

The Influence of Processing Conditions on the Electrical Properties of Polypropylene Nanocomposites Incorporating Multiwall Carbon Nanotube

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Abstract

The recent commoditisation of multiwall carbon nanotubes (CNT) in particular, as substitute for conductive carbon black (CB) based composites has attracted immense interests from different sector of industries. Typically, CNT can achieve similar or greater electrical property at a fraction of CB loading level, therefore retaining the ease of processing. It appeals especially in applications requiring stringent cleanliness property where contamination is detrimental to materials performance *e.g.* high-end electronics. The key challenges to successful fabrication of CNT thermoplastic nanocomposites that combined outstanding electrical and mechanical properties rest in understanding of its processing behaviour to obtain high degree of percolating morphology (*i.e.* inter-connective network structure of CNT in polymer matrix). In this paper, we investigated the influence of melt mixing and injection moulding parameters on the electrical conductivity of polypropylene (PP) CNT nanocomposites. The influence of polymer viscosity was also examined. Our results showed that depending on molecular weight and processing conditions, polypropylene can achieve some remarkably low percolation threshold of 1.4 and 1.8 wt% CNT, giving a volume and surface resistivities of $7.4 \times 10^2 \Omega\text{-cm}$ and $1.1 \times 10^5 \Omega/\text{sq}$ respectively. We found in this study the optimum conductivity for PP was achieved using a combination of processing conditions defined by high screw speed (above 200 rpm), high mixing temperature, moderately short mixing residence time (3-6 mins) and high mould temperature. Results also indicated that the exfoliation behaviour, given by conductivity measurements, is greatly influenced by types of intercalation pathway of polymer into CNT agglomerates.

Introduction

The rapid expansion of high-tech economy activities requires constant innovation of new high performance materials to meet the increasingly rigorous service conditions. The recent introduction of various nanofillers offering multifunctional properties has extended the scope of industrial opportunities that cannot be met using traditional fillers. Presently, one of the most promising extending agents is carbon nanotubes. Multi-wall carbon nanotube based nanocomposites has already found wide range of engineering usage, especially in the high-end electronics and automotives systems and, is expanding rapidly to other areas requiring exceptional electro-conductive/dissipative, sensing, energy storage, thermal dissipative, flame retardant and EMI shielding properties [1-4]. Because of their low loading level, typically between 1 and 5 wt%, processability, recyclability and mechanical properties of the polymer can be retained.

The pricing factor that was once a main entry barrier was driven down significantly owing to scale-up production effort led by major players especially in Europe. Today, carbon nanotubes are available in the marketplace in powder, compound or masterbatch forms at competitive prices.

One of the greatest attractions of CNT based composites to polymer producers lies in their processability using existing polymer processing equipments, most commonly extrusion and injection moulding. However, a major restraint in a broad market adoption of this new class of materials is the variation of electrical conductivity due to CNT sensitivity to processing conditions. To pave way for wider industrial acceptance of carbon nanotube thermoplastic systems, it is important for producers of carbon nanotubes to understand the requirements of end-users and, customise and sharing their processing expertise with compounders and plastics converters.

Materials and Methods

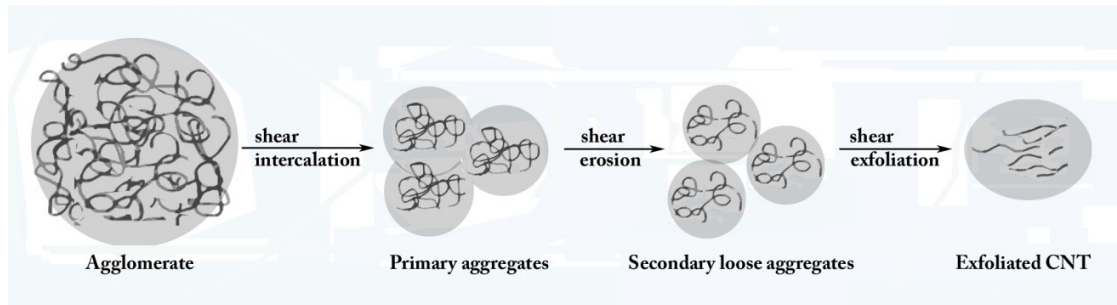
The carbon nanotube used in this study tradename NC7000 is a commercial product manufactured by Nanocyl S.A. NC7000 is a high conductivity grade of MWCNT, characterised by an average diameter of 9.5 nm, a mean length of 1.5 μm , a carbon purity of 90% and surface area of 250-300 m^2/g . Three different polypropylenes were investigated, characterised by different viscosity; (a) LPP low viscosity, (b) MPP medium viscosity and (c) HPP high viscosity.

PP CNT nanocomposites were prepared by either direct mixing with MWCNT or through dilution from masterbatch. Masterbatch of LPP and MPP containing 15 wt% MWCNT were produced using a Leistritz co-rotating twin-screw extruder adapted with a proprietary screw profile designed for high loading dispersion. Both mixing and dilution process were performed using a DSM Xplore Micro 15cc twin-screw microcompounder. Test specimens of dimension 80 x 10 x 4 mm^3 were injection moulded using a DSM Xplore 12cc injection moulding machine. Measurement for volume and surface resistivities were performed in accordance to the ASTM D449 6-87 and IEC 167 standard respectively.

Results and Discussions

Figure 1 illustrates the relationship between mixing screw speed and volume resistivity of 5 wt% loaded HPP produced by direct compounding from CNT powder. Compounding was performed at 175°C for 8 mins and the mould temperature was maintained at 50°C. Results showed that resistivity increases with increasing screw speed until 200 rpm and then decreases. A lower screw speed may allow an annealing effect to take place which could promote melt intercalation of polymer chain into the CNT agglomerate. Given by sufficient mixing residence time, the exfoliation of CNT may be governed predominantly by thermodynamic erosion process. The decrease in resistivity observed at higher limit of the screw speed tested could be attributed to effective delamination of agglomerates into primary aggregates. Under intense shearing these primary aggregates quickly developed into loosely entangled secondary aggregates and easing the exfoliation process.

The mechanism characterising exfoliation pathway of CNT may be partly adapted from literatures describing exfoliation process of nanoclay in thermoplastic melt during an extrusion process [5-6]. In this process, the morphological evolution during polymer melt intercalation (volume expansion given by a diffusion process) depends on the path and path rate of mass melt transport into the CNT agglomerate. A CNT agglomerate may be more or less visualised as a bulk agglomerate made up of sub-agglomerates which in turn, consisted of domains of micro-aggregates. For intercalation to occur, polymer must first be transported to the sub-agglomerates interface and then to the galleries within the micro-aggregates. At lower screw speed, mass transport through the micro-aggregates is comparable to sub-agglomerates, therefore facilitate for melt intercalation of the bulk agglomerates. Given by sufficient intercalation, the bulk agglomerates are exfoliated through an erosion process. In this case, the formation of hybrid is dependent on the sub-agglomerate size. However, at higher screw speed, because the transport through the micro-aggregates is slower than sub-agglomerates at the agglomerate/polymer interface, physical delamination of sub-agglomerates into primary aggregates plays an important role and the kinetics of hybrid formation is less dependent on the sub-agglomerate size.



Schema illustrates possible exfoliation pathway of CNT agglomerates during a melt mixing process

Figure 2 shows the effect of mixing temperature from 155-220°C on the volume resistivity of 5 wt% loaded HPP, compounded at 225 rpm. Resistivity was observed to decrease with increasing mixing temperature. This may be attributed to that a higher mixing temperature generally improves diffusion of polymer chain into the CNT agglomerate, resulted in a more improved melt intercalation process. The melt intercalation process was further enhanced by shear thinning (viscosity reduction) of polymer due to the more aggressive shearing of polymer chain by the screw. Additionally, the high shearing action accelerated the delamination of intercalated agglomerates into loosely entangled primary and secondary aggregates and therefore, alleviated the CNT exfoliation through a slippage process. In this case, a combination of high mixing speed and high mixing temperature appears to offer good balance between thermodynamic erosion, physical delamination and entanglement slippage in obtaining a most improved dispersion of CNT in the polymer matrix.

The influence of mixing residence time on the volume resistivity of 5 wt% HPP was studied in Figure 3. In order to discriminate the influence of mixing speed, screw speed was maintained at 225 rpm. Results showed optimum mixing residence time in between 3 and 6 min, given by lowest resistivity values. Under-mixing (below 3 mins) may result in poor dispersion of the CNT within the polymer matrix while over-mixing (above 6 mins) could cause either re-agglomeration or rupture of the CNT therefore, reduces conductivity (due to sparser population of inter-connecting CNT networks).

The relationship between mould temperature and volume resistivity of 5 wt% HPP is shown in Figure 4. It is clear that a higher mould temperature have a positive effect on the materials conductivity. This may partly be attributed to an annealing effect which mediated with the chain relaxation process. During relaxation, polymer chain reorients and therefore, improves reconciliation of flocculated CNT particles to form a conductive network bridge. In addition, increase in mould temperature can cause an increase in the mean crystalline size (provided below certain critical value) that in turn, may act as a conduit to direct CNT particles closer together to form a conductive network bridge. This conduit effect may also in part be attributed to different crystallisation behaviour at higher mould temperatures.

The influence of mould cycle time on volume resistivity of 5 wt% HPP was studied in Figure 5. In order to accentuate the crystallisation effect and discriminate contributions from other parameters, mould temperature was set to as high as 115 °C. Mould cycle time was varied from 1 to 20 mins. Surprisingly, resistivity remained somewhat constant independent of the length of mould cycle time. One possible explanation is that the CNT particles may have acted as primary nucleating agent but they intervened with the secondary spherulite growth process. In this case, crystallinity would be roughly constant since contribution to the polymer crystalline phase was derived for most part from primary nucleation process.

The electrical percolation curves for volume and surface resistivities of LPP are plotted in Figure 6 and 7 using an optimised mixing and moulding conditions derived from previous results. LPP nanocomposites were processed through a masterbatch dilution process. Results showed a remarkably low percolation threshold for volume and surface resistivities at 1.4 and 1.8 wt% respectively. Their values are $7.4 \times 10^2 \Omega \cdot \text{cm}$ and $1.1 \times 10^5 \Omega/\text{sq}$. More impressively, a volume resistivity as low as 74.8 and 5.65 $\Omega \cdot \text{cm}$ were achieved at just 1.8 and 3.5 wt% and, surface resistivity of 46.4 Ω/sq was obtained at only 3.5 wt% CNT loading.

For investigation of the effect of polymer molecular weight (viscosity) on resistivity, processing was carried out using same conditions as LPP to produce electrical percolation plots of MPP. MPP was also prepared by masterbatch dilution. The volume and surface percolation occurred at 2 and 3 wt% of CNT loading, higher than that for LPP. This would confirm that a lower molecular weight polymer is more efficient in dispersing CNT particles. This corroborated the exfoliation pathway schema depicted earlier and results pertaining the effect of screw speed and mixing temperature. A lower the molecular weight polymer (as long as above certain critical value) is more effective in wetting the interface boundary of the CNT agglomerate and therefore attaining a greater degree of melt intercalation. When coupled with high screw speed and mixing temperature, rapid delamination of intercalated agglomerates resulted in development of a more loosely entangled primary aggregates that would mediate the exfoliation process. In addition, shorter polymer chain would reduce the constriction effect on CNT that eases formation of more improved percolation network and. This resulted in an overall increase in the materials conductivity.

Conclusions

This work summarised how the collective influence of processing conditions during a twin-screw extrusion process can determined exfoliation behaviour of CNT and in turn, dispersion morphology and conductivity of PP CNT nanocomposites. In this study we found the combination parameters (within processing windows of PP) that gave the most improved electrical property was described by high screw speed, high mixing temperature, moderate mix residence time and high moulding temperature. The effect of mould cycle time is not obvious, at least from this study. Generally, a lower molecular weight polymer (as long as above certain value) is more effective in dispersing the CNT particles, provided process conditions are balanced.

References

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Case Study

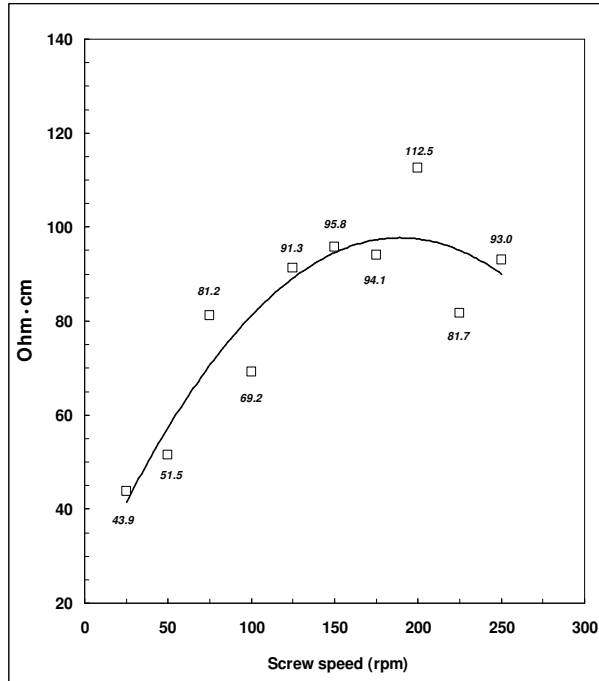


Figure 1 The influence of mixing screw speed on volume resistivity of HPP nanocomposites

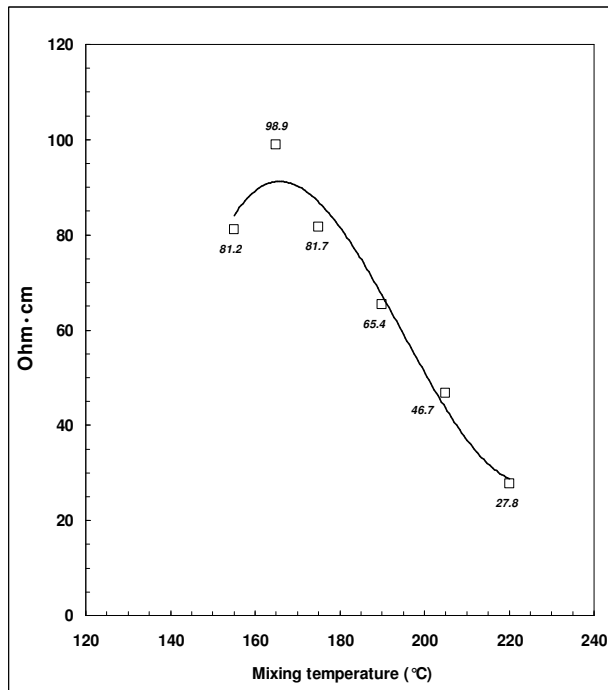


Figure 2 The influence of mixing temperature on volume resistivity of HPP nanocomposites

Case Study

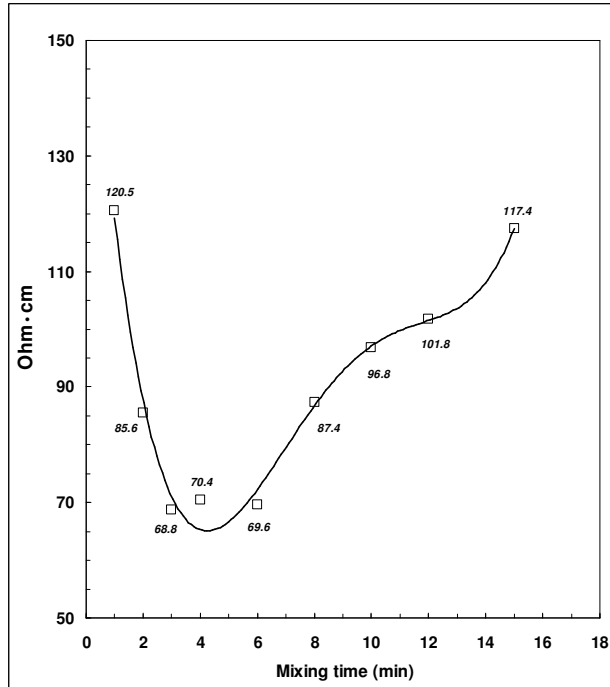


Figure 3 The influence of mixing residence time on volume resistivity of HPP nanocomposites

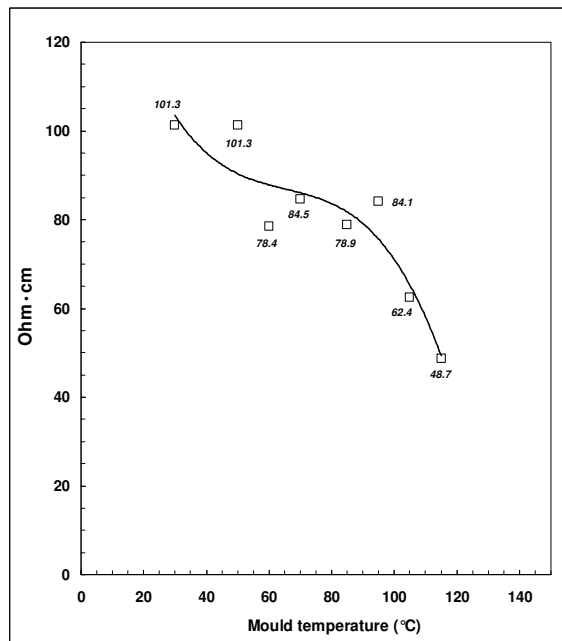


Figure 4 The influence of mould temperature on the volume resistivity of HPP nanocomposites

Case Study

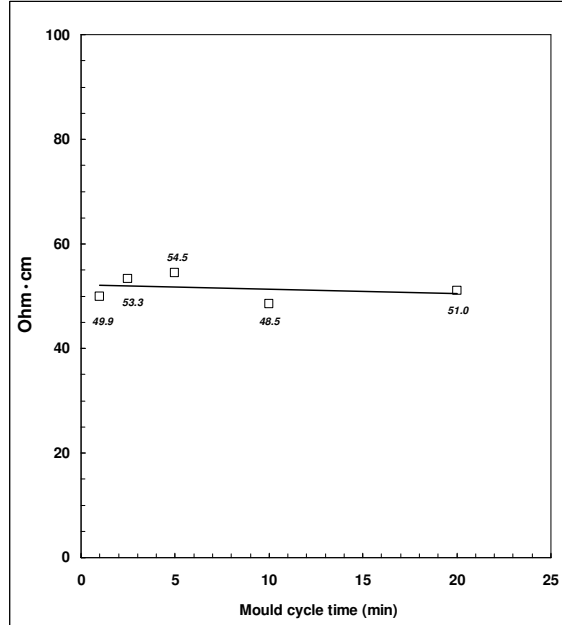


Figure 5 The influence of mould cycle time on volume resistivity of HPP nanocomposites

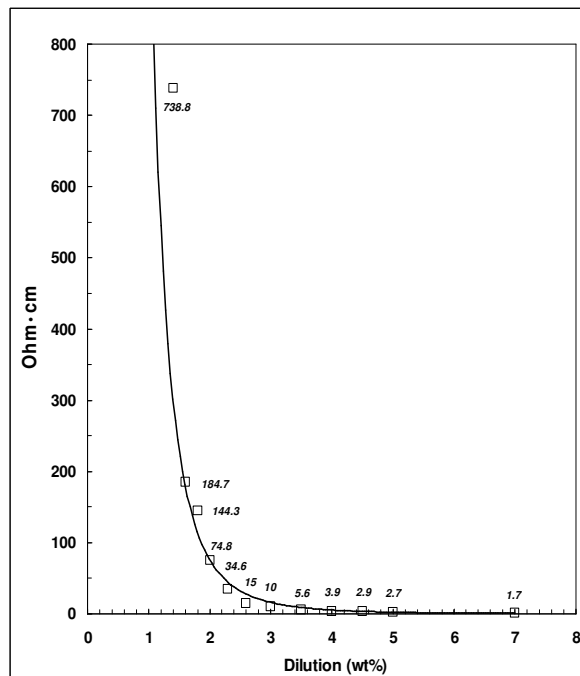


Figure 6 Electrical percolation curves of volume resistivity of LPP nanocomposites

Case Study

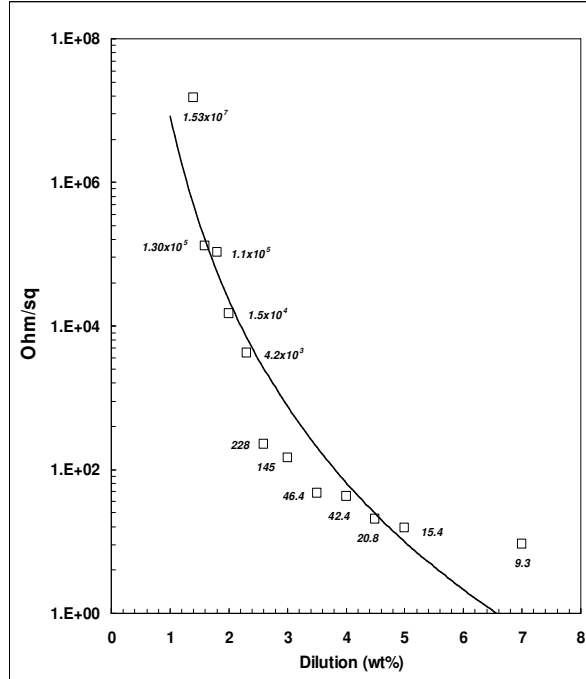


Figure 7 Electrical percolation curves of surface resistivity of LPP nanocomposites