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Masterbatch-based multi-walled carbon nanotube filled polypropylene nanocomposites: Assessment of rheological and mechanical properties

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ABSTRACT

Polypropylene (PP)/multi-wall carbon nanotubes (MWNTs) nanocomposites were prepared by diluting a PP/MWNT masterbatch by melt compounding with a twin screw extruder and prepared nanocomposites were characterized for their rheological, mechanical and morphological properties in terms of MWNT loading. The rheological results showed that the materials experience a fluid–solid transition at the composition of 2 wt.%, beyond which a continuous MWNT network forms throughout the matrix and in turn promotes the reinforcement. The tensile modulus and yield stress of the nanocomposites are substantially increased relative to the neat polypropylene. Nanotube reinforcement thus enhanced the yield stress, while reducing the ductility. The same behavior is observed in flexural tests. Charpy impact resistance of the notched samples increases slightly by the addition of MWNT, while impact resistance for the un-notched samples decreases with the addition of MWNTs. Finally, optimum in mechanical properties was observed at 2 wt.% MWNTs, which is near the rheological percolation threshold. From transmission electron microscopic (TEM) and scanning electron microscopy (SEM) images, it was observed that nanotubes are distributed reasonably uniformly indicating a good dispersion of nanotubes in the PP matrix. These results reveal that, preparation of nanocomposites from masterbatch dilution is an excellent method to obtain well-dispersed CNTs, while limiting the handling difficulties in plastics processing industrial workshops.

1. Introduction

Carbon nanotubes (CNTs) have generated a great deal of interest since Iijima announced his discovery of CNTs using high resolution TEM in 1991, due to their excellent physical and mechanical properties [1]. Since CNTs are known to have an extremely high Young's modulus and tensile strength [2], they tend to be used as reinforcement in polymers to form nanocomposite materials [3,4]. Carbon nanotubes have a tendency to form agglomerates during synthesis because of van der Waals attraction between nanotubes. In the composites, these agglomerations decrease the surface area and disturb the formation network structure which is essential to improve mechanical properties and the main task of processing is to dissolve such agglomerates as good as possible. Therefore, uniform dispersion of the nanotubes is required to realize the potentiality of the nanotubes as reinforcing fillers [5–10]. Common methods for the preparation of CNT filled polymer composites include in situ filling polymerization [11], solution mixing [12] and melt blending [13]. In situ polymerization and solution mixing techniques have many limitations, including that they may not be commercially viable and are environmentally contentious. On the other hand melt processing of nanocomposites provides the cost effectiveness, fast production and environmental benefits due to free of solvents and therefore, this technique is a promising method to produce CNT based nanocomposites as the tendency of CNTs to form aggregates may be minimized by appropriate application of shear during melt mixing [3]. Among several melt mixing processes, extrusion process has captured considerable interest due to its industrial importance and its ability to disperse the nanotubes in a polymer matrix [14]. Among the most versatile polymer matrices, polyolefins such as PP is 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 that makes them a excellent material [15]. Therefore, PP has been a popular matrix used to reinforce both single-wall [16–18] and multiwall [19–21] nanotubes. The reported results for these nanocomposites have been mixed, especially for mechanical properties, where Bhattacharyya et al. [16] reported no significant improvement in mechanical properties, and others have shown moderate improvements in tensile strength, but decreased toughness [18]. Most recently, Zhao and co-workers [22] reported the substantial increase of tensile modulus (Young's modulus) and strength by adding small amount of MWNTs to PP matrix. However, the addition of CNTs can cause significant change of viscoelasticity for the

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nanocomposites. Much research has been done on the rheological behavior of polyolefins/nanotube nanocomposites. Some researchers reported a transition to solid-like response at low oscillation frequencies in polymer nanocomposites containing carbon nanotubes [23–27]. This non-terminal solid-like rheological behavior has been attributed to a filler network formed in the nanocomposites. The formation of the network structure is strongly depended on the concentration and dispersion of nanotubes in polymer matrix [24]. Many properties such as electrical conductivity, mechanical strength and thermal stability are strongly affected by the network structure which can restrain the mobility of the polymer chains in polymer/CNT nanocomposites [26]. The extent of property improvement in CNT filled polymer composites generally depends on several factors such as volume fraction of fillers, dispersion of CNTs in polymer matrix, type of polymer employed and fabrication method, etc.

The prospective widespread usage of CNT in industrial workshops will cause emissions to the environment and result in an increase of human exposure to CNT. Upon exposure, CNTs may reach the lungs they can exert serious toxicity by inflammatory and fibrotic reactions [28]. Therefore, handling of CNTs in plastic parts manufacturing workshops is however 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 CNTs in occupational settings. Using commercial masterbatch in the production of CNT based polymer nanocomposites would be a better choice as it offers a dust free, no health and safety risks in comparison to bulk nanotube dispersion process. Other benefits of using masterbatch include elimination of dispersion difficulties, formulation development and easy handling.

Therefore, most of the durable goods manufacturing industries naturally prefer this processing route and the fluffy MWNT material is bounded in the polymer and, thus, easier to handle. Furthermore, the viscosity and, with that, the applied stress to the primary agglomerates during masterbatch production is quite high due to the high loadings, whereby the dispersion process is enhanced [29]. Importantly, the dispersion of MWNT in masterbatches should be ascertained, the dilution process has to be carried out under appropriate processing conditions to distribute the filler and avoid masterbatch aggregates in the nanocomposites. There are reports in the literature which examine the dilution of MWNT containing masterbatches [30–41]. However, literature survey reveals that, reports on the detailed investigations on the properties of MWNT/PP masterbatches are limited [42,43] when compared to the studies of nanocomposites prepared by direct incorporation of MWNT in PP [16–22,27] and this prompted us to take up this work. Moreover, distribution of masterbatch and subsequent dispersion of nanotubes in the polymer matrix after processing needs to be ascertained. Particularly in case of polypropylene, which has low interactions with nanotubes, the main problem is that primary aggregates in the base nanotube material are not wetted and dispersed good enough and remains in agglomerates. Therefore, in the present work polypropylene-multi wall carbon nanotubes nanocomposites were produced with varying MWNT content by diluting a commercial PP/MWNT masterbatch in a twin screw extruder. The prepared nanocomposites are characterized for their rheological and mechanical properties.

2. Experimental methods

2.1. Composite fabrication

Polypropylene (PP)-multi wall carbon nanotubes (MWNT) nanocomposites were produced by mixing homo PP granules (Polychim polypropylene with a melt flow index of 12 g/10 min. at 190 °C) with the commercial masterbatch "Plasticyl-2001" containing 20 wt.% of MWNT produced by extrusion process (supplied by Nanocyl S.A., Belgium. The specifications of MWNTs in the masterbatch are as follows: average diameter is 9.5 nm, average length of the nanotubes is 1.5 μm and purity > 90%). The dilution was done in a co-rotating twin screw clextral extruder at barrel temperature of 195–210 °C and at a screw speed of 50 rpm. During melt extrusion ventilation was kept on to remove trapped air in composites. After pelletizing, the nanocomposite granules were compression molded into 4 mm-thick plates using a hydraulic press at 180 °C during 2 min. for rheological experiments. For mechanical testing, nanocomposite granules were injection-molded (using KraussMaffei KM80-160E injection molding machine) into standard test specimen 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 cm^3/s. The final nanocomposites contained 1, 2, 3 and 5 wt.% MWNTs in the PP matrix. As a reference, neat PP was also similarly extruded-injection molded for rheological and mechanical studies.

2.2. Rheological measurements

Oscillatory shear measurements are performed using an advanced rheometrics expansion system (ARES). Measurements are carried out using cone and plate geometry (25 mm diameter 0.1 rad cone angle and 0.4554 mm gap) at 180 °C in air. Frequency sweeps with an angular velocity of 0.1–100 rad/s are performed in the linear viscoelastic regime at low strain of 5%. Samples are left to equilibrate for 5 min. prior to measurement.

2.3. 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 machine at a crosshead rate of 20 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 as per ISO 178 standard at a thickness to span length ratio of 1:16. Charpy notched and un-notched impact tests were carried out as per ISO 179-1 standard. All the reported values were calculated as averages over five specimens for each composition.

2.4. Morphological characterization

Samples for electron microscopy were prepared by injection molding and cryofractured carbon nanotube/polypropylene composite being mounted on a standard scanning electron microscopy. A thin layer of carbon 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.

For transmission electron microscopy (TEM), ultrathin sections were cut at ambient temperature with a Leica Reichert FCS microtome and collected on a 300 mesh copper grid. Thickness is of the ultrathin section is 125 nm. They were examined with a LEO 922 TEM operated at 120 kV and the micrographs were taken using an energy filter in zero loss mode for an optimal contrast of the nanotubes.

3. Results and discussion

The elaboration of polymer nanocomposites by melt blending remains a challenge especially in the case of polyolefins. Due to the nanometric size and the high aspect ratio of the nanoparticles, the specific surface area is high and thus responsible of strong interparticles interactions which make the dispersion in the matrix difficult. In the case of PP/CNT nanocomposites the weak nanofiller/matrix interaction and the entanglement of very long nanotubes increase the difficulty to obtain a well defined network structure. So as to evaluate the network structure of the elaborated nanocomposites, rheological measurments have been done. Indeed, the rheological properties can provide information about the percolated network structure, the interaction between filler and polymer matrix. Moreover, it is important to evaluate the rheological behavior in order to understand the effect of the nanotubes on internal structures and processing properties of polymer/MWNT composites [26]. Fig. 1 represents the frequency dependence of the storage modulus (G') and loss modulus (G'') for the PP and MWNT/PP nanocomposites measured at 180 °C. It is apparent that both the storage and loss moduli of the nanocomposites increase with increase in MWNT content. Specifically in the case of PP and 1% MWNT/PP nanocomposites, at low frequencies PP chains are fully relaxed and exhibit typical homopolymer-like terminal behavior. However, when the nanotube loadings reaches 2 wt.%, this terminal behavior disappears and the dependence of (G') and (G'') on ω at low frequency is limited. As shown in Fig. 1a, the G' starts to develop a plateau at low frequencies when the nanotube loading reaches 2 wt.%, which is indicative of a transition from liquid-like to solid-like viscoelastic behavior [26]. This non-terminal low frequency behavior can be attributed to the formation of an interconnected nanotube network in the polymer. Therefore, the solid-like (or pseudo-solid-like) behavior can be attributed to the fact that, as the nanotube content increases in the polymer matrix, nanotube–nanotube interactions begin to dominate, eventually lead to percolation and the formation of an interconnected structure of nanotubes in the matrix as shown by Pötschke et al. [44,45]. One can notice the existence of this percolation threshold at a low content. The low frequency dependence of G'' shows a similar trend as shown in Fig. 1b. However, the corresponding increase in the loss modulus is much lower than that in the storage modulus at a fixed nanotube content. The more limited increase of the loss modulus G'' as the nanofillers content increases was already reported by Pötschke et al. [44] and was attributed to the insensitivity to the interfacial energy or compatibility between the polymer and the nanoparticles.

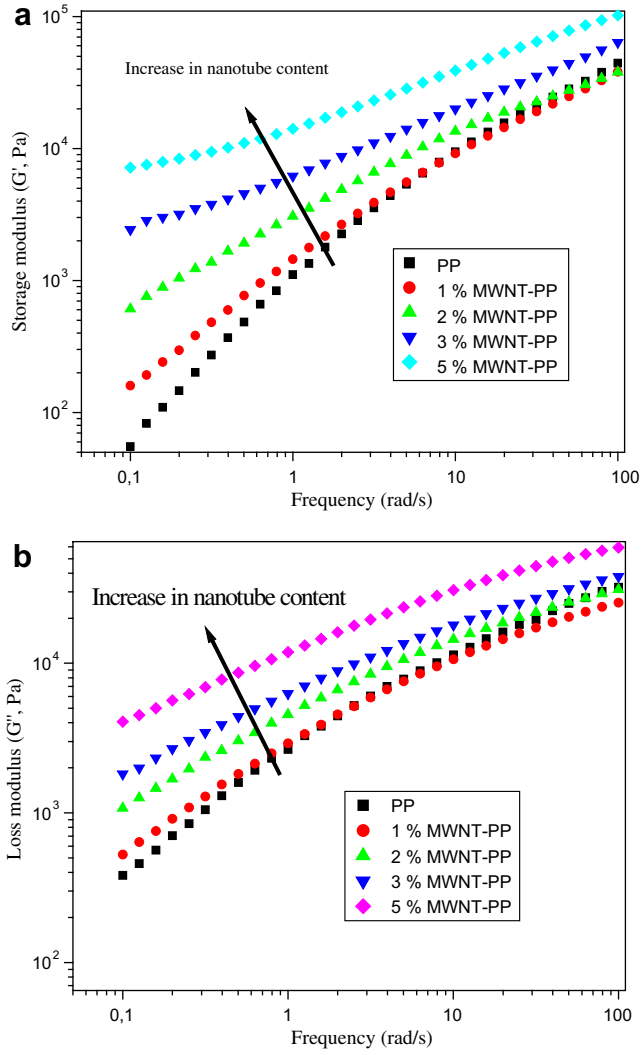

Fig. 1. (a) Storage modulus (G') and (b) loss modulus (G'') of MWNT/PP nanocomposites with frequency sweep as a function of MWNT content at 180 °C.

The complex viscosity of pure PP and the nanocomposites measured at 180 °C as function of angular frequency is shown in Fig. 2. The pure PP shows a Newtonian behavior at low frequencies with respect to its complex viscosity whereas the filled samples exhibit a significant increase in melt viscosity with decreasing frequency. On increasing the MWNT content the viscosity values increase further. The remarkable shift in the shape of the complex viscosity plots from pure PP to the composite with 2 wt.% MWNT clearly indicates that a transition from the liquid-like to solid-like behavior has taken place and the system with 2 wt.% MWNT can be regarded as rheologically percolated. The above observations are confirmed by plotting Van-Gurp Palmen plot (Fig. 2b). From Fig. 2b, one can estimate the filler concentration at which liquid–solid transition takes place. It is at 2 wt.% of nanotubes. Below this concentration the curves approach a phase angle of 90° indicating an viscous behavior, at 2 wt.% of nanotubes the rheological behavior changes from a viscous fluid to an elastic solid indicating a percolation threshold [45].

The TEM observations of the 2 wt.% MWNTs filled nanocomposites are presented in Fig. 3 in order to confirm these results. As shown in Fig. 3a one part of the nanotubes is dispersed individually while the other part is dispersed as aggregates of different sizes (Fig. 3b). Dispersion state of nanotubes in PP matrix is also confirmed by Fig. 3c which shows the dispersion at lower magnification. However, the aggregates remain in the nanoscale level with a size of hundreds nanometers. Nevertheless, SEM observation (Fig. 4) of cryofractured surface of typical 3 wt.% MWNT filled nanocomposite also demonstrates the presence of masterbatch aggregates of several micrometers which might be attributed to the unperfect mixing of the masterbatch with the neat PP. Indeed, due to the very high viscosity of the highly filled masterbatch, the melt blending of the masterbatch and the PP, even with high shear induced by the twin screw extruder, remains difficult.

The typical tensile stress–strain curves of nanocomposite samples with respect to their nanotube content are shown in Fig. 5, including extruded-injection molded PP for comparison. For PP, the typical behavior of a ductile material is observed with a very high elongation at break (620%). The strain hardening region appears at about 400% of elongation and after which tensile strength increases almost linearly with strain until fracture eventually occurs. Also in case of nanocomposites with lower loading (1 and 2 wt.% MWNT) a ductile behavior is observed with necking, but with lower strain at fracture and without strain hardening. Nanocomposites bearing higher nanotube content (3 and 5 wt.%

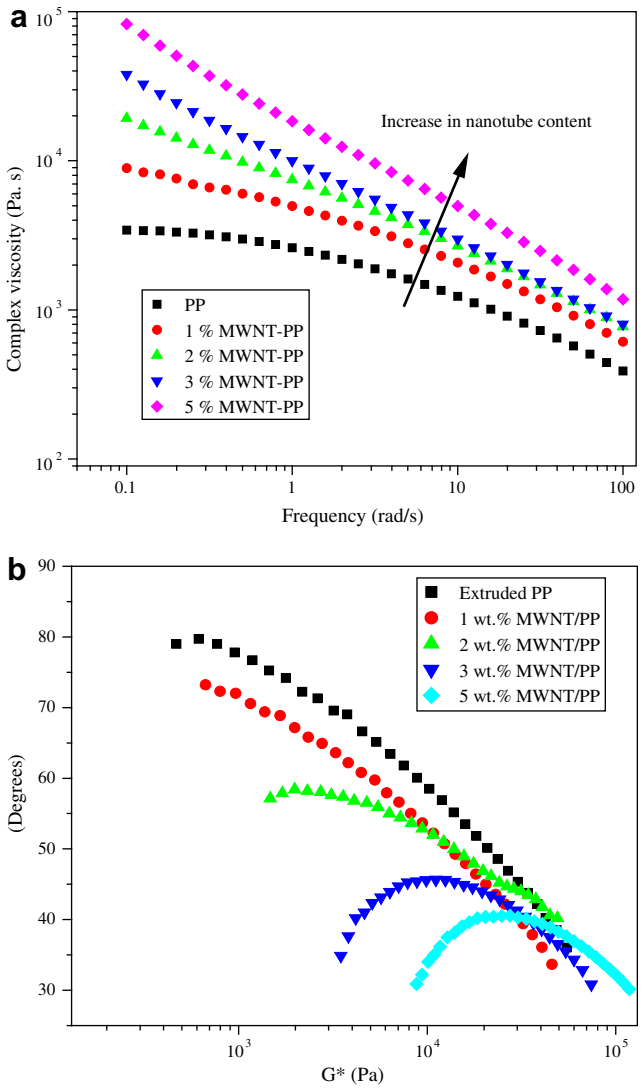

Fig. 2. (a) Complex viscosity of MWNT/PP nanocomposites with frequency sweep as a function at 180 °C. (b) Van-Gurp Palmen plot of MWNT/PP nanocomposites.

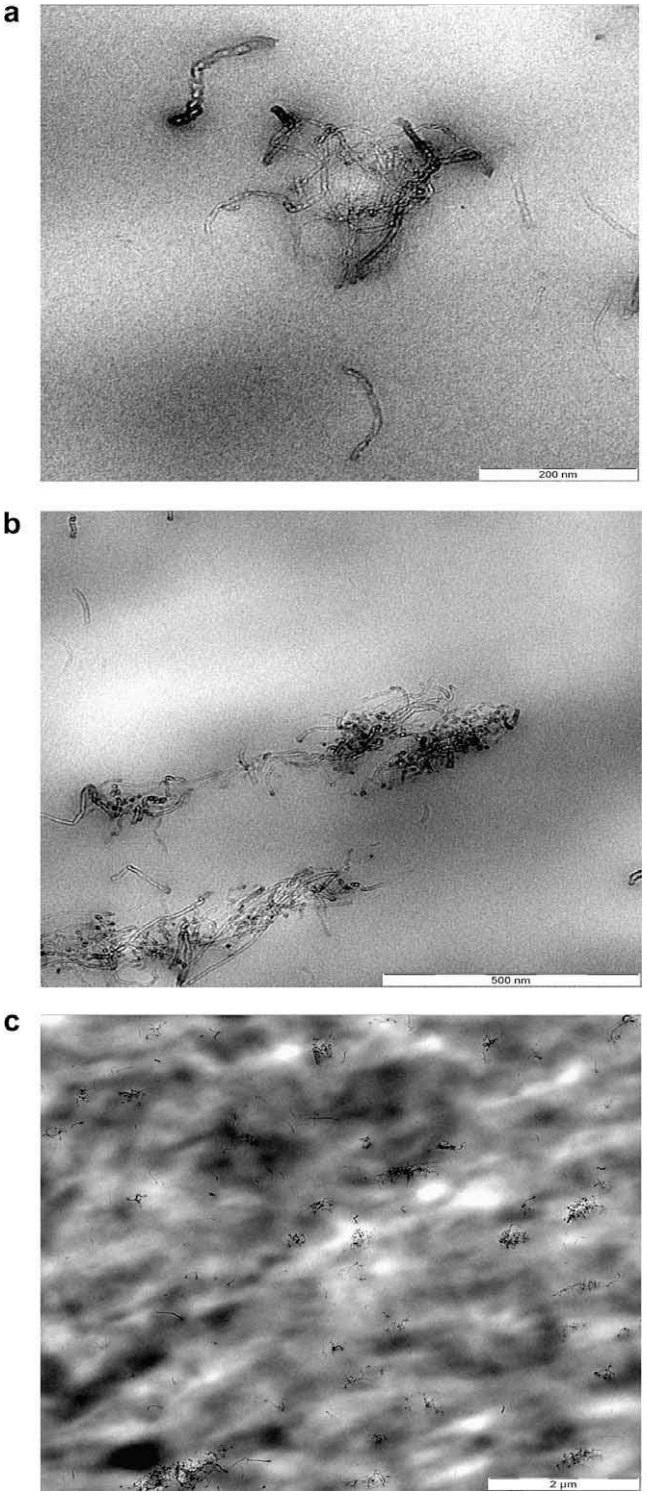

Fig. 3. Transmission electron microscopic pictures of 2 wt.% MWNT/PP nanocomposites. (a) Regions of dispersed nanotubes in PP matrix, (b) regions of nanotubes agglomerations in PP matrix and (c) low magnification TEM picture showing the nanotube dispersion.

MWNT) showed a brittle behavior with breaking after the yield point. Tensile properties of the fabricated nanocomposites are shown in Table 1. It was observed that the Young's modulus and yield stress of the nanocomposites are substantially increased relative to the neat polypropylene. The percentage increase of Young's modulus is from 26.9% to 40.2% and that of yield stress is from 17% to 30.3% with an increase of MWNT concentration. In case of strain at fracture, it decreases linearly from −30% to −90% as shown in Table 1. Moreover, samples of the neat polymer and nanocomposites showed neck formation at the yield stress. However, extent of necking decreases with increase in MWNT content. It is due to the fact that at higher MWNT content the nanotube-rich areas become bigger and tend to show characteristics of forming an interconnecting network. When such network-density becomes higher at higher MWNT concentrations they can potentially lead to intense strain localization because of hindered plastic deformation/strain of the matrix. The strain localization around the dense network of nanotubes ultimately causes matrix cracking due to severe modulus mismatch between polymer and nanotubes and hence ductile yielding behavior is substantially reduced. Therefore, decrease of the ductility at higher nanotube content might be attributed to the presence of nanotubes aggregates which act as stress concentrators. Indeed, when MWNTs content increases the number of aggregates and as a consequence the nanocomposites become brittle. Nevertheless, obtained results in the present studies via diluting a masterbatch are found to be similar to those obtained with direct mixing of MWNTs in PP matrix as reported in the literature [27,46].

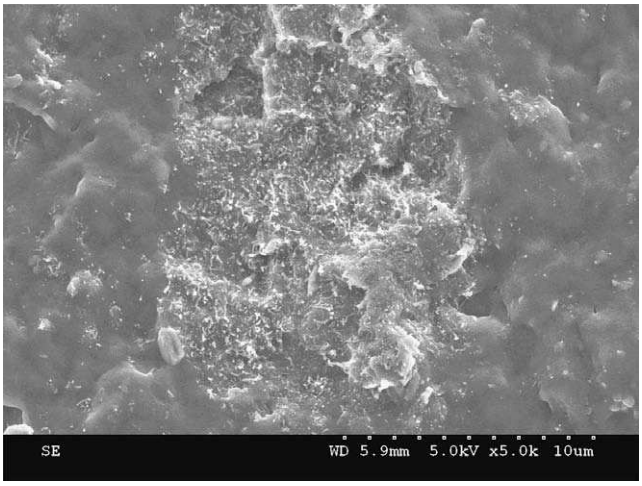

Fig. 4. Scanning electron microscopic pictures of 3 wt.% MWNT/PP nanocomposites representing a masterbatch aggregates in PP matrix.

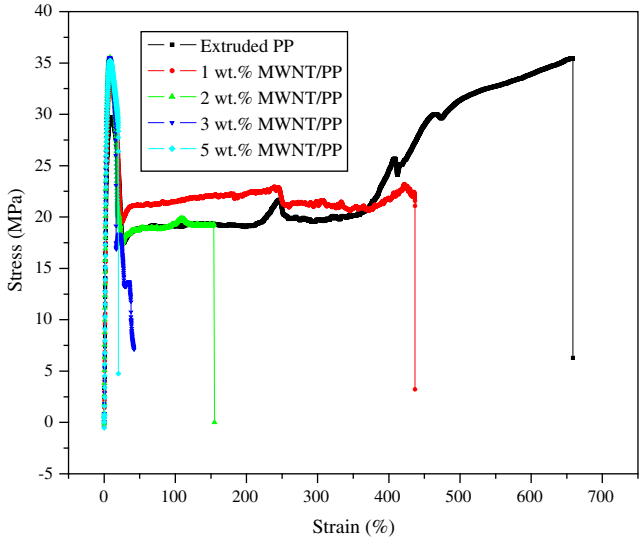

Fig. 5. Tensile behavior: stress–strain diagrams of MWNT/PP nanocomposites.

Table 1
Tensile properties of PP and PP/MWNT nanocomposites.

Material	Tensile properties		
	Modulus (MPa)	Yield stress (MPa)	Strain at break (%)
Neat PP	1280 ± 20	28.2 ± 0.5	620 ± 15
1 wt.% MWNT/PP	1625 ± 25	33.2 ± 0.6	436 ± 10
2 wt.% MWNT/PP	1728 ± 15	35.5 ± 0.5	154 ± 08
3 swt.% MWNT/PP	1795 ± 20	36.8 ± 0.5	64 ± 05
5 wt.% MWNT/PP	2150 ± 25	35.25 ± 0.8	12 ± 02

The flexural strength and modulus of MWNT/PP nanocomposites are shown in Fig. 6. All the tested samples exhibit a bending without ultimate breaking in the tested strain range. From Fig. 6, it can be seen that, flexural strength and modulus increased with increasing nanotube content up to 2 wt.%, but these properties tend to decrease after 3 wt.% of MWNT content. At higher nanotube loading (3 and 5 wt.%), decrease in flexural properties has been observed, it may probably due to the fact that the nanotubes formed a cluster or agglomerate among themselves, resulting in a filler–filler interaction and lower interfacial properties promoting an internal

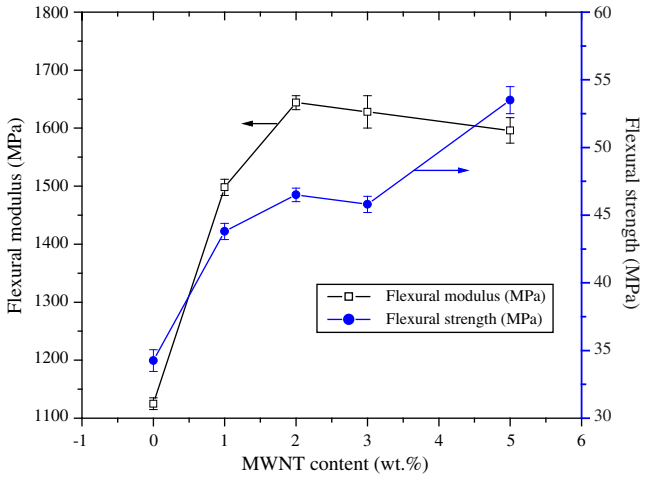

Fig. 6. Flexural properties of PP and PP/MWNT nanocomposites.

shear delamination. Finally, obtained results indicate an existence of optimum MWNT concentration of 2.0 wt.% where a fine network of filler is formed as supported by rheological measurements and it is in accordance with previous literature [43].

Apart from modulus and strength, impact properties are crucial in polymer applications. Impact properties of the notched and un-notched samples are shown in Fig. 7. With increasing filler contents impact resistance for the un-notched samples decreases with increase of MWNTs content in the PP matrix. Impact strength decreased at 1 wt.% nanotube content and decrease was less for 2 wt.% nanotube filled nanocomposites when compared to 1 and 3 wt.% nanotube bearing composites. Decrease was more pronounced in 3 wt.% nanotube filled nanocomposites (Fig. 7). Less decrease in impact strength at 2 wt.% nanotube content is probably attributed to toughening mechanism of nanotubes [47]. More pronounced decrease at higher filler content, i.e. at 3 and 5 wt.% nanotube filled nanocomposites is due to the presence of few nanotube agglomerations in the PP matrix, which provides points of stress concentrations, thus providing sites for crack initiation.

On the other hand, charpy impact strength for the notched specimens of MWNT/PP nanocomposites slightly increased as the MWCNT content increased. However, the notched specimens bearing 2 wt.% MWNT showed 40% increase in impact energy comparing to neat PP. Notched impact behavior is controlled to a greater extent by factors affecting the propagation of fracture initiated

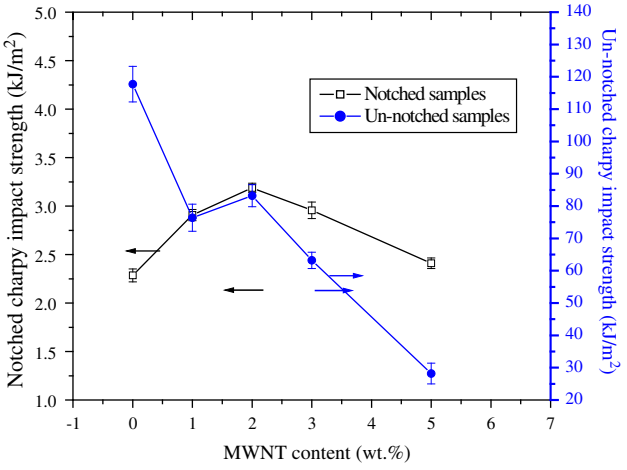

Fig. 7. Charpy impact properties of PP and PP/MWNT nanocomposites.

due to stress concentration at the notch tip. Hence the fiber-pull-out, fiber fracture and nanotube bridging effect are more distinctly visible in case of notched impact resistance and this will be discussed below.

SEM pictures of the cryofractured nanocomposite samples are shown in Fig. 8. It can be seen from Fig. 8a–c that reasonable dispersion of carbon nanotube via simple extrusion process by masterbatch dilution technique. Only few aggregates can be seen in nanocomposites bearing 3 wt.% MWNTs. Carbon nanotubes were pulled out during the fracture of the composite, nevertheless there are still few nanotubes in PP matrix indicating some adhesion between the polymer matrix and the carbon nanotubes as observed in Fig. 8a.

Fig. 9 represents some of the events of fracture behavior of nanocomposites under notched impact. It is well known from the

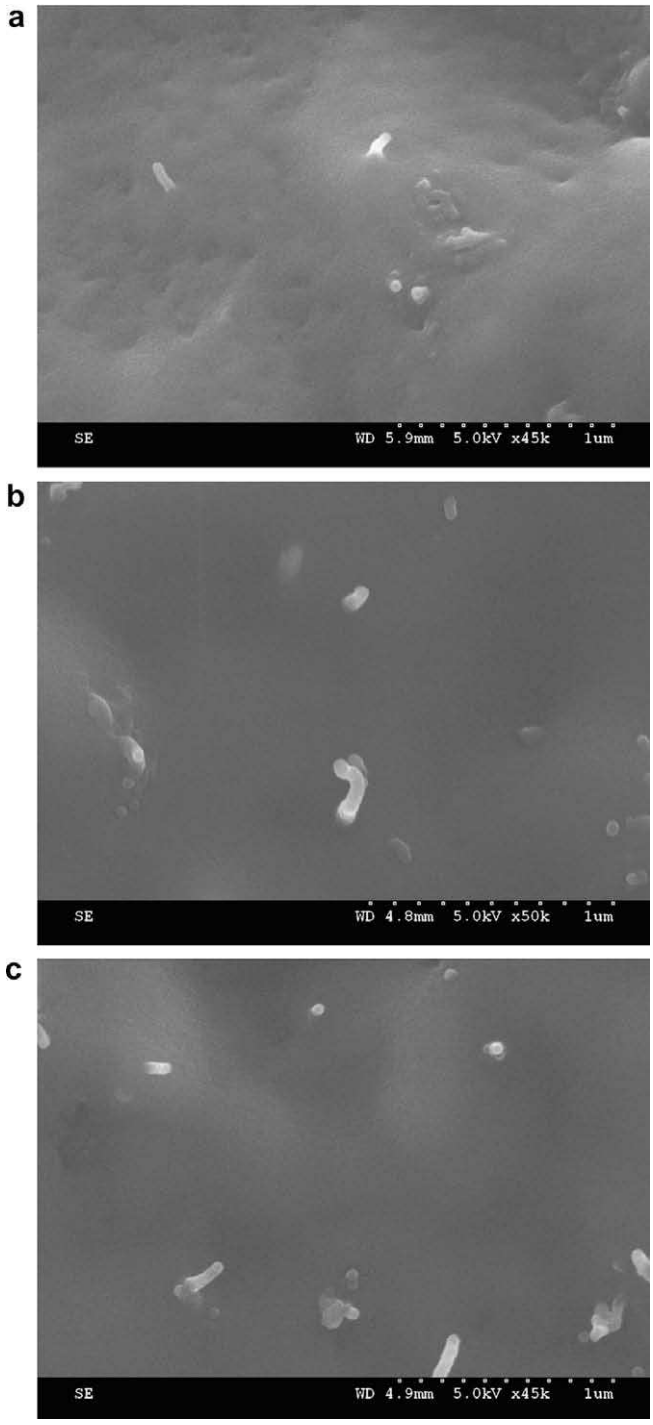

Fig. 8. SEM pictures of cryofractured nanocomposite samples: (a) 1 wt.% MWNT/PP, (b) 2 wt.% MWNT/PP and (c) 3 wt.% MWNT/PP nanocomposites.

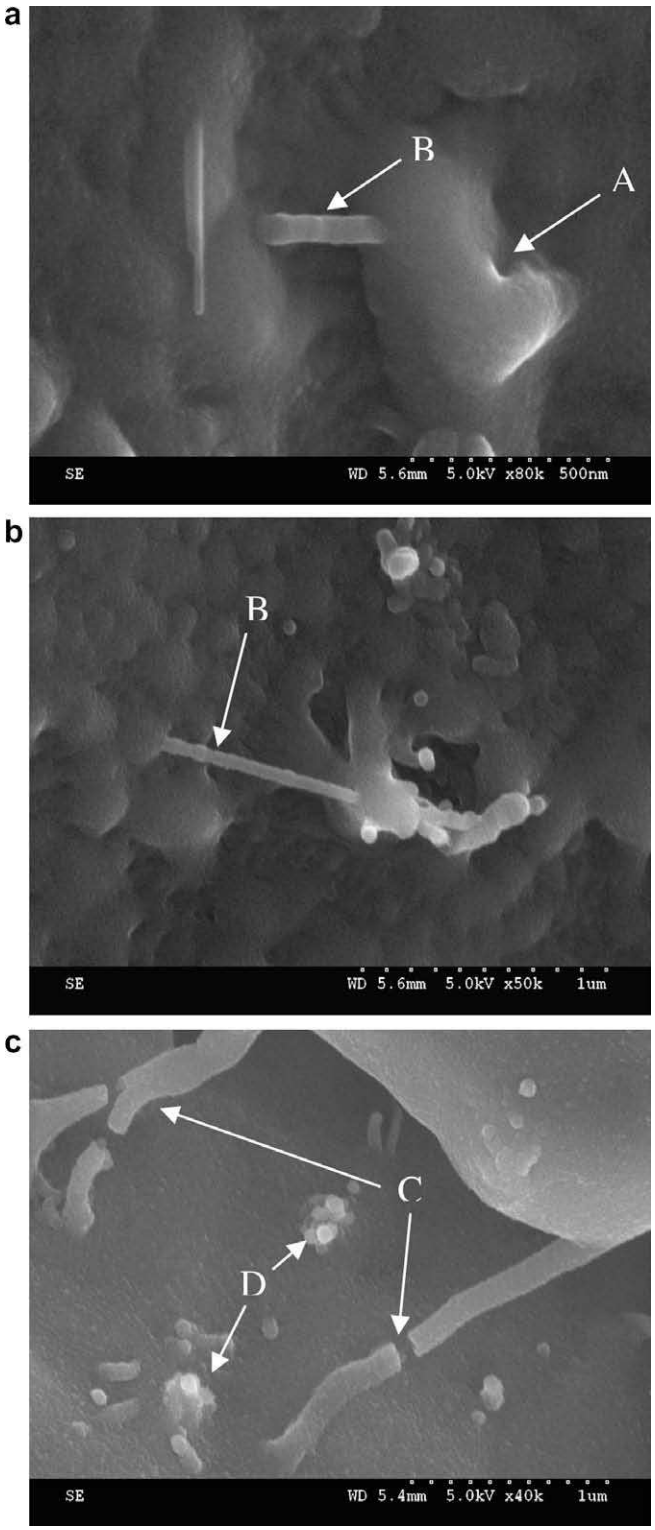

Fig. 9. (a) Fracture behavior of notched charpy impact tested samples of 1 wt.% MWNT/PP. (b) Fracture behavior of notched charpy impact tested samples of 2 wt.% MWNT/PP. (c) Fracture behavior of notched charpy impact tested samples of 3 wt.% MWNT/PP nanocomposites.

literature that for fiber-reinforced polymer composites, fibers could toughen polymer matrix through several energy-consuming events, such as fiber fracture, fiber-pull-out and fiber bridging [48]. In the present work, similar features of carbon nanotubes pull-out (Marked as "A" in Fig. 9a), bridging (Marked as "B" in Fig. 9a and b) and nanotube fracture (Marked as "C" in Fig. 9c) were observed. Fig. 9a illustrates the nanotube bridging between the matrix in the impacted samples containing 1 wt.% MWNTs. Fig. 9b shows the nanotube holding matrix lumps in high impact energy absorbed samples, i.e. 2 wt.% MWNTs filled nanocomposites. Agglomerations of nanotubes (Marked as "D" in Fig. 9c) and breaking of some nanotubes in the nanocomposites with 3 wt.% MWNTs can be observed in Fig. 9c. These observations clearly support the tensile results presented in Table 1. Increase in impact energy for 1 and 2 wt.% MWNTs filled nanocomposites is due to dispersion and distribution of individual nanotubes in the matrix. In addition, nanotube bridging, breaking and pullout can consume additional energy [49] and the large aspect ratio of nanotubes would cause complex matrix-filler interaction during nanotube bridging, breaking and pullout, which probably promotes the local plastic deformation of matrix. Lowering of impact energy at 3 wt.% MWNTs filled nanocomposites is due to poor dispersion of individual nanotubes and more number of aggregates increases the stress concentration leading to brittle failure. Overall findings suggests that nanocomposites containing 2 wt.% nanotubes gave a better performance, which is probably due to the larger areas containing well-dispersed nanotubes as indicated by TEM showing only few agglomerations.

4. Conclusions

Rheological results shows that dynamic moduli and viscosity were increased with the addition of MWNT into PP. Fluid to solid transition takes place between 1 and 2 wt.% of MWNT content, indicating a percolated network structure in the material. Young's modulus of the nanocomposites increased by the addition of nanotubes. Nanotube reinforcement enhances the yield stress, while reducing the ductility. Decrease of ductility is less when compared to classical carbon fiber reinforced PP composites. Flexural properties of the fabricated nanocomposites increases with nanotube content and maximum increase was observed for 2 wt.% CNT filled nanocomposites. Charpy impact resistance increases for notched samples and decreases for un-notched samples with the addition of MWNTs. It clearly indicates that nanotubes limits the crack propagation. But, presence of nanotubes aggregates eases the crack initiation. Better dispersion of nanotubes could avoid the crack initiation providing both high strength and ductility to the nanocomposites.

Microscopic pictures indicate an effective dispersion of nanotubes via extrusion process by masterbatch dilution technique. Thus, preparation of nanocomposites by masterbatch 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 a greater flexibility and cost-effective adaptation ability of the nanofiller content to focused applications. This opens the way to a wider industrial utilization of these materials. Further studies on the relationships between melt processing conditions and MWNT dispersion and distribution with detailed investigation on thermal properties is underway in our laboratory.

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References

[1] Iijima S. Helical microtubules of graphitic carbon. Nature 1991;354(6348):56–8.
[2] Treacy MMJ, Ebbesen TW, Gibson JM. Exceptionally high Young's modulus observed for individual carbon nanotubes. Nature 1996;381:678–80.
[3] Xiao KQ, Zhang LC, Zarudi I. Mechanical and rheological properties of carbon nanotube reinforced polyethylene composites. Compos Sci Technol 2007;67:162–77.
[4] Du JH, Bai J, Ccheng HM. The present status and key problems of carbon nanotube based polymer composites. Express Polym Lett 2007;1(5):253–73.
[5] Wong SS, Joselevich E, Wooley AT, Cheung CL, Lieber CM. Covalently functionalized nanotubes as nanometer-sized probes in chemistry and biology. Nature 1998;394:52–8.
[6] Song YS, Youn JR. Influence of dispersion state of carbon nanotubes on physical properties of epoxy nanocomposites. Carbon 2005;43(7):1378–85.
[7] Song YS, Youn JR. Modeling of effective elastic properties for polymer based carbon nanotube composites. Polymer 2006;47(5):1741–8.
[8] Wang Y, Wu J, Wei F. A treatment method to give separated multi-walled carbon nanotubes with high purity, high crystallization and a large aspect ratio. Carbon 2003;41:2939–48.
[9] Eitan A, Jiang K, Dukes D, Andrews R, Schadler LS. Surface modification of multiwalled carbon nanotubes: toward the tailoring of the interface in polymer composites. Chem Mater 2003;15:3198–201.
[10] Park WK, Kim JH. Effect of carbon nanotube pre-treatment on dispersion and electrical properties of melt mixed multi-walled carbon nanotubes/poly(methylmethacrylate) composites. Macromol Res 2005;13(3):206–11.
[11] Funck A, Kaminsky W. Polypropylene carbon nanotube composites by in situ polymerization. Compos Sci Technol 2007;67(5):906–15.
[12] Curran S, Davey AP, Coleman J, Dalton A, McCarthy B, Maier S, et al. Evolution and evaluation of the polymer/nanotube composite. Synth Met 1999;103(1–3):2559–62.
[13] Andrews R, Jacques D, Minot M, Rantell T. Fabrication of carbon multiwall nanotube/polymer composites by shear mixing. Micromol Mater Eng 2002;287(6):395–403.
[14] Huang YY, Ahir SV, Terentjev EM. Dispersion rheology of carbon nanotubes in a polymer matrix. Phys Rev–B 2006;73:125422–9.
[15] Mihaela M, Olaru A. In: Cornelia V, editor. Handbook of polyolefins. Marcel Dekker, Inc.; 1993. p. 267–90.
[16] Bhattacharyya AR, Sreekumar TV, Liu T, Kumar S, Ericson LM, Hauge RH. Crystallization and orientation studies in polypropylene/single wall carbon nanotube composite. Polymer 2001;44:2373–7.
[17] López Manchado MA, Valentini L, Biagiotti J, Kenny JM. Thermal and mechanical properties of single-walled carbon nanotubes–polypropylene composites prepared by melt processing. Carbon 2005;43(7):1499–505.
[18] Kashiwagi T, Grulke E, Hilding J, Groth K, Harris R, Butler K, et al. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. Polymer 2004;45(12):4227–39.
[19] Assouline E, Lustiger A, Barber AH, Cooper CA, Klein E, Wachtel E, et al. Nucleation ability of multiwall carbon nanotubes in polypropylene composites. J Polym Sci Part B: Polym Phys 2003;41:520–7.
[20] Xia HS, Wang Q, Li KS, Hu GH. Preparation of polypropylene/carbon nanotube composite powder with a solid-state mechanochemical pulverization process. J Appl Polym Sci 2004;93:378–86.
[21] Coleman JN, Cadek M, Blake R, Nicolosi V, Ryan KP, Belton C, et al. High performance nanotube-reinforced plastics: understanding the mechanism of strength increase. Adv Funct Mater 2004;14:791–8.
[22] Zhao P, Wang K, Yang H, Zhang Q, Du R, Fu Q. Excellent tensile ductility in highly oriented injection-molded bars of polypropylene/carbon nanotubes composites. Polymer 2007;19:5688–95.
[23] Zhang QH, Lippits DR, Rastogi S. Dispersion and rheological aspects of SWNTs in ultrahigh molecular weight polyethylene. Macromolecules 2006;39(2):658–66.
[24] Zhang QH, Rastogi S, Chen DJ. Low percolation threshold in single-walled carbon nanotube/high density polyethylene composites prepared by melt processing technique. Carbon 2006;44(4):778–85.
[25] Xiao KQ, Zhang LC, Zarud I. Mechanical and rheological properties of carbon nanotube-reinforced polyethylene composites. Compos Sci Technol 2007;67:177–82.
[26] Seo MK, Park SJ. Electrical resistivity and rheological behaviors of carbon nanotubes-filled polypropylene composites. Chem Phys Lett 2004;395:44–8.
[27] Ganß M, Satapathy BK, Thunga M, Weidisch R, Pötschke P, Jehnichen D. Structural interpretations of deformation and fracture behaviour of polypropylene/multi-walled carbon nanotube composites. Acta Mater 2008;56:2247–61.
[28] Muller J, Huaux F, Lison D. Respiratory toxicity of carbon nanotubes: how worried should we be? Carbon 2006;44(6):1048–56.
[29] Baird DG, Collias DI. Polymer processing: principles and design. John Wiley and Sons, Inc; 1998.
[30] Pötschke P, Bhattacharyya AR, Janke A, Pegel S, Leonhardt A, Täschner C, et al. Melt mixing as method to disperse carbon nanotubes into thermoplastic polymers. Fullerenes, Nanotubes Carbon Nanostruct 2005;13(1):211–24.
[31] Lin B, Sundararaj U, Pötschke P. Melt mixing of polycarbonate with multi-walled carbon nanotubes in miniature mixers. Macromol Mater Eng 2006;291(3):227–38.

[32] Pötschke P, Bhattacharyya AR, Janke A. Melt mixing of polycarbonate with multiwalled carbon nanotubes: microscopic studies on the state of dispersion. Eur Polym J 2004;40(1):137–48.
[33] Pötschke P, Brünig H, Janke A, Fischer D, Jehnichen D. Orientation of multiwalled carbon nanotubes in composites with polycarbonate by melt spinning. Polymer 2005;46(23):10355–63.
[34] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Mechanical properties and electrical conductivity of carbon-nanotube filled polyamide-6 and its blends with acrylonitrile/butadiene/styrene. Polymer 2004;45(3):739–48.
[35] Alig I, Lellinger D, Engel M, Skipa T, Pötschke P. Destruction and formation of a conductive carbon nanotube network in polymer melts: in-line experiments. Polymer 2008;49(7):1902–9.
[36] Alig I, Lellinger D, Dudkin SM, Pötschke P. Conductivity spectroscopy on melt processed polypropylene–multiwalled carbon nanotube composites: recovery after shear and crystallization. Polymer 2007;48(4):1020–9.
[37] Villmow T, Pegel S, Pötschke P, Wagenknecht U. Influence of injection molding parameters on the electrical resistivity of polycarbonate filled with multi-walled carbon nanotubes. Compos Sci Technol 2008;68(3–4):777–89.
[38] Schartel B, Pötschke P, Knoll U, Abdel-Goad M. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. Eur Polym J 2005;41(5):1061–70.
[39] Pegel S, Pötschke P, Petzold G, Alig I, Dudkin Sm, Lellinger D. Dispersion, agglomeration, and network formation of multiwalled carbon nanotubes in polycarbonate melts. Polymer 2005;49(4):974–84.
[40] Schartel B, Braun U, Knoll U, Bartholmai M, Goering H, Neubert D, et al. Mechanical, thermal, and fire behavior of bisphenol a polycarbonate/multiwall carbon nanotube nanocomposites. Polym Eng Sci 2008;48:149–58.
[41] Spiros T, Dionysis EM, Vasilis D, Vasilis GG. Polyethylene terephthalate-multiwall nanotubes nanocomposites: effect of nanotubes on the conformations, crystallinity and crystallization behavior of PET. J Polym Sci Part B: Polym Phys 2008;46(7):668–76.
[42] Adamne AM, Belina K. Effect of multiwall nanotube on the properties of polypropylenes. Int J Mater Form 2008. doi:10.1007/s12289-008-0325-4.
[43] Lee SH, Kim MW, Kim SH, Youn JR. Rheological and electrical properties of polypropylene/MWCNT composites prepared with MWCNT masterbatch chips. Euro Polym J 2008;44(6):1620–30.
[44] Pötschke P, Fornes TD, Paul DR. Rheological behavior of multiwalled carbon nanotube/polycarbonate composites. Polymer 2002;43(11):3247–55.
[45] Abdel-Goad M, Pötschke P, Zhou D, Mark JE, Heinrich G. Preparation and rheological characterization of polymer nanocomposites based on expanded graphite. J Macromol Sci Part A 2007;44(6):591–8.
[46] Bao SP, Tjong SS. Mecanical behaviours of polypropylene/carbon nanotubes nanocomposites: the effects of loading rates and temperature. Mater Sci Eng A 2008;485(1–2):508–16.
[47] Zhang H, Zhang Z. Impact behaviour of polypropylene filled with multi-walled carbon nanotubes. Eur Polym J 2007;43(8):3197–207.
[48] Thostenson ET, Li C, Chou TW. Nanocomposites in context. Compos Sci Technol 2005;65:491–516.
[49] Ajayan PM, Schadler LS, Giannaris C, Rubio A. Single walled carbon nanotube-polymer composites: strength and weakness. Adv Mater 2000;12:750–3.