Dispersion and Mechanical Properties of Polypropylene/Multiwall Carbon Nanotubes Composites Obtained via Dynamic Packing Injection Molding

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Received 6 January 2006; accepted 17 April 2006
DOI 10.1002/app.25852
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, polypropylene (PP)/multiwall carbon nanotubes (MWNTs) composites were prepared through dynamic packing injection molding, in which the oscillatory shear was exerted on the molten composite during packing and solidification stage of injection-molding. A simultaneous increase of tensile strength and impact strength has been achieved for PP/MWNTs composites containing only 0.6 wt % MWNTs. Particularly, the impact strength was found increased by almost 50% at such low MWNTs content. These improvements in properties were attributed to uniform dispersion and possible orientation of nanotube induced by shear stress. It was suggested that the dynamic packing injection molding could provide much strong shear force for better dispersion of MWNTs in PP matrix, on one hand, but breakdown the aspect ratio of MWNTs, on the other. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1880–1886, 2007

Key words: multiwall carbon nanotubes (MWNTs); polypropylene; shear force

INTRODUCTION

Polymer/multiwall carbon nanotubes (MWNTs) composites have attracted more and more attention in both academia and industry because of their ultralight structure with enhanced electrical, thermal, optical, and mechanical properties. Many researchers have tried to improve the mechanical properties of various polymers through carbon nanotubes; however, the successful examples are very limited. To optimize polymer/MWNTs composites, the key is to achieve homogeneous dispersion of MWNTs, maintain high aspect ratios, orient the MWNTs, and enhance the interfacial interaction between polymer and MWNTs. To resolve the question about the dispersion of MWNTs, two different approaches are usually used[1]: physical methods and chemical methods. Physical methods include ultrasonication, ball milling, and grinding, while chemical methods use surfactant to change the surface energy of MWNTs or form polar groups on the surface of MWNTs to improve the compatibility between the matrix and MWNTs. Xia et al.[2] used pan milling to prepare polypropylene (PP)/MWNTs composites. They found that the solid-state mechanochemical pulverizing process has three functions: (1) it can improve the cohesion between the polymer and MWNTs; (2) it can cut the MWNTs and reduce the number of defects and entanglements of long MWNTs; and (3) it can improve the dispersion of the MWNTs in PP. Lozano[3] used an intermediate-size mixer and obtained good dispersion. A significant increase in the storage modulus was obtained, but no real change in the ultimate tensile strength of the composites was observed. This might be due to the increased brittleness of the polymer matrix, resulting from PP's inability to further crystallize on deformation. Liu et al.[4] refluxed MWNTs with concentrated nitric acid to create acidic sites on MWNTs, such as carboxylic and hydroxyl groups, to improve the interfacial adhesion between MWNTs and nylon-6. The MWNTs were found uniformly dispersed into the nylon-6 matrix, resulting in a significant improvement of the modulus, the strength, and the hardness. Lin et al.[5] introduced a new way to modify MWNTs, in which the MWNTs was functionalized by PVA in carbodimide-activated esterification reactions. Through investigating the dispersion of MWNTs in PVA, they demonstrated that the functionalization of MWNTs by the matrix polymer was an effective way in the homogenous nanotubes dispersion for high-quality polymeric carbon nanocomposite materials. Yet another possibility is to expose the nanotube composite to γ radiation for altering the chemistry at

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Contract grant sponsor: National Natural Science Foundation of China; contract grant numbers: 20490220, 20404008, 50533050.
Contract grant sponsor: Special Funds for Major State Basic Research Projects of China; contract grant number: 2003CB615600.

the interface for property enhancement, as has been done in PMMA.[6]

PP is one of the most important conventional polymers with some excellent properties, such as low relative density and easy processability; however, it is not sufficient for applications as engineering plastics. Therefore, PP is generally modified by melt mixing with particulate (talc, clay)[7–9] and fibrous (glass and carbon fibers)[10–12] fillers as well as by melt blending with other polymers. The preparation of PP/MWNTs composites provides a new way to obtain high performance PP engineering plastics. In this article, we report our efforts on the dispersion of MWNTs in PP matrix by using so called dynamic packing injection molding. Thereafter, this technology is abbreviated as DPIM. The main feature of DPIM is that the specimen is forced to move repeatedly in the model by two pistons that move reversibly with the same frequency during cooling. The skin is frozen immediately after injection due to the fast cooling, and the orientation of macromolecular chains in the internal regions can be remained because the melt is forced to move repeatedly during solidification. The core is cooling down at the latest after stopping the imported oscillatory shear. Thus, the melt will subject a repeated shear force during the solidification process from the mold wall to the molding core part. In this way, the good dispersion and orientation of MWNTs along shear flow direction are expected. Our goals are mainly twofolds: (1) explore a new way to prepare PP/MWNTs composites with uniformly dispersed MWNTs; and (2) obtain high performance PP engineering plastics.

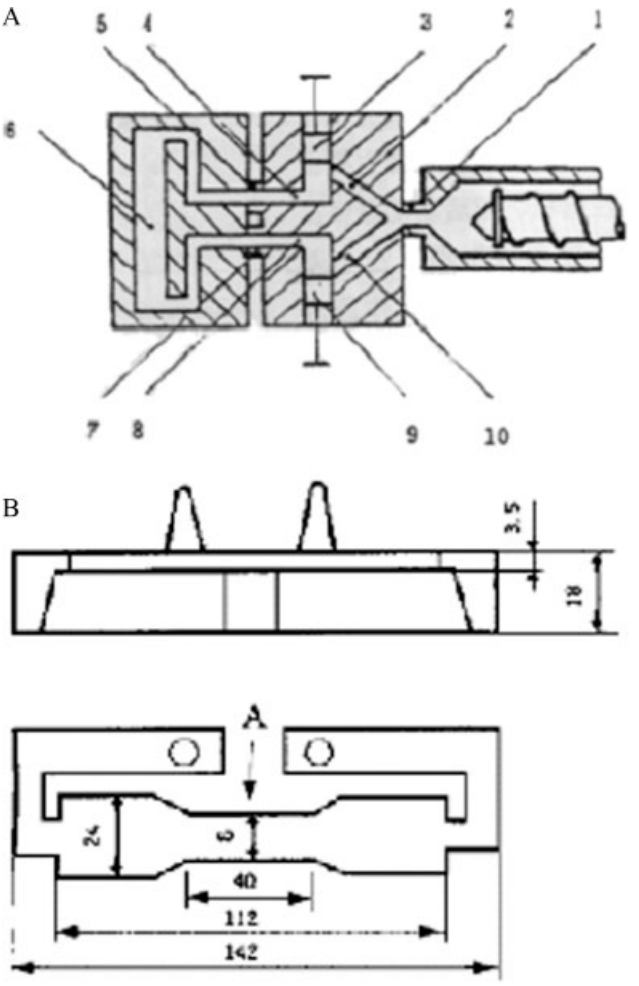

Figure 1 (a) The schematic representation of DPIM: (1) nozzle, (2) sprue A, (3) piston A, (4) runner A, (5) connector, (6) specimen, (7) connector, (8) runner B, (9) piston B, and (10) sprue B. (b) The sketch of mechanical test specimen dimensions according to ASTM638M standard.

EXPERIMENT

Materials

A commercially available isotactic PP (trade marked as T30S, Yan Shan Petroleum China), with $M_\eta = 29.2 \times 10^3$ g/mol and a melt flow index of 0.9975 g/min (190°C, 2.16 kg) and a density of 0.91 g/m^3, was used as the basal polymer. MWNTs were provided by the Chengdu Institute of Organic Chemistry of the Chinese Academy of Science (Chengdu, China). MWNTs were synthesized through the dissociation of methane at a high temperature of 700°C with a NiO/La_2O_3 catalyst. The outer and inner diameters of the MWNTs were 10–20 and 5–10 nm, respectively. They were washed with concentrated hydrochloride acid for the removal of the catalyst and its carrier and then purified with concentrated HNO_3 for the removal of amorphous carbon particles.

Preparation of PP/MWNTs composite

A master-batch consisted of iPP/MWNTs (95/5) was melt-mixed in a TSSJ-2S corotating twin-screw extruder. The temperature of the extruder was maintained at 160, 170, 200, 200, and 195°C from hopper to die and the screw speed was about 120 r/min. Then a series iPP/MWNTs nanocomposites (99.7/0.3, 99.4/0.6, 99.0/1.0, and 98.0/2.0) were obtained through adding iPP to dilute the as-prepared master-batch in the extruder. After pelletized and dried, these composites were injected into a mold with aid of an injection-molding machine. Then dynamic packing injection molding technology was applied.

Dynamic packing injection molding

To identify the important role that the repeated applied shear may play in the dispersion of MWNTs in PP matrix for as-prepared PP/MWNTs nanocomposite, special DPIM equipment was attached to the injection-molding machine. A schematic representation of DPIM instrument is shown in Figure 1(a). The processing parameters and the characteristics

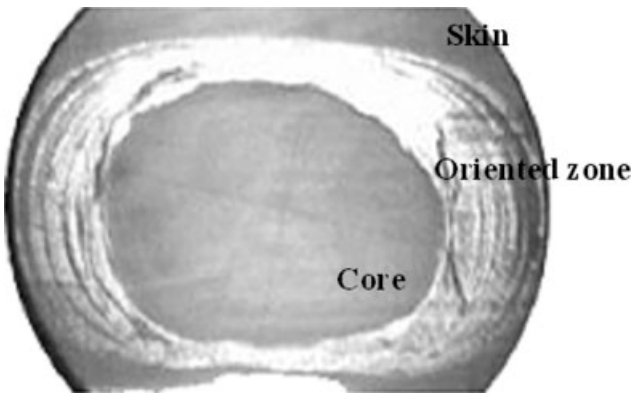

Figure 2 Optical photograph of cross section in dynamic specimen composed with triple-layer structure.

and detail experiment procedure of DPIM were described in Refs. 13–15. Its main feature was that the cooling melt was forced to move repeatedly in chamber (6) during packing stage by two pistons (3) and (9) that moved reversibly with the same frequency and a highly oriented region emerged between a skin region and a core region. To minimize the disturbances of processing parameters, only one oscillation shear frequency (1.0 Hz) was considered, the amplitude of oscillation was also constant that the reversible distance of pistons was invariant (as about 2 cm), and the duration of melt solidification was controlled at 5 min by adjusting the flux of cycle cooled water inside the mold. The specimen dimensions are shown in Figure 1(b). The shear rate was about 10 s^{-1} calculated from the geometry of mold. The composites were injected into a mold with aid of SZ 100 g injection-molding machine with barrel temperature of 190°C and injection pressure of 900 kg cm^{-2}. We also carried out injection molding under static packing by using the same processing parameters but without shearing for comparison purpose. The specimen obtained by dynamic packing injection molding is called dynamic sample, and the specimen obtained by static packing injection molding is called static sample.

Mechanical properties measurement

Instron 4301 tensile testing machine was used to measure the stress–strain curves and the tensile

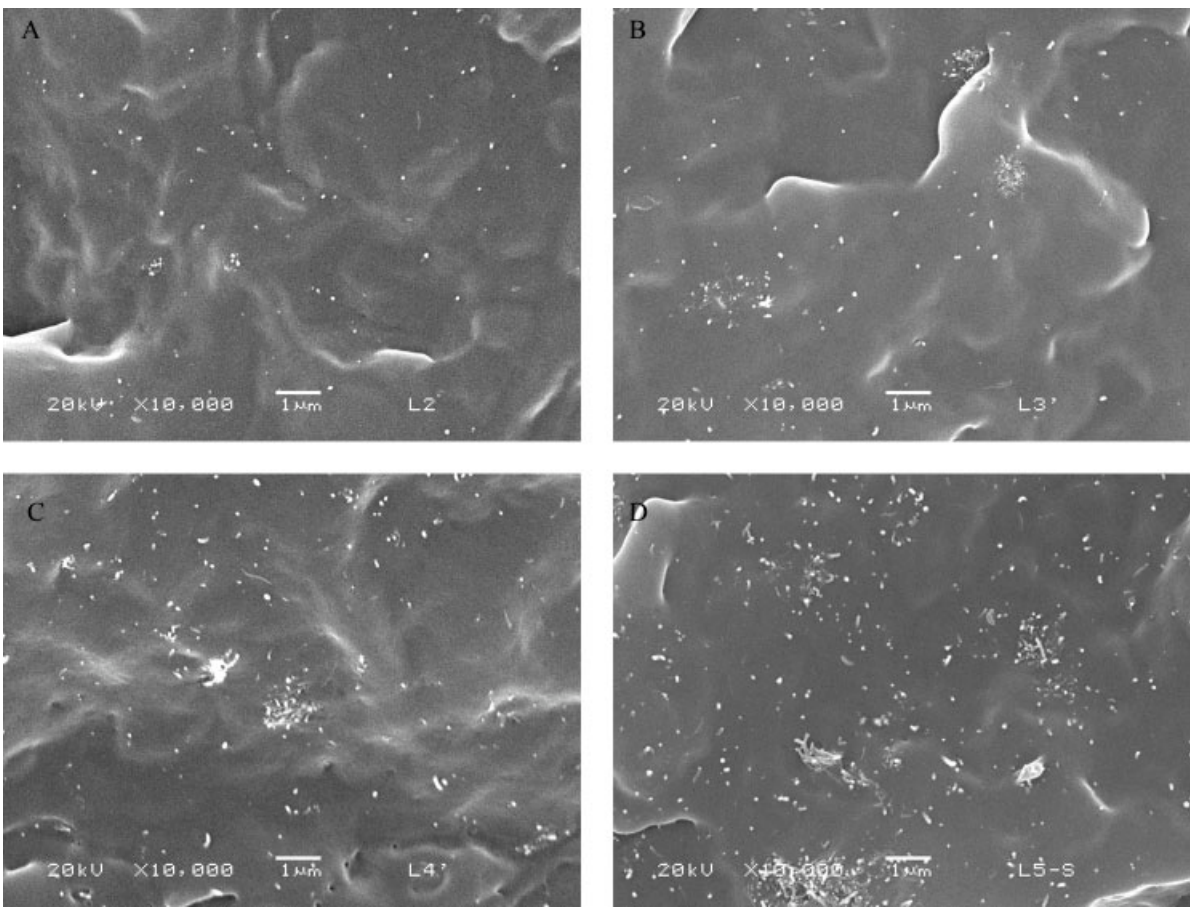

Figure 3 SEM photographs of PP/MWNTs obtained by static packing injection molding (in the core): (a) 0.3%, (b) 0.6%, (c) 1%, and (d) 2%.

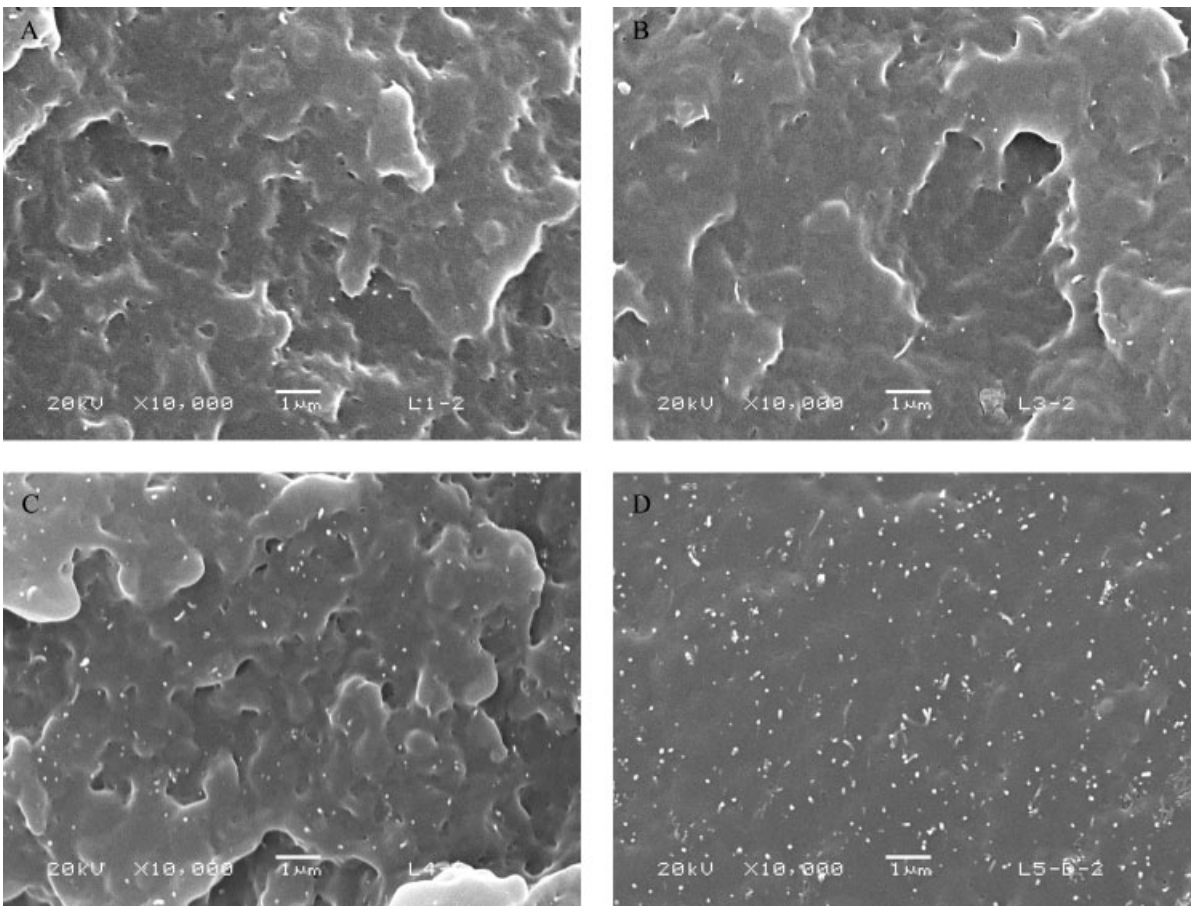

Figure 4 SEM photographs of PP/MWNTs obtained by dynamic packing injection molding (in the oriented zone): (a) 0.3%, (b) 0.6%, (c) 1%, and (d) 2%.

strengths, moving speed was 50 mm/min. For impact strength measurement, the central part of sample (40 mm long) was used. A notch with 45° was made by machine and remained width is 5.0 mm. The experiment was carried out on a 1200XJU-2.75 Impact tester according to ISO179. The values of all the mechanical parameters are calculated as over 5 specimens for each composition.

SEM experiment

The dispersion of MWNTs in PP matrix was inspected by a JEOL JSM-5900LV SEM instrument. For the SEM measurement, the specimens were fractured in the direction perpendicular or parallel to the shear flowing direction in liquid nitrogen and then the fractured surface was gold coated and observed under an acceleration voltage of 20 kV.

RESULTS AND DISCUSSION

Dispersion of MWNTs in PP matrix

It is common that the conventionally injection-molded fast crystallizing polymer generally exhibits multilayer morphology. At near the skin, the nucleation density is generally high as a result of crystallization upon contact with the cold mold surface under extensional or shear stress. The interior of the parts is composed of spherulitic structure whose sizes increase towards the core as the influence of stress history becomes weaker and weaker. As expected, the static samples prepared directly without introducing stress to the melt during packing stage show the skin-core structure. In contrast to the static sample, macroscopically the shear-induced morphology of dynamic samples can be divided into three parts, namely skin, oriented zone, and core, instead of two parts,[16,17] and is proved by Figure 2. To evaluate the dispersion of MWNTs in PP matrix, we use the central part for static samples and oriented zone for dynamic ones. The development of morphology of static samples at central part (the core) as a function of nanotube content is shown in Figure 3. The white spots indicate MWNTs ends that were pulled out off the polymer matrix. Although the magnification of these SEM images in Figure 3 is not very high (approximate ×10,000), one can clearly observe the dispersion morphology of MWNTs in PP matrix

within the large-size scale regions due to the marked difference of substantial feature between organic polymer and inorganic filler. Obviously, a better dispersion is achieved at 0.3 wt % MWNTs. Aggregates and poor dispersion of MWNTs is seen with incorporation of higher MWNTs content. Therefore, it can be concluded that it is difficult to obtain a good dispersion through general twin-screw extrusion and injection molding. Figure 4 shows the morphology of dynamic samples as a function of MWNTs content at the oriented zone where the effect of shear stress can be most demonstrated. These images within the large-size observed areas confirm the fine and homogenous dispersion of MWNTs throughout PP matrix, even for the nanocomposite containing 2 wt % MWNTs. As shown in Figure 4, individual MWNTs are dispersed within the matrix, and almost no aggregates are observed. This result suggests that better dispersion can be achieved via DPIM, and the repeated shear force is powerful for the dispersion of MWNTs in polymer matrix. One may expect that the processing parameters of DPIM, such as injected pressure, melt and molding temperatures, oscillation shear frequency, and amplitude, would certainly affect the dispersion of MWNTs in PP. In our present work, the temporary aim is to answer whether the oscillatory shear during injection molding promote the level of homogeneous dispersion of MWNTs. As to now, the positive effect of oscillatory shear on the dispersion of MWNTs has been unambiguously demonstrated through comparison between static samples and dynamic samples. The roles of processing parameters will be probed in the further study and will be discussed elsewhere.

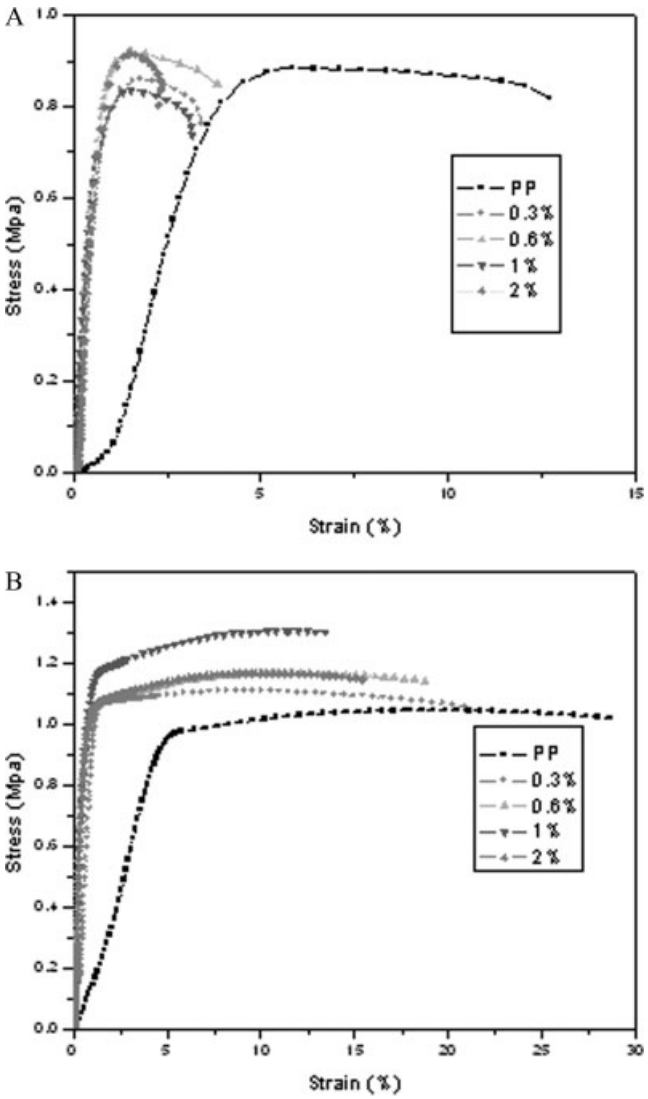

Figure 5 The typical stress–strain curves of PP/MWNTs: (a) static samples and (b) dynamic samples.

Mechanical properties

The typical stress–strain curves of dynamic samples are shown in Figure 5, including static ones for comparison. As for static samples, there is no obvious necking and the fracture mode is brittle, with ultimate elongation less than 10%. One observes a sharp decrease of elongation at break from 13% of PP to 3% of the nanocomposites when adding MWNTs to the PP matrix. As for dynamic samples, however, an obvious increase of elongation is seen, resulting from the molecular orientation in these samples. In this case one also obverses a decrease of elongation as an addition of MWNTs but quite slowly compared with the static ones. Meanwhile, from the stress–strain curves, it can be seen that the tensile modulus (Young's modulus) shows a substantial increases (judged from the slop change at initial linear regimes) by adding small amount of MWNTs for both static and dynamic samples. But the improved amplitude of modulus in dynamic samples is considerably higher than that of static samples. Now, the capability of antistrain of as-prepared samples is quantitatively being estimated in our group through dynamic mechanical analysis.

The tensile strength of the composites as a function of MWNTs content is shown in Figure 6. The values are calculated as average about 5 specimens for each composition. Two important features should be noted in Figure 6: (1) the tensile strength of dynamic samples is much higher than that of static samples in the whole composition region, due to the molecular orientation induced by shear stress in dynamic packing injection molding; and (2) as expected, the presence of the MWNTs improves the tensile strength for both static and dynamic samples, with very small for static samples but obvious for dynamic ones. For example, the tensile strength keeps almost unchanged (42 MPa) by adding 0.6 wt % MWNTs for static sample, but an increase from

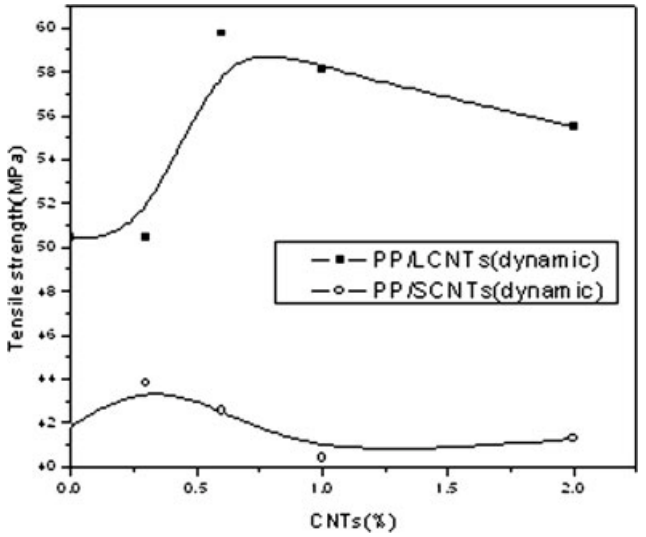

Figure 6 The tensile strength of PP/MWNTs as the function of MWNTs content.

50.5 to 59 MPa is seen for dynamic sample. Here not only the molecular orientation of PP but also the good dispersion and orientation of MWNTs may contribute to the enhanced tensile strength. The slightly decreases in tensile strength when more MWNTs is added to the PP matrix most likely originates from the difficulty of PP molecular orientation in the presence of MWNTs, and this will be further verified by using 2d-WAXD.

The Izod Notched impact strength of the samples was carried out with the fracture loading perpendicular to the shear flow direction. This is shown in Figure 7. For static samples, one finds very low impact strength (3.9 KJ/m^2) for pure PP, and it increases at 0.3 wt % of MWNTs content. Then, the impact strength keeps constant when more MWNTs are added. For dynamic samples, very high impact strength (17 KJ/m^2) is seen for pure PP. This is mainly caused by the formation of oriented layer induced by shear stress. From the Figure 7, one observes a maximum (26 KJ/m^2) occurs at 0.6 wt % MWNTs content. Then the impact strength decreases to 20 KJ/m^2 at 1 wt % and 17 KJ/m^2 at 2 wt % content, respectively. Certainly both the dispersion of MWNTs and the degree of orientation of PP play important roles to determine the impact strength in this situation. In the study that is ongoing, a high-degree oriented morphology that the fibrous MWNTs preferentially align parallel to the shear direction though the planes of PP lamellae grow perpendicular to the same direction has been observed in dynamic sample, whereas only isotropic spherulite morphology can be detected in static samples, and the crystallization behavior of PP would be significantly changed in presence of oriented nanotubes demonstrated through quiescent recrystallization investigation. A detail mechanism about the performance enhancement induced by shear and incorporation of MWNTs will be elucidated in a future work.

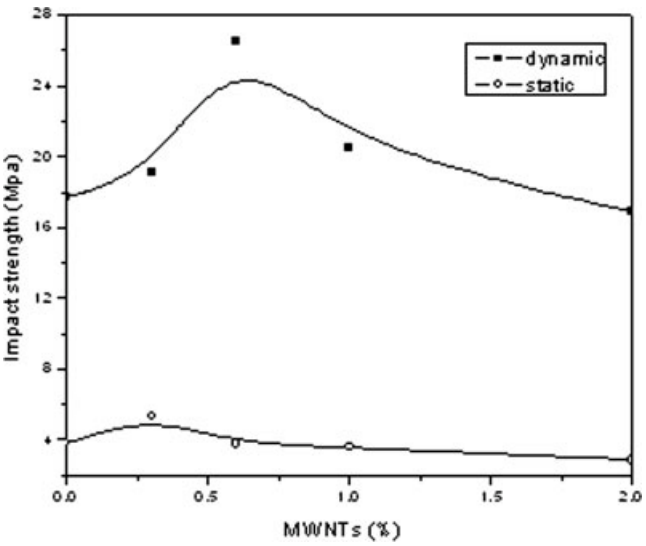

Figure 7 The impact strength of PP/MWNTs as the function of MWNTs content.

Effect of shear mixing on aspect ratio of MWNTs

Shear will helps for good dispersion on one hand, but will cut down the aspect ratio of MWNTs, on the other hand. To see the aspect ratio of MWNTs in the composites, one has to observe the fracture surface that is parallel to the shear flow direction. Figure 8 shows the morphology of the raw MWNTs. Their diameter and length were 10–20 nm and 20 μm, respectively. They have a very high aspect ratio of 1000. However, a substantial decrease of aspect ratio is observed for both static and dynamic samples. Figure 9 shows the fracture surface that is parallel to the shear flow direction. It can be seen that

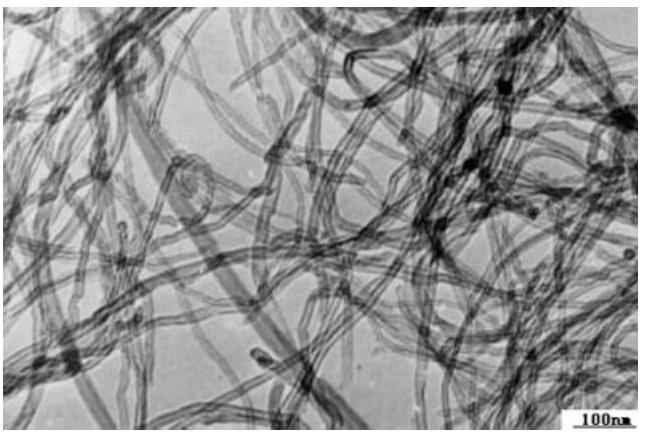

Figure 8 TEM photographs of the raw MWNTs.

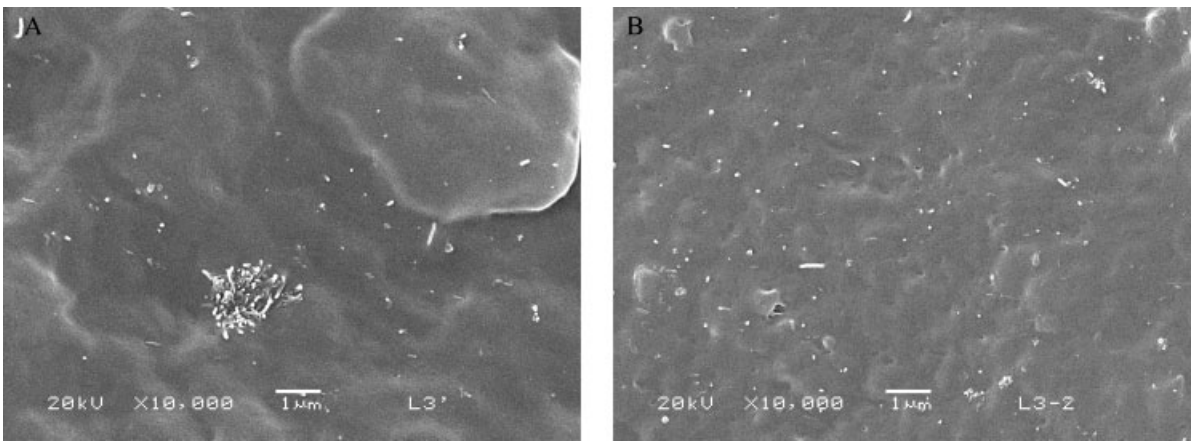

Figure 9 SEM photographs of PP/MWNTs (99.4/0.6) obtained by dynamic packing injection molding (the fracture is parallel to the shear flow direction) (a) static sample, and (b) dynamic sample.

MWNTs are much shorter than the raw MWNTs. It may be due to the action of shear force during the extruding and injection, resulting in breakage of the MWNTs. This result is in a good agreement with that obtained by Rodney.[18] One expects even a more serious decrease of aspect ration of MWNTs for dynamic samples due to the repeated shear during the processing. But our result shows that there is not much difference between static samples and dynamic one, as shown in Figure 9(a,b). To expose the MWNTS on the fractured surface as much as possible, before SEM experiment, the specimens were first etched chemically by 1% solution of potassium permanganate in a 10 : 4 : 1 (by volume) mixture, respectively, of concentrated sulfuric acid, 85% orthophosphoric acid, and water,[19] and the result is shown in Figure 9(c,d). It should be seen that even along the shear flow direction, the dispersion of MWNTs is much better for dynamic samples than that for static ones. Here again one sees the important role of shear force on the dispersion of MWNTs in polymer matrix. Also even the shear force can cut the MWNTs and reduce the number of defects and entanglements of long MWNTs, but the orientation of MWNTs is not achieved along shear flow direction. The decreased aspect ratio of the MWNTs and not much orientation along shear flow direction also be the good reasons that further improvement of the mechanical properties of the PP/MWNTs composite is not observed.

CONCLUSIONS

In summary, the PP/MWNTs composite with good dispersion were successfully prepared by the dynamic packing injection molding. An obvious increase of tensile strength and the impact strength has been achieved for dynamic samples with very small amount of MWNTs (only 0.6 wt %). Our work suggests that the repeated shear force is powerful for the dispersion of MWNTs in polymer matrix. More work is needed to achieve not only a good dispersion but also a high aspect ratio of MWNTs in polymer/MWNTs composites.

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