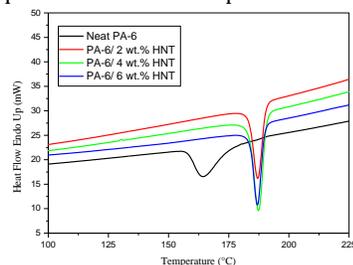


Figure. 4 DSC cooling curves for PA 6 and PA 6/HNT nanocomposites at a cooling rate of 10 °C/min

Halloysites nanotubes have become interesting nanofillers for polymers in recent past. HNTs are intrinsically strong naturally available material with tubular structure and the addition of halloysites to the thermoplastic starch matrix significantly increases the Young's modulus and tensile strength of nanocomposites. In case of HNT/Starch nanocomposites, tensile strength increased from 2.28 to 2.93 MPa and elastic modulus increased from 12.82 to 25 MPa, without decrease in the ductility as shown in Table 1. Depending on the halloysites content, the Young's modulus increases to 127.2% and the yield stress by 28.5 %. Interestingly, no loss of strain at break is observed. The enhancement of mechanical properties induced by the addition of halloysites is due to the good compatibility between the starch and the fillers. Strong interactions allow more efficient load transfer and hence better mechanical performance [8]. Therefore, good interfacial adhesion between halloysites and starch along with dispersability of halloysites in starch matrix provides better stress transfer from the matrix to reinforcements, which give rise to tensile strength [9].

Table 1. Mechanical Properties of Starch and its nanocomposites

HNTs content (wt.%)	Young's Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
0	12.82 ± 2.35	2.28 ± 0.08	87 ± 5
2	13.35 ± 1.92	2.42 ± 0.12	85 ± 1
4	18.56 ± 0.54	2.82 ± 0.03	85 ± 3
6	20.83 ± 1.96	2.91 ± 0.10	84 ± 2
8	25.01 ± 3.33	2.93 ± 0.16	83 ± 4

## Conclusion

In the present work, environmentally friendly HNTs were introduced into various thermoplastics such as polypropylene, polyamide-66, biobased polyamide 11 and thermoplastic starch matrices to generate novel nanocomposite materials through an advantageous melt-processing method. The HNT nanotubes appear to be uniformly dispersed in all polymer matrix in the studied composition range as shown by SEM and TEM observations. As expected, nanocomposites exhibit a more pronounced solid-like and stronger shear thinning behaviour than neat polymers, which is more prominent at higher HNT contents. Interestingly, good halloysite dispersion in polymer matrix increases the tensile strength and Young modulus of polymer without sacrificing the ductility, contrary to what is noticed with other nanofillers such as montmorillonites (MMTs) and carbon nanotubes (CNTs). Highly dispersed nanotubes also significantly improve the thermal stability and bring favourable changes in the dielectric characteristics of polymers. Additionally, as HNTs added in the act as nucleating agents in polymer matrix, crystallization temperature and degree of crystallinity of the nanocomposites tend to increase with growing nanotubes loading. The glass transition temperature follows similar trend, whereas the melting temperature is only marginally affected by the presence of nanotubes. Therefore, combining suitable thermoplastic polymer and naturally available

halloysitenanotubes makes sense in view of designing novel green nanocomposite materials with multifunctional properties for specific applications.

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