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Processing and Characterization of Polypropylene Filled with Multiwalled Carbon Nanotube and Clay Hybrid Nanocomposites

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Nanocomposites reinforced with hybrid fillers of carbon nanotubes (CNTs) and clays were developed, aiming at enhancing the dispersion of nanofillers with balanced mechanical properties while lowering the cost of the final product. Polypropylene-based nanocomposites were prepared by the master batch dilution technique with varying combinations of CNTs and clays as fillers by using commercially available highly concentrated master batches of polypropylene/organoclays and polypropylene/multiwalled carbon nanotubes using high-shear twin-screw extrusion. Their mechanical and morphological properties were then evaluated. It was shown that the addition of hybrid filler to polypropylene enhanced the ductility and flexural properties of nanocomposites, confirming the synergistic effect of nanofillers as a multifunctional fillers. The novelty of this work lies in the synergy arising from the combination of two nanofillers with unique dimensions and aspect ratios as well as different dispersion characteristics, which have not been specifically considered previously.

Keywords: Carbon nanotube; Clays; Hybrid nanocomposites; Mechanical properties

INTRODUCTION

The preparation and characterization of carbon nanotube (CNT)-filled polymer nanocomposites have been areas of growing academic and scientific interest because the outstanding properties of CNTs may extend the applications and final uses of polymeric materials. These modern nanocomposites may find applications as structural materials, due to their low density and enhanced mechanical properties and electrical conductivity, and also as electromagnetic induction shielding and dielectric materials.^[1-4] However, major difficulties are found in obtaining the homogeneous dispersion of nanotubes in polymer matrices, most often limiting the performances of the fabricated composite materials.^[4]

Another interesting nanostructural material that has been widely used in various applications is nanoclay. Incorporation of clay platelets as two-dimensional nanofillers in polymeric matrices has been intensively reported in the literature, and it is one of the most studied nanofillers of

today.^[5–8] Its main benefits are good availability, relatively easy surface modification, and low price among nanofillers. Only minor (10 wt.%) nanoclay addition can result in, for instance, lighter weight products maintaining equally strong mechanical properties compared with traditionally filled composites. This is a great benefit to using them in many areas such as the automotive and packaging industries. Other advantages of lower filler content include better surface appearance, enhanced barrier performance, and easier processing. The main challenges affecting the use of nanoclay include difficulties in achieving adequate dispersion and adhesion of this hydrophilic filler to hydrophobic polymer matrices like polypropylene.^[9–11]

Melt compounding is the most interesting technique for the processing of polymers as it provides cost effectiveness, fast production, and environmental benefits since it is free of solvents; therefore, it is a promising method for producing polymer nanocomposites as the tendency of nanofillers to form aggregates may be minimized by appropriate application of shear during melt mixing.^[12] Melt mixing methods have nowadays been mainly concentrated on the twin-screw extrusion process, but laboratory-scale batch mixers and microextruders are also being used. Batch mixers are conventionally utilized in preparation of master batches, but the use of twin-screw extruders is becoming more common in this era of nanocomposite research.^[13,14]

Among the most versatile polymer matrices, polyolefins such as polypropylene (PP) are the most widely used thermoplastics in food packaging, automobile, and other industrial sectors because of its well-balanced physical and mechanical properties and easy processability at a relatively low cost, making them attractive materials.^[15] Therefore, PP has been a popular matrix used to reinforce both clays and multiwalled nanotubes. The literature indicates that the extent of property improvement in nanofiller-reinforced polymer composites generally depends on several factors such as volume fraction of fillers, dispersion and/or exfoliation nanofillers in polymer matrix, type of polymer employed, and fabrication method, among others.

Increasing usage of nanofillers in academic research laboratories and in industrial workshops will cause emissions to the environment and result in an increase of human exposure to nanofillers. Upon exposure, these fillers may reach the lungs they can exert serious toxicity by inflammatory and fibrotic reactions.^[16] Therefore, handling of nanosized particles in plastic parts manufacturing workshops is often a key issue. These difficulties represent a cause of concern for human health and indicate that strict preventive and protective measures should be taken to limit inhalation exposure to nanomaterials in occupational settings. Using a commercial master batch technique in the production of polymer nanocomposites is often favored because it reportedly leads to more effective dispersive mixing.^[17,18] It is also a dust-free process, so there are lower health and safety risks than with the bulk nanotube dispersion process. Other benefits of using the master batch technique include more effective dispersive mixing and more precise control of filler concentration in the final compound compared with direct mixing, particularly for easily dusting fillers such as powdery nanoclays.

Considering the special structures and properties of CNTs and layered silicates coupled with the master batch dilution process, it is very interesting to prepare CNT/clay hybrids, which are anticipated to have promising applications in industrial sectors. Recently, this kind of hybrid has been used to prepare polymer nanocomposites through the melt-mixing or solution mixing process.^[19–22] The synergistic effects of CNTs and clay have been found to improve the properties of polymer nanocomposites, such as mechanical properties,^[19,20] flame retardancy,^[21,22] and electrical conductivity.^[23] These property improvements are attributed mainly to the increase in dispersion of fillers and the formation of a network-like structure and the interaction between CNTs and

clay.^[22,23] Undoubtedly, the key challenge remains to reach a high level of nanoparticle dissociation (i.e., either to delaminate the silicate nanoplatelets or to break down the bundles of aggregated carbon nanotubes) and their fine dispersion upon melt blending within the selected polymer matrix.

The present contribution deals with the preparation and properties of polypropylene-based nanocomposites filled with organoclays and/or carbon nanotubes. These two types of nanofillers were dispersed within the molten polymer by conventional melt processing, by diluting commercially available master batch materials. The morphology and mechanical properties of different ternary nanocompositions were studied. For the sake of comparison, corresponding binary compositions of PP filled with either clays or MWNTs were also investigated and reported.

EXPERIMENTAL METHODS

Composite Fabrication

Multiwalled carbon nanotubes (MWNT) and/or clay-filled polypropylene hybrid nanocomposites were produced by mixing homopolymer PP granules (Polychim polypropylene with a melt flow index of 12 g/10 min. at 190°C) with commercial master batches: Plasticyl-2001, containing 20 wt.% of MWNT (Nanocyl S.A., Belgium), and PolyOne MB-1001, containing 40 wt.% of clays (PolyOne Inc., USA). The dilution was done in a co-rotating twin-screw Clextral extruder at a barrel temperature of 195°–210°C and a screw speed of 50 rpm. During melt extrusion, ventilation was used to remove trapped air in the composites. For mechanical testing, nanocomposite granules were injection-molded (using a Krauss Maffei KM80-160E injection molding machine) into standard test specimens for tensile, impact, and flexural tests. The temperature profile ranged from 200° to 215°C and the mold temperature was kept at 25°C. The holding pressure and speed were 300 bar and 100 rpm, respectively, with a throughput of 50 cm³/s. The final nanocomposites contained 2 and 4 wt.% MWNTs and/or clays in the PP matrix. The composition and abbreviations of the material are presented in Table I.

Mechanical Characterization

Mechanical performance of all compounded materials was evaluated from injection molded specimens. Tensile properties of the molded dogbone specimens were tested using an Instron

TABLE I
Composition and abbreviations of the nanocomposites

<i>Composition of nanocomposites</i>	<i>Abbreviation</i>
Neat PP	PP
2 wt.% MWNT + PP	MP-2
4 wt.% MWNT + PP	MP-4
2 wt.% Clay + PP	CP-2
4 wt.% Clay + PP	CP-4
1 wt.% MWNT + 1 wt.% clay + PP	MCP-2
2 wt.% MWNT + 2 wt.% clay + PP	MCP-4

machine at a crosshead rate of 10 mm/min at 25°C according to the ISO 527 standard. The tensile strength and modulus could be directly obtained from the stress-strain curves by the provided software. Flexural properties of the nanocomposites were determined by three-point bending tests per the ISO 178 standard at a thickness-to-span length ratio of 1:16. Charpy notched and un-notched impact tests were carried out per the ISO 179-1 standard. All the reported values were calculated as averages over five specimens for each composition.

Morphological Characterization

For scanning electron microscopy (SEM), injection-molded hybrid nanocomposites were cryofractured. A thin layer of gold was sputter deposited onto the sample. Electron microscopy imaging of the nanocomposite was performed under high vacuum with a Hitachi S-4300SE/N SEM instrument operating at 5 kV.

RESULTS AND DISCUSSIONS

Mechanical Properties

Mechanical properties of the nanocomposites measured from the tensile test are presented in Table II. PP/MWNT and PP/clay binary nanocomposites showed an increase of tensile modulus and tensile strength with increase in nanofiller content, as shown in the table. The percentage increases of Young's modulus are 25% and 40.2% and those of yield stress are 35% and 46% for MP-2 and MP-4 nanocomposites. For PP/clay nanocomposites, the percentage increases of Young's modulus are 25% and 29% and those of yield stress are 22% and 29% for CP-2 and CP-4 respectively. Among the binary nanocomposites, PP/MWNT composites exhibited brittle behavior at high loading, while PP/clay nanocomposites still maintained some degree of ductility. Such a behavior might suggest better layered silicate dispersion for PP/clay nanocomposites than for MWNTs throughout the matrix, at least at the same filling level. However, using both clay and MWNTs as hybrid fillers dramatically increases the tensile properties of PP. The MCP-2 and MCP-4 nanocomposites had 40 and 50% increase in tensile modulus and 37 and 54% increase in the tensile strength respectively, with a slight reduction in elongation compared to the neat PP. This is probably due to the increased rigidity of polymer chains, resulting from

TABLE II
Tensile properties of binary and ternary nanocomposites

<i>Material</i>	<i>Tensile strength (MPa)</i>	<i>Tensile modulus (MPa)</i>	<i>Strain at break (%)</i>
Neat PP	28.2 ± 2.1	1280 ± 20	620 ± 15
MP-2	35.5 ± 0.5	1728 ± 15	154 ± 08
MP-4	37.6 ± 0.8	1881 ± 15	38 ± 05
CP-2	35.2 ± 0.5	1562.5 ± 12.2	185 ± 12
CP-4	36.5 ± 0.7	1734.2 ± 10.3	168 ± 10
MCP-2	38.89 ± 0.3	1772.8 ± 12	210 ± 12
MCP-4	39.31 ± 0.4	1914.5 ± 13	165 ± 13

the restriction effect of nanofillers. Further, it is very interesting to see that the ternary composites of PP/MWNT/clay have not only higher tensile strength and modulus but also a slightly larger elongation than the corresponding binary nanocomposites.

The flexural strength and modulus of neat PP and binary and ternary nanocomposites are shown in Figure 1. All the tested samples exhibit a bending without ultimate breaking in the tested strain range. From Figure 1, it can be seen that flexural strength of nanotube-filled composites is more than that of clay-filled nanocomposites. However, clay-filled PP nanocomposites showed better flexural modulus than nanotube-bearing nanocomposites. A unique nanofiller effect can be seen in hybrid nanocomposites, where both flexural modulus and strength are higher than in corresponding binary composites. The MCP-2 and MCP-4 nanocomposites showed an increase of 58 and 65% in flexural modulus and 49 and 64% increase in the flexural strength, respectively, when compared to neat PP. These improvements have been attributed to the clay-assisted dispersion of nanotubes in the PP matrix. Therefore, the finely dispersed MWNT-clay filler throughout the polymeric matrix and the strong adhesion between the hybrid filler and the PP matrix are responsible for the significant reinforcement of the mechanical properties of the hybrid nanocomposites.^[19]

Figure 2 shows the notched and un-notched impact strength values of the neat PP and its nanocomposites. The un-notched impact strength in all the filled nanocomposites is less than that of neat PP. The impact strength of binary composites further decreases with increase in filler content. But when hybrid composites are considered, the impact strength of hybrid composites at lower filler content (i.e., MCP-2) is higher than that of corresponding binary composites samples (i.e., MP-2 and MC-2). At higher filler content, the impact strength of hybrid composites was less than that of corresponding binary composites. The improvement in impact strength at lower filler content over that of binary samples could be attributed to the exfoliation of clays and good dispersion of nanotubes, which in turn increases the ductility of the material.^[24,25]

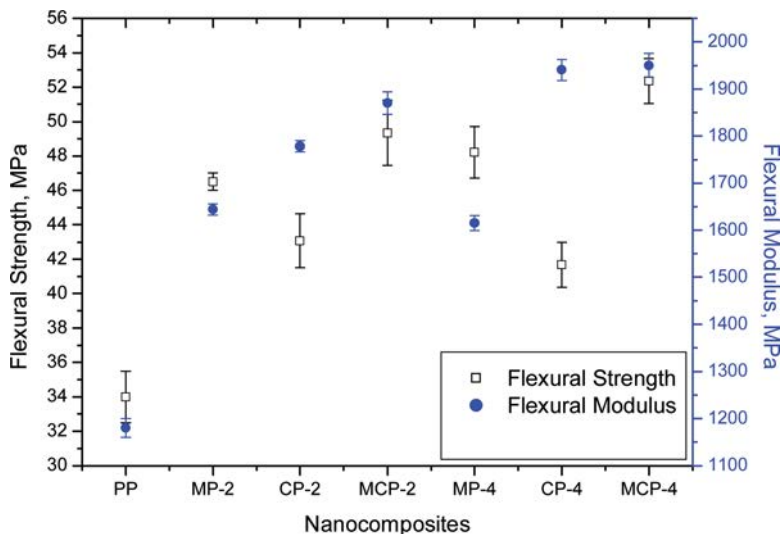


FIGURE 1 Flexural properties of binary and ternary nanocomposites.

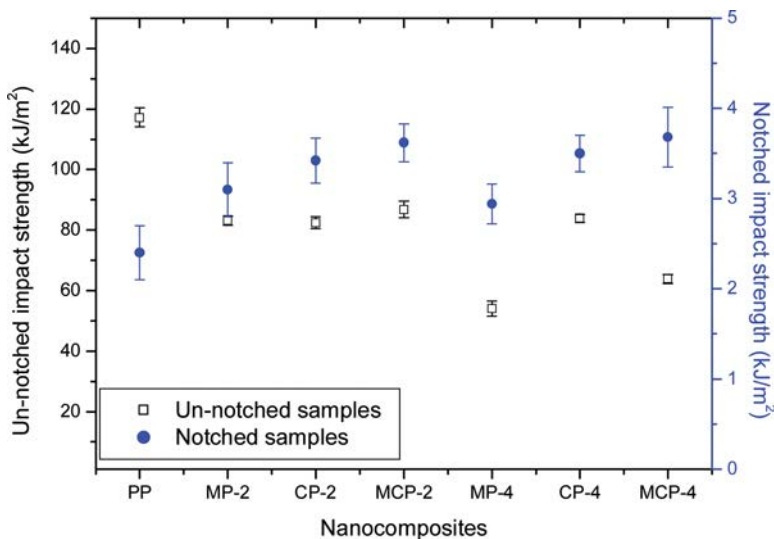


FIGURE 2 Impact properties of binary and ternary nanocomposites.

Decrease at higher filler content, i.e., in MCP-4, is due to the presence of a few nanotube agglomerations and clay tactoids in the PP matrix, which leads to crack initiation and subsequent failure. The impact strength of notched specimens of binary and ternary nanocomposites increased as the filler content increased. However, hybrid composites MCP-2 and MCP-4 showed an increase of 50 and 53% respectively when compared to neat PP. This increase is much higher than for binary composites. Notched impact behavior is controlled to a great extent by factors affecting the propagation of the fracture initiated due to the stress concentration at the notch tip. Increased impact energy in ternary nanocomposites is due to the enhanced dispersion and distribution of individual nanotubes and exfoliation of clays in the matrix. In addition, nanotube bridging, breaking, and pullout can consume additional energy,^[26] and the large aspect ratio of nanofillers would cause complex matrix-filler interaction during filler bridging, breaking, and pullout, which probably promotes the local plastic deformation of the matrix.

Morphological Characterization

The uniform dispersion of nanofillers in polymeric matrices is one of the most important factors for producing nanocomposites with better performance. In the present study, SEM was used to observe the dispersion of the MWNTs and clay-filled hybrid nanocomposites. Figure 3(A) shows a typical fracture surface of the nanocomposite MCP-2 (containing 1 wt.% MWNT and 1 wt.% clay filler) after impact testing. It clearly shows the uniform distribution of small bright dots and lines, which are the ends of the broken MWNTs on the fracture surface.

In Figure 3(B), a very small area (marked ‘a’) is observed with a higher density of MWNTs, probably from the master batch, a highly concentrated nanotube aggregate left over during melt processing. A further observation is that most MWNTs are broken upon failure rather than just

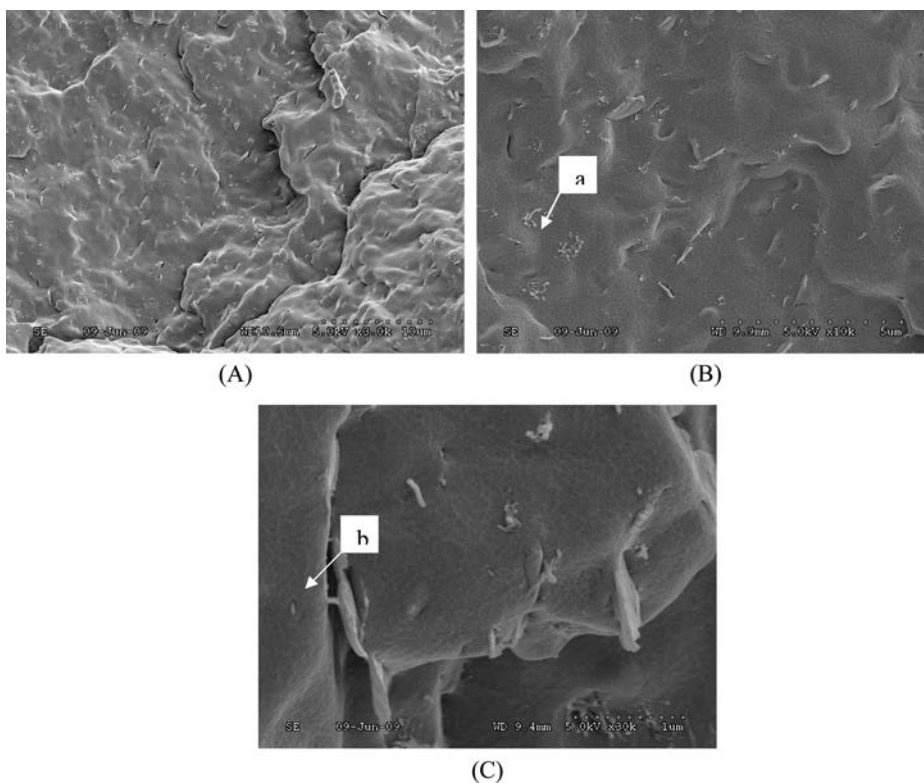


FIGURE 3 SEM images showing typical morphology of the failure surface of hybrid nanocomposites.

pulled out of the matrix, which is clear evidence of a strong interfacial adhesion between MWNTs, clay fillers, and the PP matrix. An observation can be made of a nanotube interconnected with two polymer lumps (marked “b” in Figure 3(C)). This is another indication of the strong interaction between the MWNTs and the PP matrix. From Figure 3(C), one can clearly see the separately distributed MWNTs, and, more interestingly, clay platelets connected to MWNTs are also observed. The SEM image clearly exhibits the adhered nanotubes and clay platelets on the matrix. Therefore, the finely dispersed nanotube-clay filler throughout the polymeric matrix and the strong interaction between the hybrid filler and PP matrix are responsible for the significant reinforcement of the mechanical properties of the prepared composite.

CONCLUSIONS

The master batch dilution technique has been successfully utilized for the preparation of carbon nanotubes and clay platelets filled polypropylene nanocomposites. A synergistic effect of two-dimensional clay platelets and one-dimensional nanotubes on the PP matrix has been observed. With incorporation of smaller quantities of clays and nanotubes, the tensile strength

and Young's modulus were significantly improved, by about 50 and 54%, respectively, compared with neat PP. Further, it is very important to note that the ternary composites showed larger elongation than the corresponding binary nanocomposites. Flexural properties of the hybrid were largely higher than those of binary composites and neat PP. Hybrid nanocomposites showed better Charpy impact resistance than the individual filler-filled nanocomposites. Scanning electron microscopic pictures indicate an effective dispersion of nanotubes by the extrusion process using the master batch dilution technique. Thus, preparation of nanocomposites by the master batch dilution technique is an excellent method to obtain well-dispersed CNTs, while limiting the handling difficulties (potential health and safety hazards) in plastics processing industrial workshops and also offering greater flexibility and cost-effective ability to adapt the nanofiller content to targeted applications. This opens the way to wider industrial utilization of these materials.

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