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Excellent tensile ductility in highly oriented injection-molded bars of polypropylene/carbon nanotubes composites

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Abstract

Multi-wall carbon nanotubes (MWNTs) grafted with alkyl chain were used for reinforcement of polypropylene (PP). For achieving excellent tensile properties, the as-prepared PP/MWNTs composites were subjected to a unique injection molding, as so-called dynamic packing injection molding, to induce a highly oriented structure with both PP chains and MWNTs aligned along the shear flow direction. Not only Young's modulus and tensile strength were enhanced, as expected for oriented materials, but also more importantly composites containing only 0.1–0.3 wt% MWNTs were much ductile compared with the polymer matrix. The addition of PP-*g*-MMA made a drop in the elongation at break to only 15%; however, it could be improved to 80–100% after incorporation of small amount of MWNTs. This improvement in ductility could be ascribed to: (1) the increased mobility of both the PP chains and MWNTs, as they are oriented along tensile deformation direction and (2) the bridging effect of the oriented MWNTs on the crack development during tensile failure.

Keywords: PP/CNTs composite; Orientation; Tensile ductility

1. Introduction

Recently, polymer/carbon nanotubes (CNTs) nanocomposites have gained intensive interest because of their unique and valuable properties, such as, in mechanical [1–3], thermal [4,5], and electronic [6] properties compared to the pristine polymers. One of the advantages of CNTs as a reinforcement filler is their large surface area that can induce a better adhesion with the polymeric matrix, which is an important factor for an effective enhancement of the composite properties [7,8]. However, carbon nanotubes are strongly affected by Van der Waals attraction just due to their small size and large surface area. These forces give rise to the formation of aggregates, which in turn, make dispersion of CNTs in polymer difficult, resulting in rather poor mechanical and electroconductive properties. Therefore the key point to fully explore CNTs reinforcing potential or enhance the properties of a polymer matrix is uniform dispersion, exfoliation, and orientation [9,10], and improving the interaction between CNTs and a polymer matrix is also important.

Currently, three methods are commonly used to incorporate CNTs into thermoplastic polymer: (1) melt mechanical mixing of CNTs with polymers [11,12]; (2) solution mixing or film casting of suspensions of CNTs in dissolved polymer [13,14] and (3) in situ polymerization of CNTs-polymer monomer mixture [15,16]. Meincke et al. [17] fabricated nylon 6/multi-wall carbon nanotubes (MWNTs) and achieved almost a doubled increase in modulus, from 2.6 GPa, for pure nylon 6, to 4.2 GPa for the composites by adding 12.5 wt% of MWNTs. This was, however, accompanied by a significant reduction in ductility, from 40% to just 4%. Manchado et al. [18] observed an increase in modulus from 0.85 GPa to 1.19 GPa by adding 0.75 wt% of arc-single-wall carbon nanotubes (SWNTs) into isotactic polypropylene (iPP). The ductility was found to drop only marginally, from 493% to 402%. To explore the importance of CNTs orientation for improving the mechanical properties, Gorga and Cohen [10] fabricated the PMMA/CNTs nanocomposites using oriented CNTs. An

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increase in the stiffness from 2.7 GPa to 3.7 GPa has been achieved by addition of 10 wt% of MWNTs. In addition, an increase in toughness by 170% was also observed. Paiva et al. [19] introduced a new way to modify MWNTs, in which the MWNTs were 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. Fukushima et al. [20] investigated in detail the mechanical and electro-conductive properties of bucky plastics prepared in situ by free radical polymerization of imidazolium ion-based ionic liquids gelling with single-walled carbon nanotubes. A great enhancement (120-fold) of the tensile modulus was reported, with not much change of the elongation at break. Zeng et al. [16] prepared PA1010/MWNTs composites via in situ polymerization and found a significant increase of Young's modulus and storage modulus of PA1010 by ca. 87.3% and 197%, respectively, at 30.0 wt% of MWNTs content, accompanying a decreases of elongation at break. Yet another possibility is to expose the nanotube composite to gamma radiation for altering the chemistry at the interface for property enhancement, as has been done in PMMA [34]. In summary, not withstanding an increase in stiffness, most reported polymer/CNTs composites exhibit lower toughness than the matrix polymers. The same story was also found for polymer/clay nanocomposites. Recently, Shah et al. [21] have reported a simultaneous increase in stiffness and toughness for PVDF/clay and PS/clay nanocomposites when the measurement temperature was above the glass transition of polymer matrix. According to the authors' suggestion that the motion and orientation of nanoparticles induced by elongation deformation were responsible for the additional energy dissipation, a high mobility nanoparticle seems crucial for super-toughness. To increase the mobility of CNTs in polymer matrix, it is necessary to destroy the entanglement of long CNTs and align them along the deformation direction.

In this article, we will report a largely improved ductility of PP/MWNTs composites achieved via dynamic packing injection molding. In our work, PP/MWNTs composite were first prepared via twin-screw extruder and by adding a compatibilizer. Then the composites were subjected to dynamic packing injection molding (DPIM), in which the melt is firstly injected into the mold and then forced to move repeatedly in a chamber by two pistons that move reversibly with the same frequency as the solidification progressively occurs from the mold wall to the molding core part. In this way, a highly oriented structure with both PP chains and MWNTs aligned along the shear flow direction was achieved. Surprisingly, the PP/MWNTs composite obtained via DPIM possessed excellent tensile performances, particularly, the tensile ductility was found larger compared with neat iPP. The observed high ductility was discussed based on the increased mobility of MWNTs as they were oriented along tensile deformation direction and the bridging effect of the oriented MWNTs on the crack development during tensile failure.

2. Experimental

2.1. Materials

A commercially available isotactic polypropylene (trade marked as T30S, Yan Shan Petroleum China) with $M\eta = 29.2 \times 10^3$ g/mol and a melt flow index (MFI) 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. The compatibilizer, PP grafted maleic anhydride (PP-*g*-MA) (MA content = 0.9 wt%, MFI = 6.74 g/min at 190 °C) in which maleic anhydride group is randomly grafted on a PP backbone, was purchased from Chen Guan Co. (Sichuan, China). The main range of diameter of the raw multiwall carbon nanotubes (MWNTs) is about 10–20 nm and their length is about 5–15 μm, the purity is larger than 95%. The raw MWNTs were executed grafting reaction with octadecylamine according to the method suggested by Qin et al. [22].

2.2. Preparation of PP/MWNTs composite

A series of composite consisting of iPP/PP-*g*-MA/MWNTs (90/10/x wt%; $x = 0$, 0.1, 0.3) were melt-mixed in a TSSJ-2S co-rotating twin-screw extruder. The temperature was maintained at 160 °C, 175 °C, 190 °C, 200 °C, 200 °C and 195 °C from hopper to die and the screw speed was about 120 rpm/min. Thereafter, the specimens are termed as PPCNTx (where x represent the weight content of PPCNT multiplied by 10, such as PPCNT3 means that the MWNTs content is 0.3 wt%) and PPCNT0 is regarded as matrix resin (iPP/PP-*g*-MA 90/10 wt%) for comparison purpose.

After pelletized and dried, the composites were injected into a mold with the aid of a SZ 100 g injection-molding machine with barrel temperature of 190 °C and injection pressure of 900 kg/cm^2. In order to prepare materials with oriented structure during packing stage, special molded equipment named as dynamic packing injection molding (DPIM) was attached on the machine. The processing parameters and their characteristics and detailed experimental procedure of DPIM are described in Refs. [23–25]. The major feature of DPIM is that the melt was firstly injected into the mold then forced to move repeatedly in a chamber by two pistons that moved reversibly with the same frequency as the solidification progressively occurs from the mold wall to the molding core part. The shear rate was about 10/s calculated from geometry of the mold. 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 was signed as PPCNTx-d; otherwise the specimen obtained by static packing injection molding is called static sample, and was signed as PPCNTx-s.

2.3. Tensile property measurement

The tensile experiments were carried out with the aid of Shimadzu AG-10TA Universal Testing Machine. The oriented direction is parallel to tensile deformation direction. The moving speed of crosshead was 5.00 mm/min and 50.00 mm/min for modulus and tensile strength measurements, respectively. And the moving speed shift point was 0.25 mm. The measured temperature was 25 °C. The tensile strength and modulus could directly be obtained from the stress–strain curves by the provided software. The values were calculated as averages over six specimens for each composition.

2.4. Scanning electron microscopy (SEM)

To learn the toughening mechanism, the fractured surface of the prepared PP/MWNTs composites was inspected by a JEOL JSM-5900LV SEM instrument in the direction perpendicular or parallel to the tensile direction. To clarify the orientation of MWNTs, the testing samples were chemically etched in alkyl solvent. Then the fractured surfaces or etched surfaces were gold-coated and observed under an acceleration voltage of 20 kV.

2.5. 2D SAXS measurements

Two-dimensional SAXS measurements were carried out on the dynamic packing injection molded samples using an in-house setup with a rotating anode X-ray generator (Rigaku RU-H300, 18 kW) equipped with two parabolic multilayered mirrors (Bruker, Karlsruhe), giving a highly parallel beam (divergence about 0.012) of monochromatic Cu Kα radiation ($\lambda = 0.154$ nm). Intensity was collected with a two-dimensional gas-filled wire detector (Bruker Hi-Star). A semitransparent beam-stop placed in front of the area detector allowed monitoring intensity of the X-ray beam.

2.6. Two-dimensional WAXS measurements

The 2D wide-angle X-ray scattering experiments (2D WAXS) were conducted using a Rigaku Denki RAD-B diffractometer. The wavelength of the monochromatic X-ray from Cu Kα radiation was 0.154 nm. The samples were placed with the orientation (flow direction) perpendicular to the beams.

3. Results and discussion

3.1. Oriented structure in injection-molded bars

As already demonstrated in our previous works [26–28], samples obtained via dynamic packing injection molding usually show a highly oriented structure. As an example, Figs. 1 and 2 are the 2D SAXS and 2D WAXS patterns, respectively, of dynamic packing injection-molded bar of PP/MWNTs composite containing 0.3 wt% MWNTs (PPCNT3-d), the corresponding patterns of static counterpart (PPCNT3-s) are also included for comparison. For the 2D SAXS pattern of PPCNT3-d, two strong scattering spots in the meridian direction indicate that preferential growth of all lamellae is perpendicular to the shear direction. Meanwhile, all reflections of 2D WAXS present themselves by arcs rather than circles, indicating significant molecular orientation. Strong reflections of (*hk*0) plane in PP along the equator reflect that molecular chains are preferentially oriented along shear direction. Four reflections around the meridian also emerge in the (110) plane of PP, indication of lamellar branching through homoepitaxy between α-crystals themselves [29]. In contrast to PPCNT3-d, for PPCNT3-s, only isotropic reflection circles are observed in both 2D WAXS and 2D SAXS patterns, which imply a random orientation of PP molecular chain as well as PP lamellae.

The dispersion and orientation of MWNTs in polymer matrix are keys for high performance composite materials. One expects a highly oriented structure for the dynamic samples. Shown as an example (Fig. 3(a)) is the SEM image of the dynamic sample containing 0.3 wt% MWNTs (PPCNT3-d). MWNTs preferentially oriented along the shear flow direction. From the SEM images, one can evaluate the diameter of the observed MWNTs fibers, which is about 0.4–0.6 μm. Since the diameter of single MWNT is only 10–20 nm (product

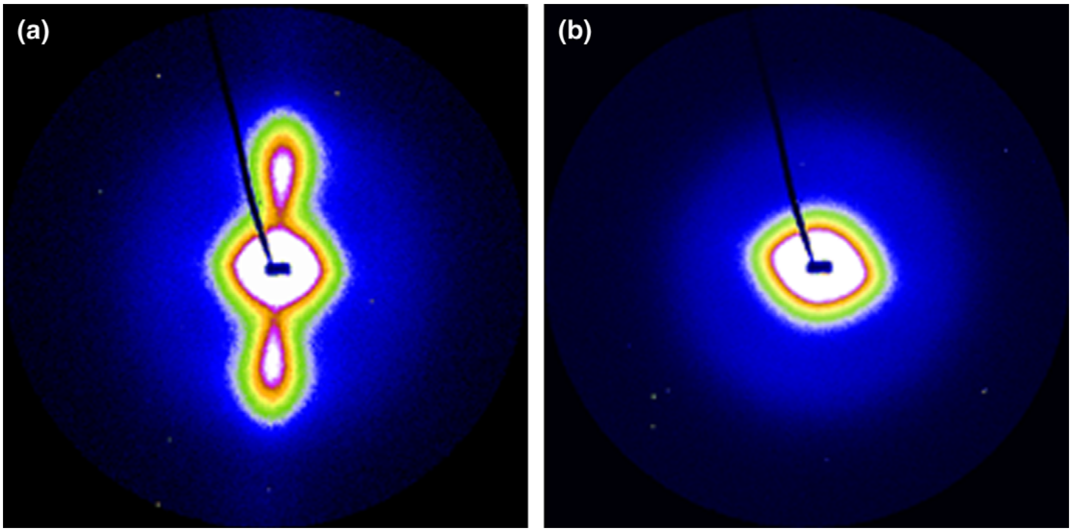

Fig. 1. Scattering patterns of 2D SAXS at 25 °C of: (a) PPCNT3-d and (b) PPCNT3-s. Shear direction is vertical.

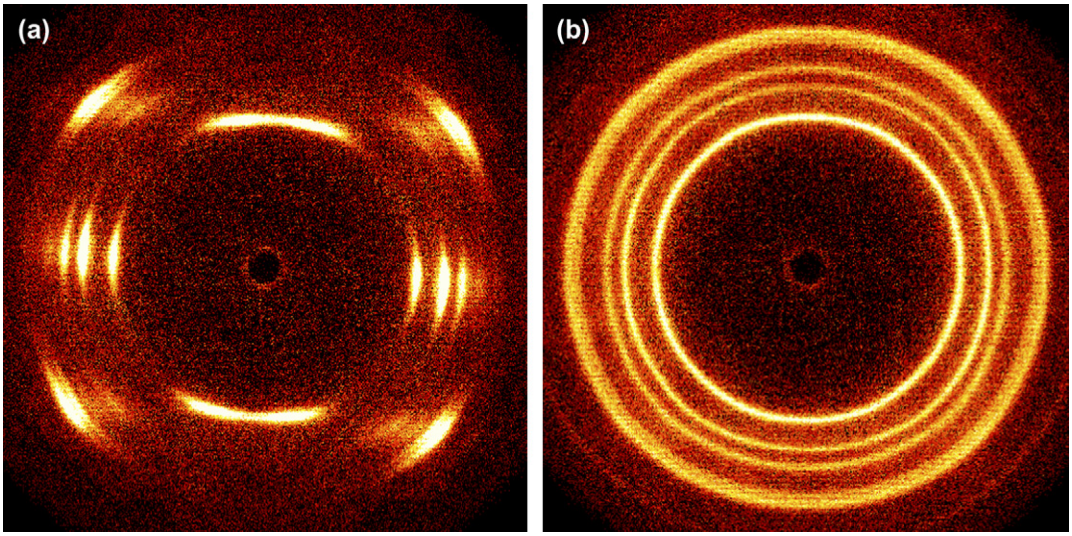

Fig. 2. Scattering patterns of 2D WAXS at 25 °C of: (a) PPCNT3-d; (b) PPCNT3-s. Shear direction is vertical.

information provided by the manufacturer), the observed MWNTs fibers could be wrapped by the matrix polymer, probably due to the shear induced interaction between PP matrix and MWNTs during dynamic packing injection molding. Another possible structure is that the observed MWNTs fibers are actually bundles composed by 20–30 individual nanotubes. To see clearly the dispersion of MWNTs in the composites, the fractured surface perpendicular to tensile deformation direction was examined. Fig. 3(b) shows the fractured surface for the same sample as shown in Fig. 3(a), but viewed perpendicularly to the tensile deformation direction. One observes indeed that MWNTs are dispersed in PP matrix as bundles instead of single nanotube. The diameter of MWNTs bundles is about 0.4–0.6 μm and is composed by 20–30 individual nanotubes. Although tens of single nanotube will aggregate into a bundle, the bundles separate from each other and disordered entanglement between MWNTs fibers is eliminated through shearing dispersion. So it can be concluded that a composite with good dispersion and preferential orientation of MWNTs bundles has been achieved via dynamic packing injection molding. It is also found that the edge between bundles of carbon nanotubes and matrix is faint (Fig. 3(b)), and the diameter of the bundles founded in Fig. 3(a) are more larger than that in Fig. 3(b) because of being wrapped by polymer matrix. So it can be conclude that (1) the strong interface adhesion between the modified carbon nanotubes and the polymer matrix could be formed; (2) instead of individual carbon nanotubes, bundles composed by 20–30 individual nanotubes are uniformly dispersed in the PP matrix and (3) a composite with preferential orientation of MWNTs along shear flow direction has been achieved via dynamic packing injection molding.

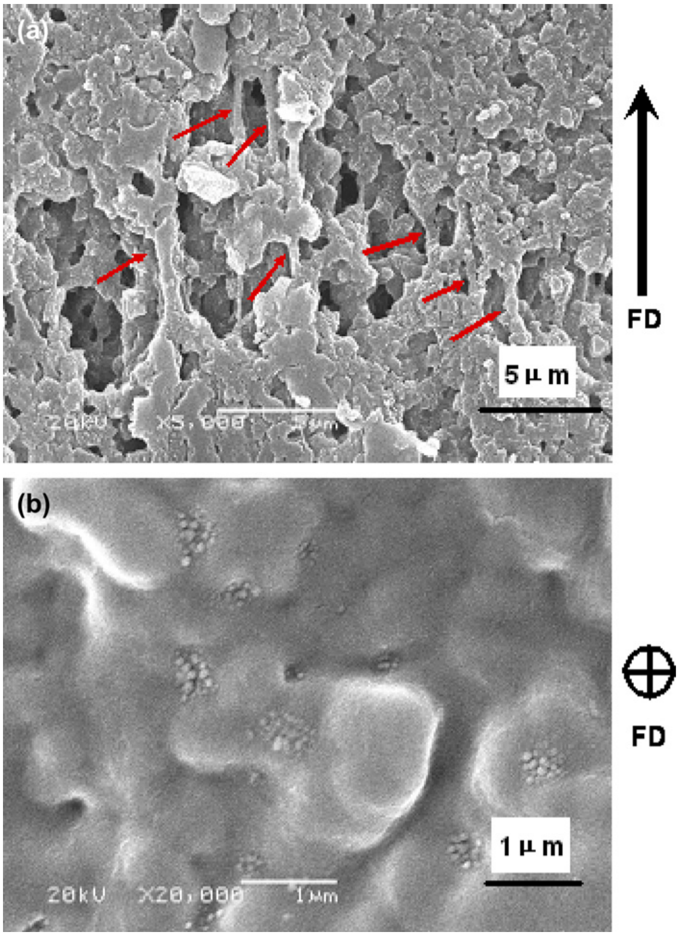

Fig. 3. SEM images of the dynamic sample containing 0.3 wt% MWNTs (PPCNT3-d): (a) etched by alkyl solvent along the shear flow direction and (b) fracture surface perpendicular to the shear flow direction.

3.2. Enhancement in tensile properties

The typical stress–strain curves of dynamic samples are shown in Fig. 4, including static ones for comparison. And the average values of various composites are show in Fig. 5. As for the static samples, there is no obvious necking and the fracture mode is brittle, with ultimate elongation less than 15%. One also observes not much change of modulus and tensile strengths by adding very small amount of MWNTs to the PP matrix via conventional injection molding. It should be noted that the elongation of PP matrix here is quite small,

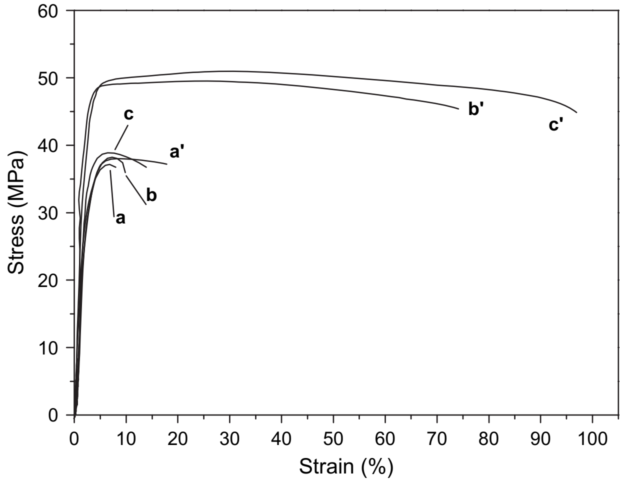

Fig. 4. The stress–strain behavior of both dynamic samples and static samples: (a) PPCNT0-s; (b) PPCNT1-s; (c) PPCNT3-s; (a′) PPCNT0-d; (b′) PPCNT1-d and (c′) PPCNT3-d.

which is usually larger than 50%, depending on the molecular characteristics and testing conditions. We have measured the elongation of neat iPP without PP-*g*-MA. It was around 50% as prepared with the same injection molding parameters. The drop in the elongation in our case must be due to the addition of PP-*g*-MA. As for the dynamic samples, however, an obvious increase in elongation is seen, resulting from the oriented structure via dynamic packing injection molding. There is an order of magnitude increase in the ductility (elongation) as well as the toughness of the composites as measured by integrated area under the stress–strain curves, compared with the basal polymer. By adding 0.1 wt% and 0.3 wt% of MWNTs, the increase in the ductility is about 800% and 1000%, respectively, compared with the static sample of iPP/PP-*g*-MA matrix; at about 400% and 540%, respectively, compared with the dynamic sample of iPP/PP-*g*-MA matrix. Even compared to the neat iPP resin without PP-*g*-MA, the elongation is also obviously increased. Meanwhile the tensile modulus (Young's modulus) and strength show substantial increase by adding small amount of MWNTs for dynamic samples. The Young's modulus of iPP/PP-*g*-MA matrix via DPIM is 2.1 GPa and increased to 2.6 GPa and 2.8 GPa by adding 0.1 wt% and 0.3 wt% MWNTs, respectively; correspondingly the tensile strength is enhanced from 38.0 MPa to 49.8 MPa and 51.1 MPa.

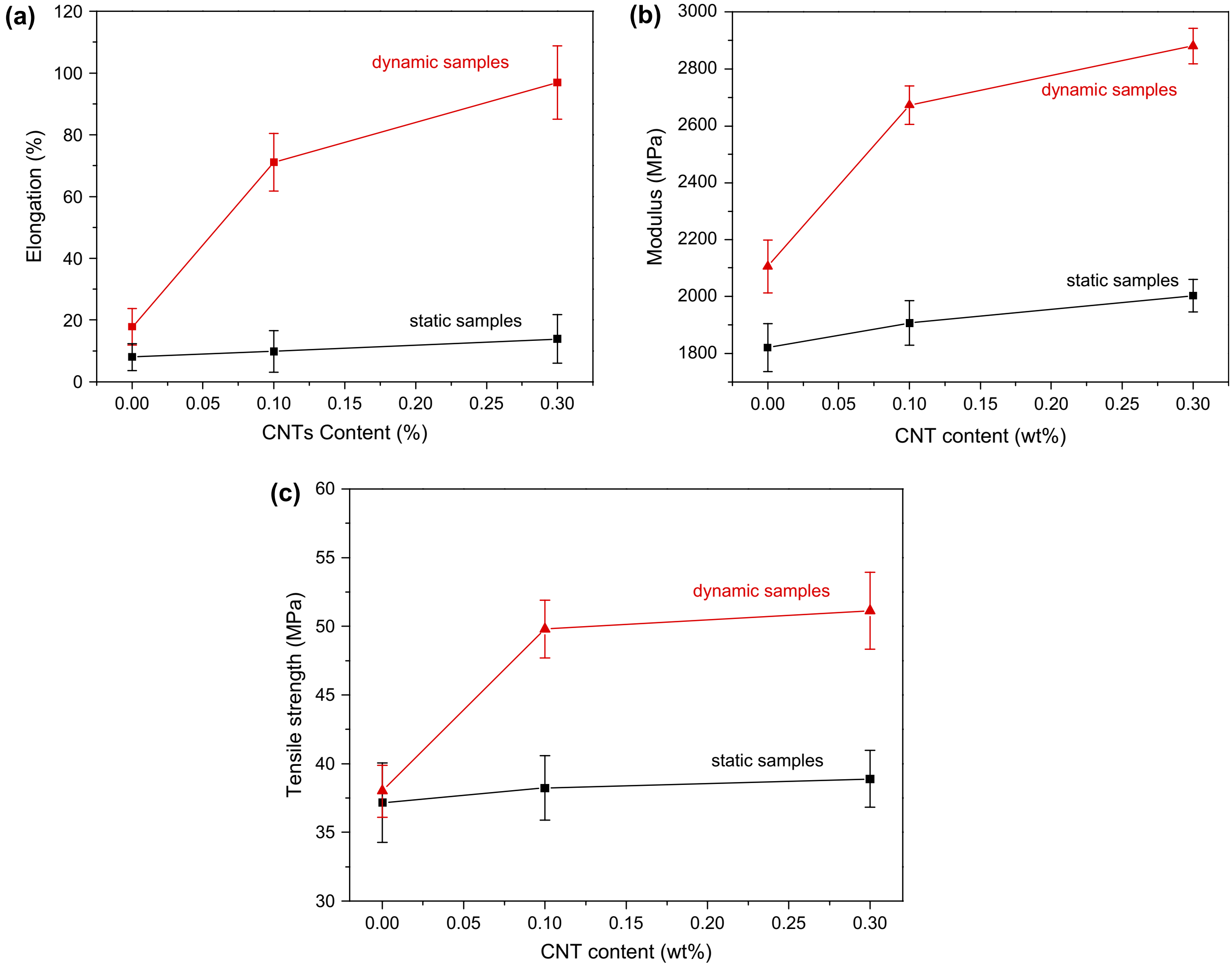

Fig. 5. CNT content dependences of: (a) elongation, (b) Young's modulus and (c) tensile strength in the as-prepared composites.

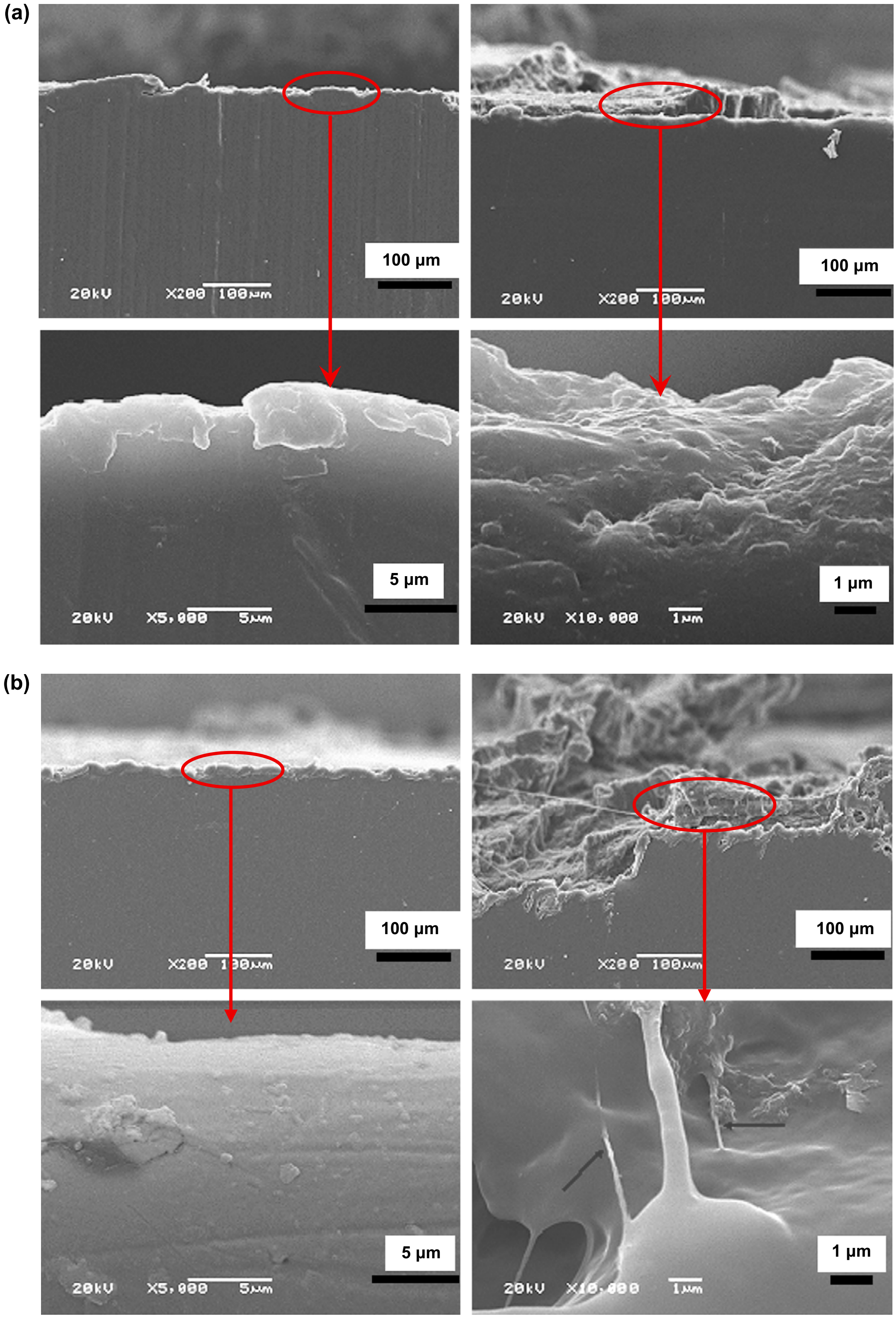

Fig. 6. The SEM images of the fracture surface along the flow direction of the dynamic (right line) and static (left line) samples: (a) PPCNT0; (b) PPCNT1 and (c) PPCNT3.

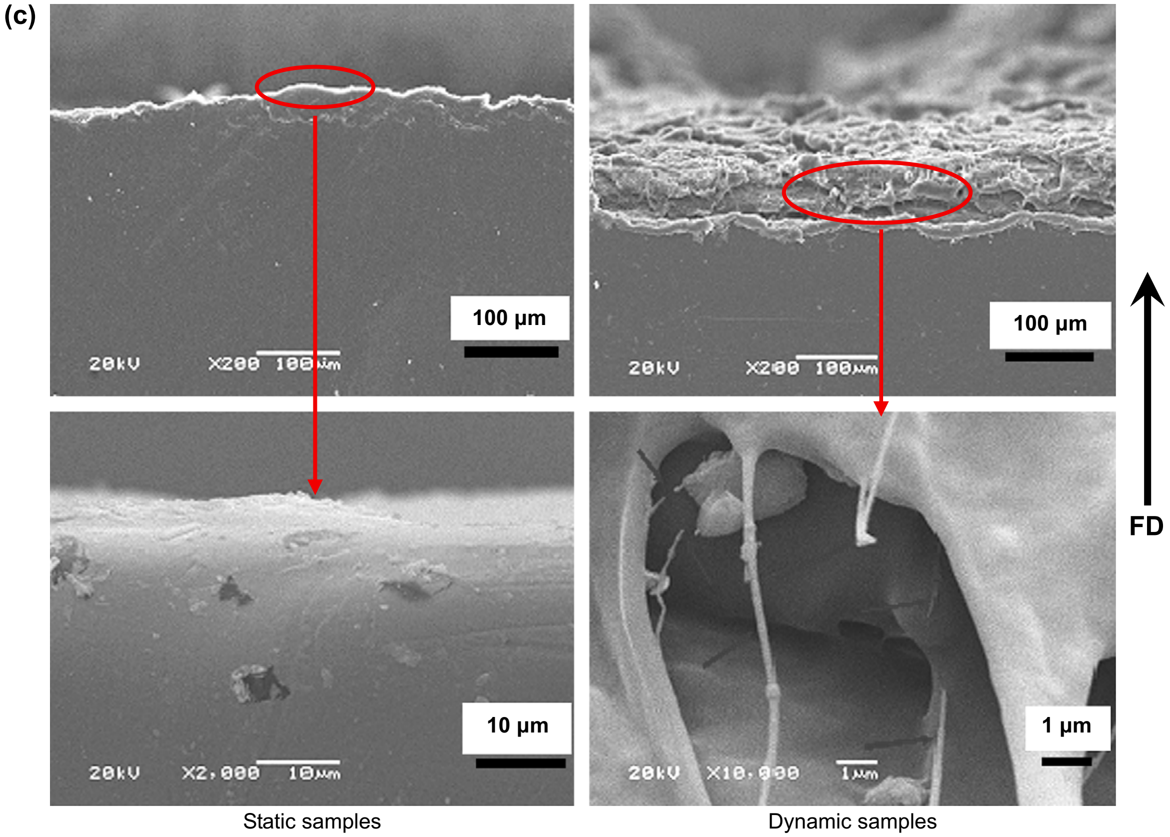

Fig. 6. (*continued*).

3.3. Mechanism for the enhanced ductility

Our present result is somewhat conflictive to a general consideration that the unoriented PP usually possesses a relatively high ductility contrasting to the oriented one. As the doubt about ductility of oriented PP matrix is higher than the unoriented one, we have repeated the experiment and the result is same. Moreover, in this study, the ductility of PP matrix seems low compared to the value in the past literature. The reason is complicated and may be as: (1) the incorporation of low molecular weight PP-*g*-MA disturbs the assembly or entanglement of PP chains; (2) the scission PP chains commonly occurs during melt compounding, particularly in the presence of PP-*g*-MA and (3) some unknown factors for our injection-molding equipment. Our work is under going and the substantial reason will be deeply explored. On the other hand, since the major goal of this study is to investigate the roles of nanotubes and orientation structure on the ductility of as-prepared composites, if the compositions of basal polymer and the processing parameters are same, which ensures the mechanical properties of basal polymer in various samples as approximately constant, thus a relative comparison between the samples is possible. Semi-crystalline polymers being composed of crystalline lamellae and entangled amorphous chains show a complicated behavior under tensile strain. They exhibit large plasticity when being deformed above the glass transition temperature T_g of the amorphous phase. Cohen and coworkers [30,31] used three different sizes of $CaCO_3$ particles as fillers to successfully improve the impact toughness of high-density polyethylene (HDPE) and iPP, and attributed the effect to the combined mechanisms of crack deflection and local plastic deformation of the polymer around the particles following debonding. Recently, molecular-dynamics studies have suggested that the mobility of the nanoparticles in polymer might be crucial for introducing new energy-dissipating mechanism that leads to enhanced toughness in the nanocomposite [32]. Furthermore, Shah et al. [21] presented experimental evidence that both nanoparticle orientation and alignment under tensile stress were responsible for this energy-dissipation mechanism, and the mobility of polymer matrix was a precondition for this mechanism to be effective. The increased mobility of both PP matrix and MWNTs by orienting them along tensile deformation direction can be used in part to explain the enhanced ductility for the dynamic samples. In our work, the experimental temperature of tensile testing is about 25 °C, above the T_g of the PP matrix, so the macromolecular chain should have good ability to move under tensile stress, particularly when it is oriented. However, the oriented PP matrix alone cannot cause very much increase of ductility and toughness, which can be concluded by comparing the elongation between the dynamic PP sample and the static PP sample. A significant increase of ductility can only be achieved by adding oriented MWNTs, which could move along the deformation direction easily during tensile deformation, leading to the largely improved ductility of the composite. Moreover, it should be noted that, in another system, for the PP/organoclay nanocomposites, the tensile ductility of oriented nanocomposite was also found obviously higher than the unoriented one, which suggested again the importance of oriented nanoparticles to the large promotion of tensile ductility.

MWNTs have a large aspect ratio (more than 100) once they are fully oriented. In our samples, the role that MWNTs may bridge cracks cannot be negligible. For this reason, the fractured surface of the samples along the tensile direction is carefully examined; this is shown in Fig. 6 for both the dynamic and static samples. The pictures on the left line are the SEM images of the static samples while the ones on right are for the dynamic samples. The fractured surface of the static samples is smooth, indicating again that the static samples fracture in brittle mode. For dynamic samples, the fracture surface represents an absolutely different morphology. They are rugged on large scale, even on small magnification, the distorted matrixes are observed. On large magnification, the alignment of MWNTs fibers along the deformation direction is clearly observed. The diameter of these MWNTs fibers is about 0.4–0.6 μm. Our new finding is that most of MWNTs fibers are located in the center of the crack and serve as a bridge for connecting the cracks. One may visualize a sliding process of the cracks along the oriented MWNTs until breakup, resulting in also a large elongation thus a great improvement of toughness. Another argued explanation for the enhanced ductility could be due to the fact that the presence of MWNTs could result in a dramatic change in the crystalline morphology, transforming the large spherulites into thin fiber-like crystallites, particularly under the effect of shear. This will increase the number of spacing that can participate in energy dissipation thus improve the ductility of the hybrid. But the validity of this explanation needs to be approved by further experimental proofs. Moreover, the strong interfacial adhesion between the modified carbon nanotubes and the polymer matrix, which causes the successful stress transfer from PP matrix to filler [33], may also be devoted to the enhancement of toughness.

4. Conclusion

Highly oriented structure with both PP lamellae and MWNTs oriented along the shear flow direction has been obtained via dynamic packing injection molding. Not only the Young's modulus and tensile strength can be enhanced, but more importantly, the oriented composites show an order of improvement in ductility than the iPP/PP-*g*-MMA matrix. This could be understood as due partially to the increased mobility for both PP chains and MWNTs as they are oriented along tensile deformation direction. On the other hand, we have found out the evidence that oriented MWNTs with large respect ratio, could also serve as a bridge for crack development, leading to an increased elongation thus a great improvement of toughness.

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References

[1] Sreekumar TV, Liu T, Min BG, Guo H, Kumar S, Hauge RH, et al. Adv Mater 2004;16:58.
[2] Kumar S, Dang TD, Arnold FE, Bhattacharyya AR, Min BG, Zhang XF. Macromolecules 2002;35:9039.
[3] Sen R, Zhao B, Perea D, Itkis ME, Hu H, Love J. Nano Lett 2004;4(3):459.
[4] Geng HZ, Rosen R, Zheng B, Shimoda H, Fleming L, Liu J, et al. Adv Mater 2002;14:1387.
[5] Zou YB, Feng YC, Wang L, Liu XB. Carbon 2004;42:271.
[6] Benoit JM, Corraze B, Lefrant S, Blau WJ, Bernier P, Chauvet O. Synth Met 2001;121:1215.
[7] Park SJ, Cho KS, Ryu SK. Carbon 2003;41:1437.
[8] Naik NK, Meduri S. Compos Sci Technol 2001;61:1429.
[9] Fischer D, Pötschke P, Brünig H, Janke A. Macromol Symp 2005;230:167.
[10] Gorga RE, Cohen RE. J Polym Sci Part B Polym Phys 2004;42:2690.
[11] Jin ZX, Pramoda KP, Goh SH, Xu GQ. Mater Res Bull 2002;37:271.
[12] Andrews R, Jacques D, Minot M, Rantell T. Macromol Mater Eng 2002;287(14):395.
[13] Haggenmuller R, Gonmas HH, Rinzler AG, Fischer JE, Winey KI. Chem Phys Lett 2000;330:219.
[14] Safadi B, Andrews R, Grulke EA. J Appl Polym Sci 2002;84(14):2660.
[15] Jia ZJ, Wang ZY, Xu CL, Liang J, Wei BA, Wu DH. Mater Sci Eng A 1999;271:395.
[16] Zeng HL, Gao C, Wang YP, Watts PC, Kong H, Cui XW, et al. Polymer 2006;47:113.
[17] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Polymer 2004;45:739.
[18] Manchado MA, Valentini L, Biagiotti J, Kenny JM. Carbon 2005;43:1499.
[19] Paiva MC, Zhou B, Fernado KAS, Lin Y, Kennedy JM, Sun YP. Carbon 2004;42:2849.
[20] Fukushima T, Kosaka A, Yamamoto Y, Aimiya T, Notazawa S, Takigawa T, et al. Small 2006;2(4):554.
[21] Shah D, Maiti P, Jiang DD, Batt CA, Giannelis EP. Adv Mater 2005;17(5):525.
[22] Qin YJ, Liu LQ, Shi JH, Wu W, Zhang J, Guo ZX, et al. Chem Mater 2003;15:3256.
[23] Guan Q, Shen KZ, Li J, Zhu J, Zhu JM. J Appl Polym Sci 1995;55(15):1797.
[24] Zhang G, Jiang L, Shen KZ, Guan Q. J Appl Polym Sci 1999;71(5):799.
[25] Zhang Q, Wang Y, Fu Q. J Polym Sci Part B Polym Phys 2003;41(1):1.
[26] Wang K, Zhao P, Yang H, Liang S, Zhang Q, Du RN, et al. Polymer 2006;47:7103.
[27] Wang Y, Na B, Fu Q, Men YF. Polymer 2004;45:207.
[28] Na B, Wang Y, Zhang Q, Fu Q. Polymer 2004;45:6245.
[29] Lotz B, Wittmann JC. J Polym Sci Part B 1986;24:1559.
[30] Bartczak Z, Argon AS, Cohen RE, Weinberg M. Polymer 1999;40:2347.
[31] Thio YS, Argon AS, Cohen RE, Weinberg M. Polymer 2002;43:3661.
[32] Gersappe D. Phys Rev Lett 2002;89:058301.
[33] Hwang GL, Shieh Y-T, Hwang KC. Adv Funct Mater 2004;14(5):487.
[34] Clayton LM, Sikder AK, Kumar A, Cinke M, Meyyappan M, Gerasimov TG, et al. Adv Funct Mater 2005;14:101.