Mechanical and Morphological Properties of PP/MWNT/MMT Hybrid Nanocomposites

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Abstract

Polypropylene/Multiwall carbon nanotubes/Montmorillonite (PP/MWNTs/MMT) hybrid nanocomposites were prepared by using twin-screw extruder incorporating the polypropylene grafted maleic anhydride (PP-g-mA) as compotibilizer is used for better dispersion of nanoclay in the polymer matrix. The effect of MWNTs and MMT on the polypropylene matrix was investigated in terms of mechanical properties of tensile, flexural, impact and morphological properties using Transmission electron microscope (TEM), X-ray diffraction (XRD) and scanning electron microscope (SEM). These were compared with the pure PP matrix. The resulting composite shows about 81% increase in tensile modulus and 96% in the impact strength when compared with pure PP.

Keywords: Multiwall carbon nanotubes (MWNTs); Hybrid Nanocomposites; Transmission electron microscope (TEM);X-ray diffraction (XRD); Scanning electron microscope (SEM):

1. Introduction

Polymeric nanocomposites (PNCs) or polymer nanostructured materials represent a radical alternative to conventional-filled polymers. The reinforcement of polymers is done by fillers, which play a major role in strengthening the composite. In contrast to the conventional systems where the reinforcement is on the order of microns, discrete constituents on the order of a few nanometers (~10,000 times finer than a human hair) exemplify PNCs. Uniform dispersion of these nanoscopically sized filler particles produces ultra-large interfacial area per volume between the nanoelement and host polymer. Thus, new combinations of properties derived from the nanoscale structure of PNCs provide opportunities to traditional performance trade-offs associated with conventional reinforced plastics, optimizing the promise of nano-engineered materials.

Polypropylene is a semi crystalline engineering thermoplastic and is known for its balance of strength, modulus and chemical resistance. It have many potential applications in automobiles, appliances and other commercial products in which creep resistance, stiffness and some toughness are demanded in addition to weight and cost savings. The incorporation of organic and inorganic particulate fillers has been proved to be an effective way of improving the mechanical properties and in particular the toughness of polypropylene [1]. Recently, polymer nanocomposites including nanoparticle, nanoplatelet, nanofiber, and carbon nanotube-reinforced thermoplastic and thermosetting polymer matrix composites are of interest.

Nanoparticle filled polymers are attracting considerable attention since they can produce property enhancement that are sometimes even higher than the conventional filled polymers at low volume fraction range. MMT is the most commonly used tool for the preparation of nanocomposites. MMT possesses layered structure with an actahedral aluminum layer located between two layers of silicon tetrahedral. Each layered sheet is about 1nm thick with lateral dimensions of 100-1000 nm. Recently, MMT were used in the preparation of nanocomposites with polymers in the case the platelets were nanoscale reinforcement for the polymer matrix [2].

The mechanical properties of carbon nanotube are exciting, since they are considered as the ultimate carbon material even made [3]. The most important application of carbon nanotubes, based on their mechanical strength is as reinforcements in composite materials [4]. Compared with clay and other organic fibers which usually lack one or more of these properties, carbon nanotubes show a unique combination of stiffness, strength and tenacity [5]. Also in comparison to the conventional organic and inorganic fillers, Carbon nanotube has therapeutic properties and hence can address the most common drawbacks peculiar to the conventional binary composites at minimal loading. For example carbon nanotubes is soft and elastic in the radial direction and hence can favorably address the problems of poor elongation and flexural strength found in most conventional binary composites and due to its high young modulus and tensile strength, it has a better potential for reinforcement than any other known nanomaterials[6].Calcium carbonate nanofiller have resulted in some improvement in the mechanical properties of PP, namely the modulus and impact strength [7].Incorporation of $CaCo_3$ nanoparticle into PP matrix can produce attractive polymer nanocomposites with improved modulus and toughness [8].The presence of SiO_2 nanoparticles in the polymer matrix led to an increase of both Young's

modulus and impact strength [9].Montmorillonite gives improved mechanical strength, higher fracture toughness and lower wear rates [10].

The purpose of this paper is to investigate the mechanical properties of neat PP and PP/MWNT/MMT hybrid nanocomposites .Tensile, flexural and impact tests were performed and investigated mechanical performance of hybrid nanocomposites. Morphological properties of hybrid nanocomposites were studied by TEM, X-RD, and SEM.

2. Experimental

2.1 Materials

The polypropylene (H110MA) with density of 0.910 g/cc and MFI of 11 g/10 min (measured at 230^{o}C under 2.16 kg load), obtained from Reliance Ltd., India was used as the base polymer matrix for the present study. PP-g-MA was used in this study supplied by Exxon mobile India Pvt Ltd. India, under the trade name Exxlor PO 1020 and has melt flow index 125gm/10 min with percentage of grafting of MA is 0.75%. Clay i.e. Na+-MMT (unmodified having CEC 92.6 meq/100 g clay), were obtained from Southern clay Products Inc, USA. Multiwalled carbon nanotubes (MWNTs) with 95% purity were obtained from Sunnano, China.

2.2 Preparation of PP/MWNT/MMT hybrid nanocomposites

Melt blending of PP, PP-g-MAH (10 wt %),MWNTs of 0.5,1.5,2.5 and 3.5 wt% and nanoclays (Na+-MMT) of 0.5, 1.5, 2.5 and 3.5 wt% was carried out in an intermeshing counter rotating twin screw extruder (ctw-100, Haake-Germany) having barrel length of 300mm and angle of entry 90^{o}. Prior to extrusion, the matrix polymer and the nanoclay were dehumidified in a vacuum oven at 60^{o}C for a period of 6 hours. PP was fed at the rate of 5 kg/hour and the nanoclay was subsequently introduced at the melting zone. The process was carried out at a screw speed of 150 rpm and a temperature difference of 160, 170 and 180^{o}C between feed zones to die zone, followed by granulation in a pelletizer (Fission, Germany) and drying. These granules were further injection molded using injection molding machine (SP 130 Windsor Clocknar Ltd) having clamping force 800kN fitted with a dehumidifier at a temperature range of 195–220^{o}C and mold temperature of 80^{o}C, for preparation of test specimens of tensile, flexural and impact strength as per ASTM standards. The codes and composites are summarized in table 1.

Table .1 sample codes and composites

Sample code	Composition (wt %)
PP	PP(100)
PPHNC-1	PP(89)+PP-g-MA(10)+MWNT(0.5)+MMT(0.5)
PPHNC-3	PP(87)+PP-g-MA(10)+MWNT(1.5)+MMT(1.5)
PPHNC-5	PP(85)+PP-g-MA(10)+MWNT(2.5)+MMT(2.5)
PPHNC-7	PP(83)+PP-g-MA(10)+MWNT(3.5)+MMT(3.5)

2.3 Mechanical characterization

Specimens of virgin PP and PP/MWNT/MMT hybrid nanocomposites of dimensions 165X13X3 mm were subjected to tensile test as per ASTM D-638 using universal testing machine (UTM) LR-100K(Lloyd Instrument Ltd U.K).A cross head speed of 50mm/min and gauge length of 50mm was used for carrying out the test. Specimens of virgin PP and hybrid nanocomposites of dimensions 80X12.7X3 mm were taken for flexural test under three point bending using the same universal testing machine accordance with ASTM-D 790 at a cross head speed of 1.3 mm/min and a span length of 50mm.Similarly,Izod impact strength was determined from the specimens having dimensions 63.5X12.7X3mm with a “V” notch depth of 2.54 mm and notch angle of 45^{o} as per ASTM-D 256 using impact meter 6545(Ceast. Italy).For analyzing the mechanical properties test specimens were initially conditioned at 23+1^{o} C and 55+2% RH. Five replicate specimens were used for each test and the data reported are the average of five tests.

2.4 Wide angle X-Ray diffraction (WAXD)

Wide angle X-ray scans (WAXS) were made using a Philips X’Pert MPD (Japan) X-ray diffractometer in the reflection mode which had a graphite monochromator and a Cu Ka radiation source (k ¼ 1.54A˚) at a scan rate of 0.5^{o}/min over the range of 2h ¼ 8–30^{o}. X-ray analyses were performed at room temperature on as molded specimens. Both for the pure PP and hybrid nanocomposites, XRDs were recorded using, operated at 40Kv and 30mA.

2.5 Transmission Electron Microscope (TEM)

Thin sections for transmission electron microscopy (TEM) analysis were microtomed from the central and skin regions of an tensile test specimen bar, the cuts were made parallel and perpendicular to the flow direction 3–4 cm away from the end of a 13 cm tensile test specimen bar and halfway between the top and bottom surfaces of the bar. Ultra-thin sections ranging from 70 to 100 nm in thickness were cryogenically cut with a diamond knife using Reichert-Jung FC4E ultra cryomicrotome cutter (Mager Scientific, Inc., Dexter, MI)

at temperature of 100°C.Sections were collected on 300 mesh copper TEM grids and subsequently dried with filter paper. The sections were examined by TEM using a JEOL-EM-2000 FX Electron Microscope with 200 kV accelerating voltage.

2.6 Scanning Electron Microscope (SEM)

The morphology of the impact fractured surfaces of neat PP and its hybrid nanocomposites, the fracture surfaces were coated with thin layers of gold of about 10 A. All specimens were examined with JEOL, JSM 840A scanning electron microscope with an accelerating of 10kv.

3. Results and discussions

3.1. Mechanical properties

3.1.1 Tensile properties

Fig. 1 plots the tensile properties of the samples as a function of weight percentage of hybrid nanofiller content (MWNT and MMT) from 0 to 7 wt%. The result shows that hybrid nanofiller content has better influence on the tensile strength of pure PP. As the hybrid nanofiller content increases, the tensile strength reaches maximum at the hybrid nanofiller content of 5 wt%, and increased by 28.5% of tensile strength and 81% of tensile modulus, respectively, when compared with those of pure PP samples. It can be seen from Fig. 5(a, b and c) that the intercalated and exfoliated hybrid nanofiller served as the short fasciculus inside the composite. The addition of short fasciculus to the PP matrix could reinforce the PP matrix and contributed to the increase of the tensile properties of the PP/MWNT/MMT hybrid nanocomposites at the 5 wt% hybrid nanofiller content. The tensile properties decreased when the hybrid nanofiller content was further increased to 7 wt%.This might be mainly attributed to the fact that the percentage of aggregated (namely non-exfoliated) hybrid nanofiller content (see Fig. 5 d). The micro sized holes to be shown in Fig. 6d were indicative of pull out of aggregated hybrid nanofiller content particles. When the composite samples were tested under tensile loading, cracks might initiate at the aggregated hybrid nanofiller content and propagated throughout the samples. Therefore, the tensile strength was lower at the higher hybrid nanofiller concentration.

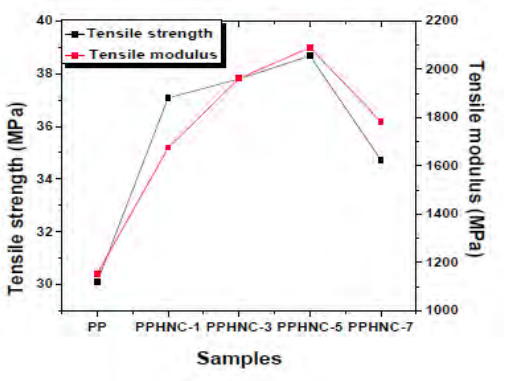

Fig.1.Tensile properties of PP and hybrid nanocomposites

3.1.2 Flexural properties

Fig. 2 plots the flexural properties of the samples as a function of weight percentage of hybrid nanofiller content (MWNT and MMT) from 0 to 7 wt%. The results show that hybrid nanofiller content has significant improvement on the flexural properties of pure PP. As the hybrid nanofiller content increases, the flexural strength reaches maximum at the hybrid nanofiller content of 5 wt%, and increased by 21% of flexural strength and 30% of flexural modulus at the hybrid nanofiller content at 5 wt%, when compared with those of pure PP samples. The flexural modulus decreased when the hybrid nanofiller content was further increased to 7 wt%.This might be mainly attributed to the fact that the percentage of aggregated (namely non-exfoliated) hybrid nanofiller content.

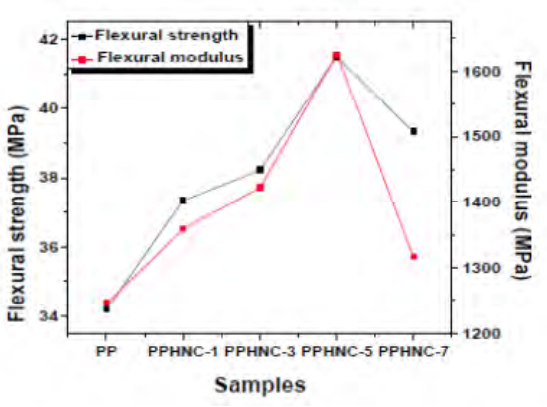

Fig.2.Flexural properties of PP and hybrid nanocomposites

3.1.3 Notched impact strength

Fig. 3 plots the notched impact strength of the hybrid nanocomposites as a function of hybrid nanofiller content. The notched impact strength increased from 22.33 J/m to 43.83 J/m by the incorporation of hybrid nanofiller particles for the nanocomposites containing up to the 5 wt% hybrid nanofiller content while decreased for the hybrid nanocomposites containing the 7 wt% of hybrid nanofiller content. Toughness improvement of hybrid nanocomposites can be attained when hybrid nanofiller content in PP matrix can resist the propagation of cracks up to the 5 wt% hybrid nanofiller content as indicated by the increase of notched impact strength. The rougher surfaces of the hybrid nanocomposites in Fig. 6 (a, b & c) than those of pure PP matrix in Fig. 6(e) are indicative of the improvement in toughness. However, as the hybrid nanofiller content was increased to 7 wt%, aggregation of hybrid nanofiller content would take place. When the effect of aggregation of hybrid nanofiller content particles (Fig. 6d) overwhelmed the effect of rough fracture surfaces was decreased.

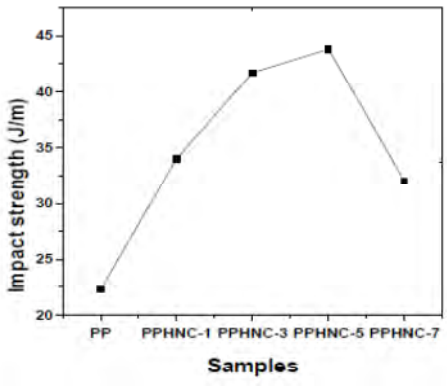

Fig.3.Impact properties of PP and hybrid nanocomposites

3.2 X-RD analysis

The X-ray diffraction patterns of both hybrid nanocomposites and pure PP matrix were shown in Fig. 4. These were determined over the same diffraction angle for basic comparison. The XRD patterns of both the PP matrix and the PP/MWNT/MMT hybrid nanocomposites depicted that MWNTs and MMT has better dispersion in the PP matrix. This is because the X ray pattern shows much more defined peak intensity was decreased by the incorporation of hybrid nanofiller content in the PP matrix. This implies that hybrid nanofiller contents were well dispersed in the nanocomposites and thus lead to the formation of intercalated and exfoliated (characteristics of nanomaterials) in this hybrid nanocomposites system.

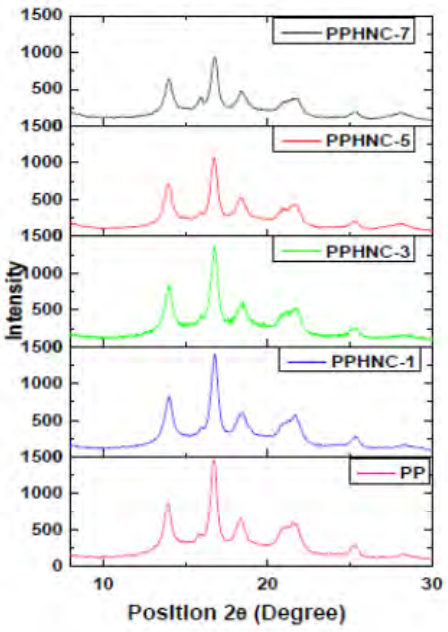

Fig.4. XRD curves of PP and hybrid nanocomposites

3.3 TEM analysis

TEM morphologies of the PP/MWNT/MMT hybrid nanocomposites are presented in Fig. 5a–d. It can be seen from Fig. 5a-c that the hybrid nanofiller has been further intercalated and exfoliated in the hybrid nanocomposite up to 5 wt%. The reason is that net like macromolecules formed the interlayer of the hybrid nanofiller during the melting process. However, some of the hybrid nanofiller actually consist of several layers, indicating that they were not fully exfoliated to the single layer. However, as the hybrid nanofiller content was increased to 7 wt%, aggregation of hybrid nanofiller content would take place, When the effect of aggregation of hybrid nanofiller content particles (Fig. 5d).

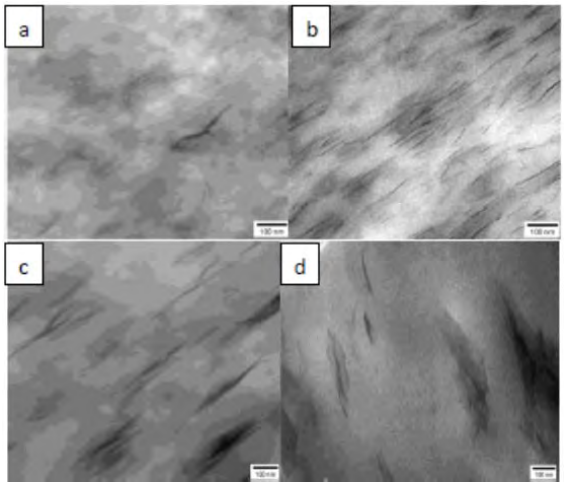

Fig.5. TEM micrograph of hybrid nanocomposites a)PPHNC-1,b)PPHNC-3,c)PPHNC-5 and d)PPHNC-7

3.4 SEM analysis

The fracture surfaces of the hybrid nanocomposites and pure PP were observed using SEM. Fig. 6a–e displays some representative SEM images of the fracture surfaces of the notched impact samples. Fig. 6 (e) shows that the surfaces of the pure PP samples were smooth and featureless, representing brittle failure of homogenous materials. As shown in the SEM images for the hybrid nanocomposite samples up to 7 wt% hybrid nanofiller content, the fracture surfaces were significantly different from those of pure PP samples. The fracture surfaces were broken into small and rough fracture pieces, contributing to improvement of the toughness of the hybrid nanocomposites. However, the improved toughness by the rough fracture surfaces for the cases of 7 wt% would be overwhelmed by the effect of aggregation of hybrid nanofiller content particles since micro cracks would relatively easily initiate at the micro sized aggregated hybrid nanofiller particles, resulting in a reduced macroscopic toughness as shown in Fig. 3.

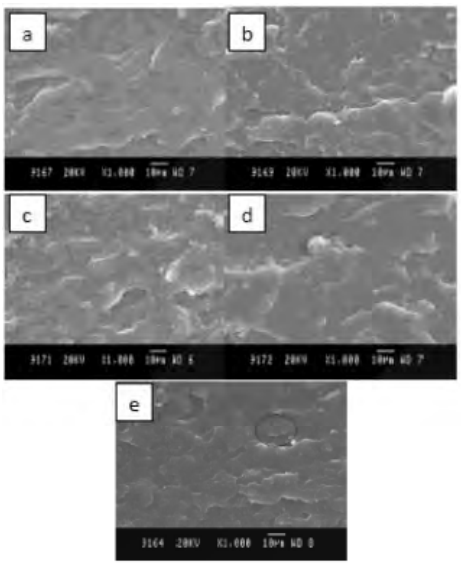

Fig.6. SEM micrograph of hybrid nanocomposites a)PPHNC-1,b)PPHNC-3,c)PPHNC-5, d)PPHNC-7 and e)pure PP

4. Conclusions

The mechanical properties and morphological properties of PP/MWNT/MMT composites prepared by melt mixing process have been studied. XRD and TEM results showed that hybrid nanofiller can be intercalated and exfoliated up to the 5 wt% hybrid nanofiller content. The mechanical results showed that the tensile strength, flexural strength, tensile modulus, flexural modulus and impact strength of PP/MWNT/MMT hybrid nanocomposites reached the maximum at the 5 wt% hybrid nanofiller content, increased by 28.5% , 81 wt% and 96 wt% respectively as compared with those of pure PP samples. Flexural strength and flexural modulus of PP/MWNT/MMT hybrid nanocomposites reached the maximum at 5 wt% hybrid nanofiller content, increased by 21% and 30% respectively.

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