PROCESSING AND MECHANICAL BEHAVIOUR OF HALLOYSITE FILLED POLYAMIDE-6 NANOCOMPOSITES

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1 Introduction

Reinforcing thermoplastic polymers with nanotubes or nanoplatelets to form nanocomposites is a way to increase the usage of polymeric materials by improving their mechanical properties, namely Young's modulus or yield stress with filler contents as low as 2–6% by weight [1-2]. Effects of fillers on the mechanical performances of composites strongly depend on their property, shape, dimension, size and aggregate degree, surface characteristics and concentration [2]. Nonetheless, most of the reported literature indicates that there is a significant reduction in the elongation at break and impact strength in these materials when the nanofiller content increases and therefore, the use of nanocomposites can be limited by the losses in toughness. Thus, considerable efforts have been given to overcome this problem [2].

Recently, halloysite nanotubes have become the subject of research attention as a new type of additive for enhancing the mechanical and thermal performance of polymers [3]. Halloysite can be mined from the consequent deposit as a raw mineral. Common halloysites can be found in form of fine, tubular structures with a length of 300~1500 nm, and inner diameter and outer diameters of 15-100 nm and 40-120 nm, respectively [4]. With their high aspect ratio and reasonable mechanical strength, HNTs are a potential alternative to carbon nanotubes (CNTs) as a reinforcing filler for polymers because HNTs are much less expensive than CNTs. Polyamide 6 (PA-6), is an important commercial polymer widely used in many engineering applications due to its excellent mechanical performances and easy processability.

In the present study, polyamide (PA-6) / halloysite nanotubes (HNTs) nanocomposites were prepared. The morphology, mechanical performance and fracture behaviour of the nanocomposites were investigated.

2 Experimental

2.1 Materials

Polyamide-6 (PA-6)-halloysites nanotubes (HNT) nanocomposites were produced by mixing homo PA granules (Akulon F130-C1, DSM Engineering Plastics) with the commercial masterbatch ''Plasticyl PA-2001'' containing 30 wt.% of HNT (Natural nano Inc., USA). The materials were dried to 80°C for 4 hours before processing.

2.2 Nanocomposites Preparation and Testing

The masterbatch dilution was done in a single screw extruder (Haake Rheocord) at barrel temperature of 220, 225, 230 and 235°C from hopper to die, at the screw speed of 80 rpm. The extrudates were then pelletized and dried again. Subsequently, the nanocomposite pellets were directly injection-moulded (KraussMaffei KM80-160E machine) into standard test specimen for tensile and impact tests. The mould temperature was maintained at 40°C, whereas the barrel zone temperatures were set at 210, 215 and 220°C. The holding pressure and speed were 300 bar and 100 rpm, respectively with a throughput of 50 cm^3/s. The final nanocomposites contained 2, 4, 6 wt.% HNTs in the PA matrix.

Morphological characterization of the nanocomposites was performed using scanning electron microscope (SEM) instrument (Hitachi S-4300SE/N) operating at 5 kV. Dynamic mechanical analysis (DMA) was carried out (DMA+150, Metravib) in the tensile mode at a frequency of 10 Hz. The strain amplitude was 20 μm and the static force was 10 N. Fracture toughness was determined by the essential work of fracture (EWF) method on double-edge notched tension (DENT) specimens cut from calendered films at a dimension of 100×50×0.4 mm. Mechanical testing were carried out on a tensile

machine (Instron 1185) and a Zwick impact pendulum. Observation of cryofractured surfaces of test samples by Scanning electron microscopy (SEM) imaging was performed under high vacuum with a SEM instrument (Hitachi S-4300SE/N) operating at 5 kV.

3 Results and Discussions

3.1. Morphology

SEM analysis of halloysites filled polyamide nanocomposites is illustrated in figure 1.
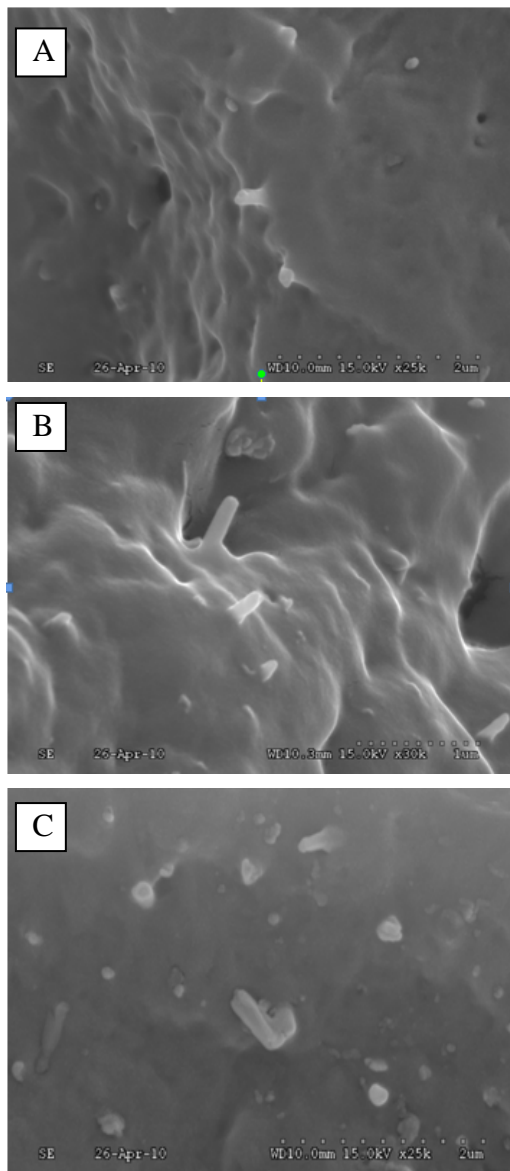

Figure-1. SEM picture of (A) 2 wt.% HNT/PA-6, (B) 4 wt.% HNT/PA-6, (C) 6 wt.% HNT/PA-6, nanocomposites

HNTs with tubular structure are uniformely dispersed in the PA-6 matrix. In case of nanocomposites with 2 and 4 wt.% halloysites an homogenous dispersion of HNTs with individual nanotubes in PA-6 matrix is observed. On the opposite, in case of 6 wt.% HNTs filled nanocomposites very few aggregates are visible, which is probably due to higher loading of fillers. In addition, the interfacial interactions between HNTs and PA-6 matrix seem to be very strong as no debonded HNTs are observed on the fractured surface of the nanocomposites.

3.2. Viscoelastic properties

DMA analysis can provide useful information reflecting the interfacial interaction between the nanocomposites components. It is also an effective tool to study the strain response of polymers exposed to vibrational forces. DMA analysis shows as expected that the storage modulus (E', Figure-2) of all nanocomposites is higher than that of neat PA-6. Storage modulus of PA-6 increases with increasing halloysites content, which is caused by the restrictions of the segmented motion of the PA chains. The incorporation of halloysites into PA-6 matrix remarkably enhances stiffness and load bearing capability of the material.
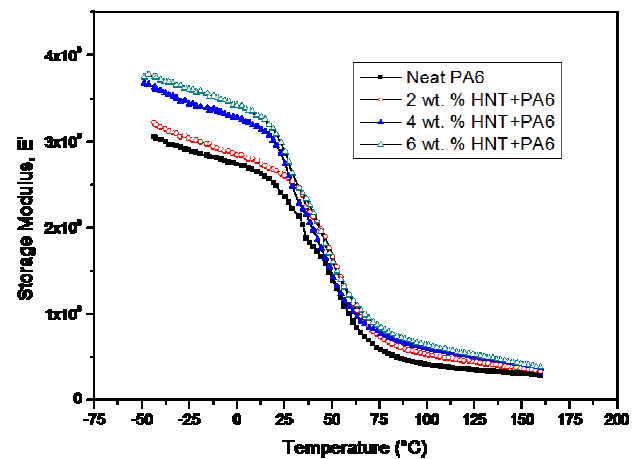

Figure-2. Storage modulus (E′) with temperature sweep for PA-6 and PA6/HNT nanocomposites at different HTN contents.

The tan δ (also called loss factor) peak is commonly referred to the glass transition temperature (Tg) of reinforced PA-6 and the nanocomposite systems (Figure-3).
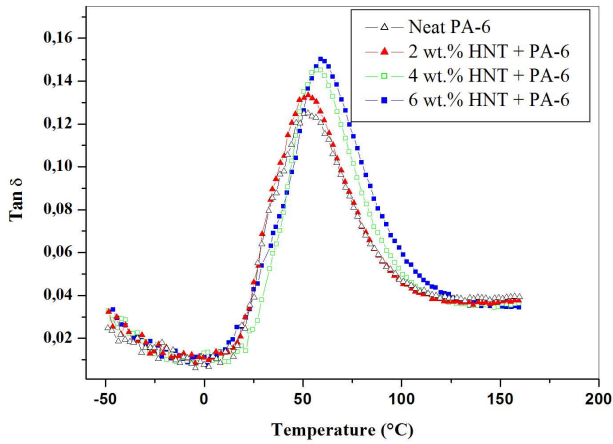
Figure-3. Tan ∂ vs temperature traces for PA6 and PA6/HNT nanocomposites at different HTN contents.

The dynamic relaxation peak was observed at around 56°C, which referred to as α peak of PA-6. The α relaxation peak is believed to be related to the breakage of hydrogen bonding between polymer chain which induces long range segmental chain movement in the amorphous area. This is assigned to the Tg of PA-6. All the nanocomposites showed Tg values higher than neat PA-6 (Tg values are 51°C for PA-6 and at 53, 57 and 58°C for 2, 4 and 6 wt.% halloysites filled nanocomposites respectively). Glass transition temperature provides an indirect indication of the interfacial interaction between nanofillers and the polymer matrix. It is reported that the restricted segmental motion can elevate the Tg of polymer composites and that such a restriction effect arises from the addition of nanofillers [5]. The above mentioned results confirm this trend and reflect the restriction of the motion of polymer chains, and indicate effective interfacial interaction between the HNT and the PA6 matrix, which is consistent with the reported literature [6].

3.3. Mechanical behaviour

The main objective of introducing nano fillers to polymers is to improve the mechanical properties of the polymeric materials. Table-1 shows the tensile and impact properties of the studied materials.

The addition of HNTs into the PA-6 matrix produced an increase in the elastic modulus and the tensile strength compared to neat PA-6. Depending on the HNT content, the Young's modulus increase ranges from +24.6% to +30.4 % and that of yield

stress from +18.5% to +30.3%. Interestingly, there is no loss of elongation at break. This behaviour is quite remarkable as most of the nanofillers including carbon nanotubes increase the tensile modulus and strength at the expense of elongation at break [7].

Material	Tensile modulus (MPa)	Tensile strength (MPa)	Tensile strain @break (%)	Notched impact strength (kJ/m^2)
PA-6	2015±18	55.1±1.3	201±3	1.8±0.2
PA-6 + 2 wt.% HNT	2452±15	65.3±0.6	203±4	2.2±0.1
PA-6 + 4 wt.% HNT	2584±22	70.5±0.5	198±10	2.5±0.1
PA-6 + 6 wt.% HNT	2628±20	71.8±0.6	192±14	2.4±0.2

Table-1. Tensile and impact properties of PA-6 and PA6/HNT nanocomposites.

The better tensile properties of PA-6/HNTs nanocomposites compare to neat PA-6 are in consistent with the DMA results, which is due to the good compatibility between the PA-6 and HNTs. Strong interactions allow more efficient load transfer and hence better mechanical performance [8]. Therefore, good interfacial adhesion between HNTs and PA-6 along with dispersability of HNTs in PA-6 matrix provides better stress transfer from the matrix to reinforcements, which give rise to tensile strength.

The notched Charpy impact strength also increases upon HTN addition and with increasing HNTs loading. The enhancement of impact strength may be ascribed to the fact that halloysite nanotubes in PA-6 play a role in hindering the crack path caused by impact.

The mechanical testing data suggest an engineered combination of mechanical strength, stiffness and toughness is plausible by halloysites reinforcement.

3.4. Fracture behaviour

Essential Work of Fracture (EWF) methodology was developed by Broberg [9] in order to characterize the fracture toughness of ductile polymers and tough composites. The total specific EWF (w_e), and specific plastic work (βw_p) were calculated from the

linear fits of specific work of fracture versus ligament length (Table-2).

Material	w_e (kJ/m²)	βw_p (MJ/m³)	R^2
PA6	32.5	11.1	0.96
PA6+2wt% HNT	42.0	13.8	0.90
PA6+4wt% HNT	44.9	11.5	0.96
PA6+6wt% HNT	36.2	12.3	0.66

Table-2. Tensile specific essential fracture work (w_e) and specific plastic work (βw_p) of PA-6 and PA-6/HNT nanocomposites

A significant improvement in w_e is noticed with increase in halloysite content up to 4 wt.%. The total specific essential work fracture increases by +29% for 2 wt.% HTN and by +38% for 4 wt.% HNT compared to neat PA-6, whereas βw_p values remains almost unchanged upon halloysites addition. These results indicate that halloysite nanotubes toughen the matrix effectively and are consistent with the reported literature [10].

In case of 6wt.% halloysite filled PA-6 nanocomposites, due to the poor linear regression coefficient, it was concluded that EWF analysis is no longer valid when the HNT content reached 6 wt.% in PA-6 matrix. This is attributed to the poor dispersion of halloysites in PA-6 matrix. Similar conclusions were drawn in case of polypropylene/coal gangue composite materials [11]. Thus the optimum halloysite content is 4 wt.% for enhancement of fracture toughness of PA-6.

In order to better understand the fracture mechanism, field-emission SEM micrographs of PA-6 and PA-6/4 wt.% HNT specimens were taken after tensile EWF measurements (Figure-4). Very smooth surface is observed for neat PA-6. The morphology of fracture surface of PA-6/4 wt.% HNT nanocomposites is different. The predominant deformation mechanism in these materials is wavy shear banding of the matrix, which can be readily seen in the micrograph. This indicates that a significant energy is absorbed in these specimens during tensile EWF measurements. Furthermore, cavitation can be seen in some areas of the nanocomposites, thereby promoting fibrillation and shear banding of polymer matrix. The fracture toughness (EWF) follows the same trends up to

4wt.% (Table-2), the lower value noticed for 6wt.% halloysites being ascribed to the presence of aggregates in that case.
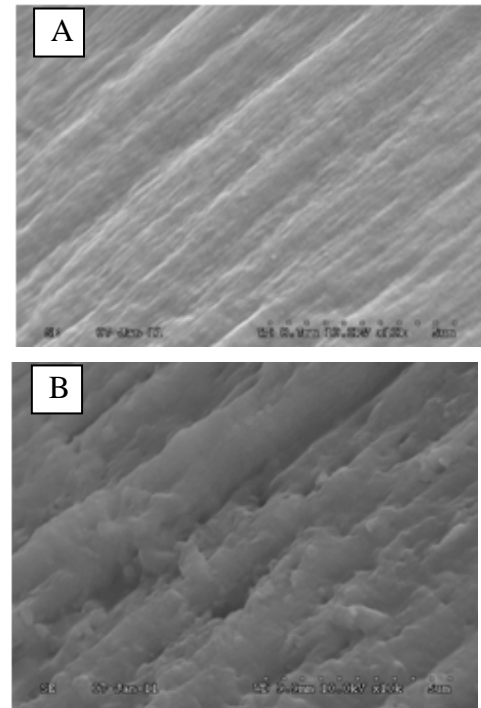

Figure-4: SEM fractographs of (A) PA-6 and (B) PA6/4wt.% HNT nanocomposite after tensile EWF test.

4 Conclusions

Polyamide-6 (PA6) / halloysites nanotubes (HNT) nanocomposites were successfully prepared by melt-extrusion using a masterbatch dilution process. A homogeneous dispersion of HNTs in polyamide matrix was achieved. Upon addition of halloysites into PA-6, the glass transition temperature increases indicating a strong interfacial adhesion between HNTs and PA6 matrix. Interestingly, the tensile modulus, yield stress and notched impact strength of polyamide 6 also significantly increases without any loss of elongation at break. Essential work of fracture (EWF) concept was used to evaluate fracture behaviour of PA6 and its PA-6/HNT nanocomposites with low filler content. The addition of nanotubes resulted in positive toughening effects without reducing the plastic deformation of matrix.

References

[1] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials, *Material Science and Engineering: Review*, 28(1-2), pp 1-63, 2000.

[2] K. Prashantha, J. Soulestin, M.F. Lacrampe, P. Krawczak, Present status and key challenges of carbon nanotubes reinforced polyolefins: A review on nanocomposites manufacturing and performance issues, *Polymers and Polymer Composites*, 17 (4), pp 205-245, 2009.

[3] K. Prashantha, M.F. Lacrampe, P. Krawczak, Processing and characterization of halloysite nanotubes filled polypropylene nanocomposites based on a masterbatch route: Effect of halloysites treatment on structural and mechanical properties. *Express Polymer Letters*, 5(4), pp 295-307, 2011.

[4] M. Du, B. Guo, D. Jia, Newly emerging applications of halloysite nanotubes: a review, *Polymer International*, 59(5), pp 574-582, 2010.

[5] R. Krishnamoorti, R.A. Vaia, E.P. Giannelis, Structure and Dynamics of Polymer-Layered Silicate Nanocomposites, *Chemistry of Materials*, 8, pp 1728-1734, 1996.

[6] H.B. Lu, S. Nutt, Restricted relaxation in polymer nanocomposites near the glass transition, *Macromolecules*, 36, pp 4010-4016, 2003.

[7] K. Prashantha, J. Soulestin, M.F. Lacrampe, P. Krawczak, G. Dupin, M. Claes, Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties, *Composites Science and Technology*, 69, pp 1756-1763, 2009.

[8] B.X. Yang, J.H. Shi, K.P. Pramoda, S. Hong Goh, Enhancement of stiffness, strength, ductility and toughness of poly(ethylene oxide) using phenoxy grafted multi walled carbon nanotubes, *Nanotechnology,* 18, No.125606, 2007.

[9] K.B. Broberg, The propagation of a brittle crack*, International Journal of Fracture*, 1, pp 1-19, 1968.

[10] C.Z. Liao, S.C. Tjong, Mechanical and fracture behaviors of elastomer-rich thermoplastic polyolefin/SiCp nanocomposites, *Journal of Nanomaterials*, Article ID 327973, 2010.

[11] G. Gong, B.H. Xie, M;B. Yang, W.Yang, W.Q. Zhang and M.Zhao., Mechanical properties and fracture behavior of injection and compression molded polypropylene/coal gangue powder composites with and without a polymeric coupling agent. *Composites: Part A*, 38, pp 1683-1693, 2007.