BIOSCIENCES BIOTECHNOLOGY RESEARCH ASIA, Ocotber 2014. Vol. **11**(Spl. Edn. 1), p. 135-141

Effect of MWNTs on Mechanical Properties of PP/MMT Nanocomposites

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doi: http://dx.doi.org/10.13005/bbra/1402

(Received: 15 August 2014; accepted: 10 October 2014)

This article addresses the effect of Multiwalled carbon nanotubes (MWNTs) on the mechanical properties of polypropylene (PP)/ Montmorillonite (MMT) nanocomposites. PP/MWNT/MMT hybrid nanocomposites have been prepared by melt mixing using maleic anhydride grafted polypropylene (MAH-g-PP) as compatibilizing agents. Melt mixing was achieved using twin screw extruder. The MAH-g-PP used as compatibilizer helped the dispersion of the MWNTs in PP/MMT matrix. The effect of MWCNTs on the PP/MMT nanocomposites was investigated in terms of mechanical properties and morphological using Transmission electron microscope (TEM), X-ray diffraction (XRD), tensile test, flexural test and notched Izod impact test. These were compared with the conventional polypropylene-clay nanocomposite. The resulting composite shows about 33% increase in tensile modulus and 20% in the impact strength when compared with binary combination of PP/MMT nanocomposite.

Key words: Multiwall Carbon Nanotubes (MWNTs); Montmorillonite (MMT); Hybrid Nanocomposites; Scanning electron microscope (SEM): Mechanical characterization:

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 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 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 property of carbon nanotube is exciting, since they are considered as the ultimate carbon material ever 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

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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[6] and due to its high young modulus and tensile strength, it has a better potential for reinforcement than any other known nanomaterial .Calcium carbonate nanofiller have resulted in some improvement in the mechanical properties of PP, namely the modulus and impact strength[3,7]. Incorporation of $CaCo_3$ nanoparticle into PP matrix can produce attractive polymer nanocomposites with improved modulus and toughness[4,8].The presence of siO_2 nanoparticles in the polymer matrix led to an increase of both Young's modulus and impact strength[5,9]. Organ modified Montmorillonite gives improved mechanical strength, higher fracture toughness and lower wear rates[6,10].

The purpose of this paper is to report the mechanical properties of neat PP and PP/MMT nanocomposites and PP/MWNT/MMT hybrid nanocomposites .Tensile, flexural and impact tests were performed to evaluate mechanical performance. Morphological properties of nanocomposites were studied by SEM.

EXPERIMENTAL

Materials

The polypropylene (H110MA) with density of 0.910 g/cc and MFI of 11 g/10 min (measured at 230°C under 2.16 kg load), obtained from Reliance Ltd., India was used as the base matrix for the present study. PP-g-MA was used in this study is 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.

Preparation of PP/MMT nanocomposites and PP/MWNT/MMT hybrid nanocomposites

Melt blending of PP, PP-g-MAH (10wt %) and the nanoclays (Na^+-MMT) of 1, 3, 5 and 7wt% and melt blending of PP, PP-g-MA (10wt %) 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°. Prior to extrusion, the matrix polymer and the nanoclay were dehumidified in a vacuum oven at 60°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°C between feed zones to die zone, followed by granulation in a pelletizer (Fission, Germany) and drying. Same manufacturing parameters and conditions were used for PP/MWNT/MMT hybrid nanocomposites manufacturing. These granules were further injection molded using injection moulding machine (SP 130 Windsor Clocknar Ltd) having clamping force 800kN fitted with a dehumidifier at a temperature range of 195–220°C and mold temperature of 80°C, for preparation of test specimens of tensile, flexural and impact strength as per ASTMD. The codes and composites are summarized in table 1.

Mechanical characterization

Specimens of virgin PP and PP/MWCNT/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 45o as per ASTM-D 256 using impact meter 6545(Ceast. Italy).For analyzing the mechanical properties test specimens were initially conditioned at 23+1°C and 55+2% RH. Five replicate specimens were used for each test and the data reported are the average of five tests. Corresponding standard deviations along with measurement uncertainty values for the experimental data showing the maximum standard deviation is also included.

SEM Analysis

The morphology of the impact fractured surfaces of neat PP and its nanocomposites, the fracture surfaces were coated with thin layers of gold of about 1 A°. All specimens were examined with JEOL, JSM 840A scanning electron microscope with an accelerating of 10kv.

RESULTS AND DISCUSSION

Mechanical properties

The mechanical properties of PP/MMT nanocomposites and PP/MWNT/MMT hybrid nanocomposites are summarized in table 2. As shown in Fig.1.PP/MMT system shows a slight increase in Young's modulus at low filler loading. When the loading of the MMT clay was up to 5 wt% a reasonable increase in stiffness was observed as filler loading increases. The PP/MWNT/MMT hybrid nanocomposites system shows higher increase in Young's modulus at low hybrid nano filler loading. When the loading of PP/MWNT/MMT hybrid nano filler was up to 5 wt% high reasonable increase in stiffness was observed as hybrid nano filler loading increases.

The behavior of the Tensile strength with respect to clay content was significant improvement in the order to that of Young's modulus as shown in Fig. 2. But with respect to hybrid system very good improvement in tensile strength the rate of decrease in the strength reduces between 5 wt% and 7 wt%.Both flexural properties of PP/MMT and PP/MWNT/MMT system was very good significant improvement as shown in Fig.3 and Fig.4.The effect of impact strength studied over a wide range of MMT clay

Table 1. Sample codes and composites

Sample code	Composition (wt %)
PP	PP(100)
PPNC-1	PP(89)+PP-g-MA(10)+MMT(1)
PPNC-3	PP(87)+PP-g-MA(10)+MMT(3)
PPNC-5	PP(85)+PP-g-MA(10)+MMT(5)
PPNC-7	PP(83)+PP-g-MA(10)+MMT(7)
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)

Table 2. Mechanical properties of PP/MMT nanocomposites and PP/MWNT/MMT hybrid nanocomposites

Sample	Tensile properties		Flexural properties		Impact
	Tensile strength (MPa)	Tensile modulus (MPa)	Flexural strength (MPa)	Flexural modulus (MPa)	strength (J/m)
PP	30.10	1152.38	34.20	1246.00	22.33
PPNC-1	32.58	1228.66	35.26	1269.56	30.83
PPNC-3	33.30	1472.17	36.35	1364.96	33.73
PPNC-5	33.60	1569.04	38.05	1412.50	36.53
PPNC-7	33.25	1357.03	34.80	1285.50	28.93
PPHNC-1	37.08	1674.84	37.34	1358.94	34.00
PPHNC-3	37.80	1962.32	38.23	1476.35	41.73
PPHNC-5	38.68	2090.73	39.33	1525.43	43.83
PPHNC-7	38.01	1783.93	38.69	1536.50	32.00

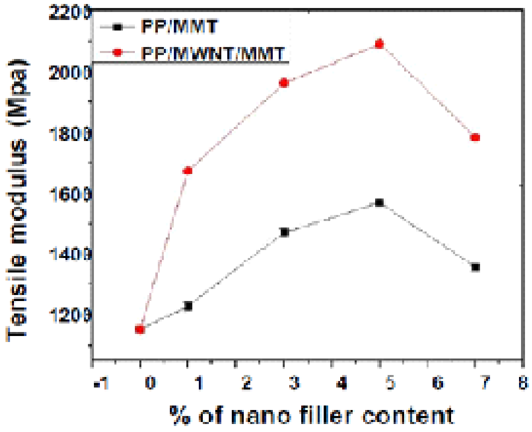

Fig. 1. Tensile modulus for both PP/MMT and PP/MWNT/MMT nanocomposites

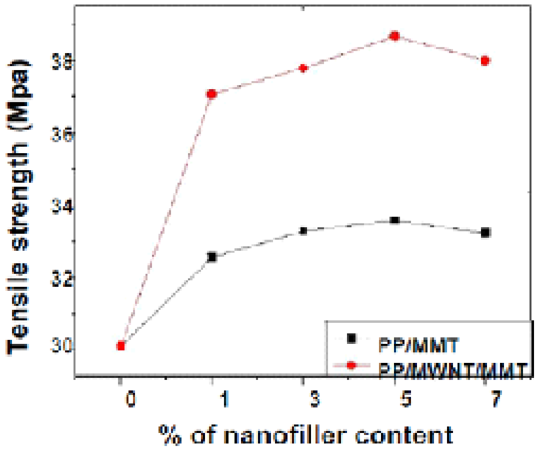

Fig. 2. Tensile Strength for both PP/MMT and PP/MWNT/MMT nanocomposites

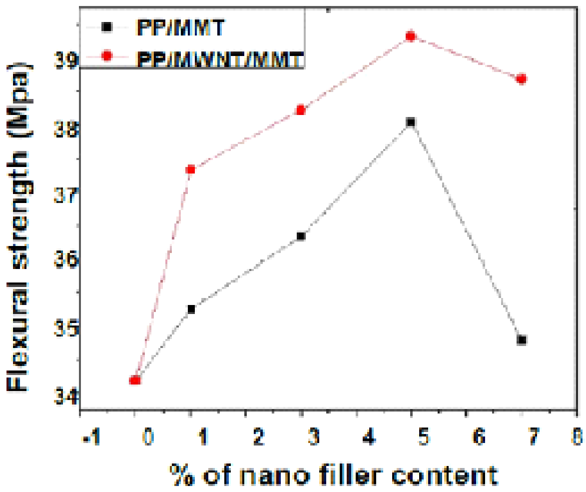

Fig. 3. Flexural Strength for both PP/MMT and PP/MWNT/MMT nanocomposites

and MWNT/MMT hybrid nano filler loading on polypropylene is shown in Fig. 5 very good significant improvement in hybrid nanocomposites over conventional nanocomposites system. From the above results, the tensile modulus and impact strength of hybrid nanocomposites is increased 33% and 20% as compared with the conventional nanocomposites.

SEM analysis

Figure 6 shows the impact fractured surface of PP and its nanocomposites. From figure 6(e) the surface shows a fairly homogenous polymer with minimal high stress zones. The high stress zones depicted by the impact fractured hole size is large and number of holes are less. In figure 6(a, b and c) arrows indicate there is a distinct change in the fractured surface when compared to PP sample. The impact fractured hole size is small and number of holes are more. These structures show several high stress zones which indicate the increased reinforcement of the polymer matrix and good dispersion of the nanoclay in nanocomposites. It is finer and more particulate in nature. This high density grain boundary shows a strengthened matrix. These structural phenomena may be linked to the increase in the strength; modulus, impact strength and hardness of the nanocomposites as shown in table1.In figure 6(d)

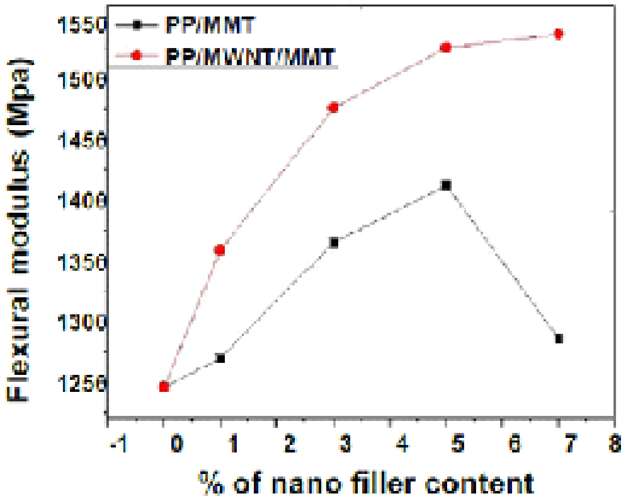

Fig. 4. Flexural modulus for both PP/MMT and PP/MWNT/MMT nanocomposites

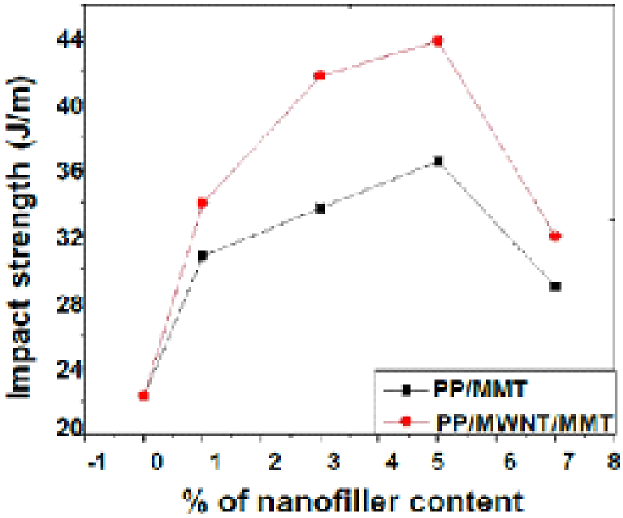

Fig. 5. Impact Strength for both PP/MMT and PP/MWNT/MMT nanocomposites

two distinct structures are seen. One is particulate in nature and the other is a large agglomerated structure. The large agglomeration may be a micron sized clay tactoid caused by poor nanoclay dispersion. The fractured surface shows areas where no dispersion occurred and agglomerated clay sites. These structures impact on the interfacial interactions of the polymer molecules causing poor interfacial adhesion leading to a reduction in mechanical properties and embrittlement in the PP nanocomposite structure. The fracture surfaces of the hybrid nanocomposites were observed using SEM. Fig.6a–d displays some representative SEM images of the fracture surfaces of the notched impact samples. 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

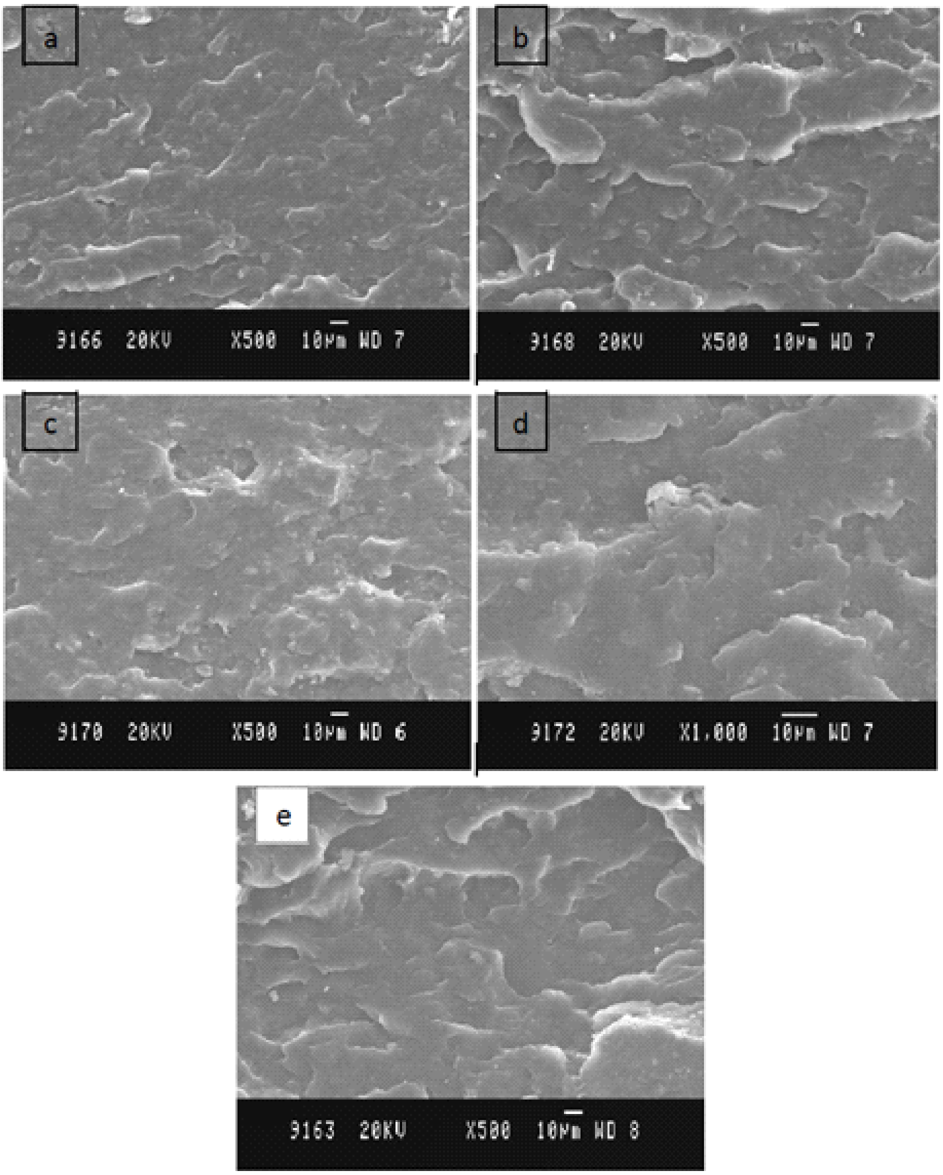

Fig.6. SEM micrographs of nanocomposite fracture surfaces at RT (a) PPNC-1;(b) PPNC-3; (c) PPNC-5; (d) PPNC-7; (e) PP

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

CONCLUSION

PP/MMT nanocomposites and PP/MWNT/MMT hybrid nanocomposites were successfully prepared by employing melt intercalation technique. In this study multiwall carbon nanotubes have been used to improve mechanical performance of PP/MMT nanocomposite due to its higher aspect ratio and surface area which facilitates its better dispersion in the matrix. The tensile modulus and impact strength of PP/MMT nanocomposites system increased 33% and 20% with the incorporation of 5% of hybrid nanofiller. Further good toughness and stiffness were coexistent in the PP/MWNT/MMT hybrid nanocomposites system compared with PP/MMT nanocomposites system.

ACKNOWLGEMENTS

The author would like to thank the Central Institute of Plastics Engineering and Technology, Chennai, India for manufacturing the nanocomposites. The author also would like to thank AMET University, chennai-603112.

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