Available online at www.sciencedirect.com
SCIENCE DIRECT
Polymer 47 (2006) 4497–4500
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Morphological manipulation of carbon nanotube/polycarbonate/polyethylene composites by dynamic injection packing molding

Sha-Ni Li, Bo Li, Zhong-Ming Li *, Qiang Fu, Kai-Zhi Shen

State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, Sichuan, People's Republic of China

Received 23 February 2006; received in revised form 30 March 2006; accepted 23 April 2006
Available online 19 May 2006

Abstract

Multiwalled carbon nanotubes (CNTs) filled polymer composite based on polycarbonate (PC) and polyethylene (PE) was fabricated by shear controlled orientation in injection molding (dynamic samples) and conventional injection molding (static samples). The morphological observation by scanning electronic microscope (SEM) indicated that PC phase in situ generated more and finer microfibrils in the dynamic samples than in the static ones, and the CNTs predominantly localized in the PC microfibrils without obvious migration to PE matrix and also aligned along the microfibrils. With such unique morphology, the tensile properties of the dynamic samples were simultaneously considerably increased compared to their complementary samples, especially in the presence of 0.5 wt% of CNTs, which indicates both stretch alignment of CNTs and molecule orientation can bring out a significant reinforcement on PE. Furthermore, the static samples displayed double yielding points in on the stress–strain curves, and interestingly, a small quantity of CNTs in PC fibrils strengthened this phenomenon.

Keywords: Carbon nanotubes; Dynamic injection packing molding; Microstructure

1. Instruction

Considering effective realization of excellent anisotropic properties of carbon nanotube (CNT) in CNT reinforced polymer composites [1–8], there is still a great challenge in achieving alignment of CNT in the matrix. Among several approaches to align nanotubes [9–11], the electrospinning technique is the most attractive way to incorporate CNT into polymer matrices to form composite nanofibers, combining the benefits of nanofiber with the merits of CNT [9]. However, the distribution and alignment of CNT in the nanofibers are strongly depended on CNT type and dispersion quality in the polymer solution. Moreover, not all the polymer matrices had the proper solutions for CNT dispersion before electrospinning process.

In our recent work, we successfully prepared an in situ microfibrillar CNT/polycarbonate (PC)/polyethylene (PE) composite through an extrusion-hot stretching–quenching process, in which the CNTs are preferably dispersed in the PC microfibrils [12]. Unexpectedly, the mechanical properties of this composite only have limited improvement, because there are too many processing procedures, which deteriorate the properties of the materials, and the microfibrils with a high CNT concentration cannot be attainable due to too high viscosity of the dispersed phase.

In recent years, dynamic injection packing molding (DIPM) technology has been found to be an effective approach for generating highly oriented structure of either molecules or phase, and therefore, greatly enhancing mechanical properties [13]. In this communication, we report our efforts to fabricate a new CNTs filled polymer composite through DIPM technology. This composite contains both highly oriented PE molecules and CNT/PC microfibrils in which most CNTs are localized and oriented. The present work is part of a series works on properties enhancement of general-purpose plastics (usually polyethylene and polypropylene), mostly achieved by new processing techniques or incorporation of some general-purpose engineering plastics (such as polycarbonate, nylon, etc.) to polyolefins (PO) [14].

2. Experiment part

The materials (including PC, EVA, PE, and CNTs) and the treatment of CNTs were same as before [12]. Solution-phase

* Corresponding author. Fax: +86 28 8540 5401.
E-mail address: zm_li@263.net.cn (Z.-M. Li).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.04.051

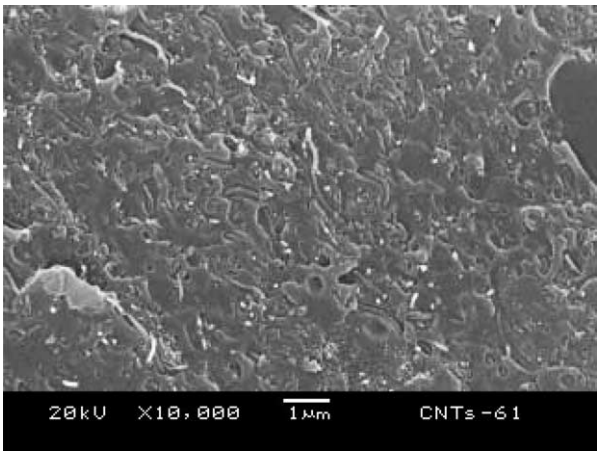

Fig. 1. SEM micrograph of the CNTs/EVA/PC composite containing 5 wt% CNTs, prepared by melt blending techniques.

processing was used to prepare the CNT/EVA (20/80 by weight) masterbatch with a high CNT content [12]. CNT/EVA/PC (5/20/75 by weight) compound was produced by melt mixing CNT/EVA masterbatch with PC. The representative morphology of CNT/EVA/PC composites with 5 wt% CNTs is shown in Fig. 1. Apparently, individual MWNT (multiwalled carbon nanotube) is randomly dispersed (without preferred alignment or orientation after dispersion) within the matrix. After pelletized, CNT/EVA/PC compound and PE (0.5/2/7.5/90 by weight) pellets were molded using DIPM technology. The main feature of this technology was that the hot melt was subjected to high shear stress in a chamber before frozen, which was given by two pistons moved reversibly with the same frequency. The detailed experiment procedures were described in Ref. [15]. We also carried out injection molding under static packing (conventional injection molding) with the same processing parameters but without shear for comparison. These two types of samples are called dynamic samples and static samples, respectively. The tensile testing of the samples obtained was carried out on an Instron universal material testing system at 25 °C with a gauge length of 25 mm and a crosshead speed of 50 mm/min. Molecule orientation in DIPM samples was determined by small angle X-ray scattering (SAXS) measurements, details of the SAXS setup can be found in Ref. [16].

3. Results and discussion

Fig. 2(a) and (b), respectively, show the typical morphology of the sub-skin layer for the static and dynamic CNTs filled samples (the SEM micrographs for the samples without CNTs were not shown for brevity). Apparently, there are injection-induced PC microfibrils in the two samples, which are perfectly oriented along the shear direction. In the dynamic sample (Fig. 2(b)), PC microfibrils are more uniform with narrow diameter distribution, compared to these in the static sample (shown in Fig. 2(a)). It indicates that a shear stress field in DIPM can decrease size of dispersed phase and narrow size distribution. Moreover, there are some holes in the static

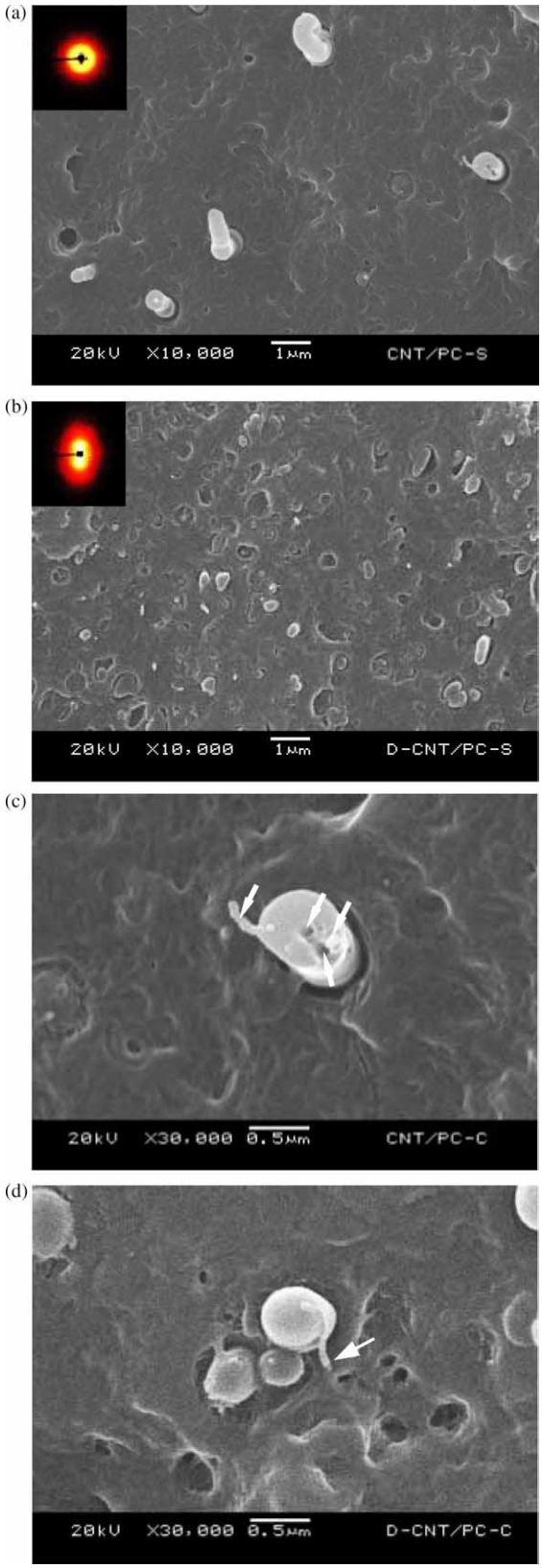

Fig. 2. SEM micrographs of CNTs filled PC/PE samples prepared by conventional and dynamic injection molding. (a) Conventional injection (static) sample, the holes mean pulling out of PC microfibrils; (b) dynamic injection (dynamic) sample; (c) CNTs in the PC microfibrils of static sample; (d) CNTs in the PC microfibrils of dynamic sample. The inset shows SAXS diagram of sample, and the bright white arrows show CNTs or the holes after CNTs pulling out.

sample after fibers pulling out, while in the dynamic sample, the fibers are almost cut off just from the fracture surface, which implies a more effective interfacial stress transfer for the dynamic sample. The shear induced compatibilization and fewer defects in the dynamic sample are probably responsible for the high interfacial interaction between the fibers and the matrix PE. Observed from the micrograph at a higher magnification (Fig. 2(c)), it is interesting that MWNTs predominantly localize in the PC microfibrils without obvious migration to PE matrix, which is in line with our previous study [12]. These phenomena imply that there is strong interfacial bonding between CNT and EVA copolymer, which is due to the fact that functionalization of the MWNTs with –COOH groups increases the anchoring (or interacting) sites along the nanotubes with EVA copolymer [17]. It is believed that the majority of CNTs are localized in PC phase based on the following facts: (a) CNTs/EVA was first melt mixed with PC phase prior to injection molding, so CNTs have sufficient time to interact with PC; (b) considering PC phase always with much higher viscosity than PE phase, especially when the incorporation of CNTs, it should be hard for CNTs immigration to PE phase during injection molding; (c) the EVA used in our laboratory has a relatively VA content (28 wt%), which is in favor of strengthening the adhesion between EVA and PC.

The typical stress–strain curves of static and dynamic samples are shown in Fig. 3, and the tensile properties including elastic modulus, ultimate tensile strength, failure strain, and toughness (characterized by area under the stress–strain curve, before strain of about 35%) are summarized in Table 1. As shown in Table 1, tensile strength, Young's modulus, and toughness of 0.5 wt% CNT filled dynamic samples were increased at least 213.0% from 26.0 to 81.4 MPa, 162.6% from 876.7 to 2302.0 MPa, 195.9% from 1.5 to 4.4 kJ/m^2, but failure strain decreased 83.2% from 209.7 to 35.3% compared with those of CNT filled static samples, respectively. The outstanding

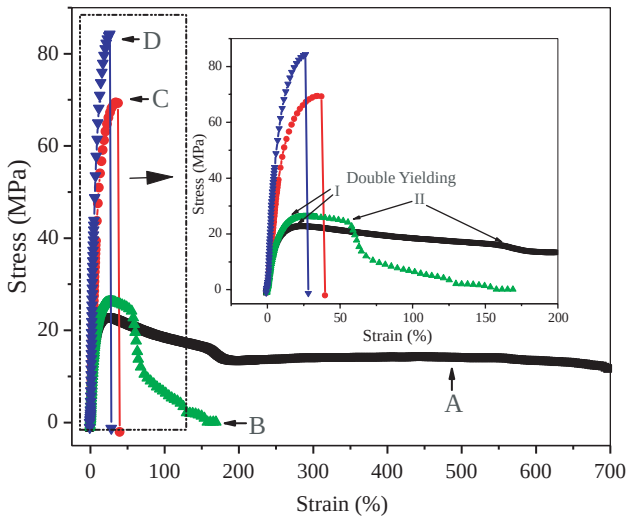

Fig. 3. Typical strain–stress curves for all samples at a crosshead speed of 50 mm/min and at 25 °C. (A) static PC/PE sample; (B) static CNT filled PC/PE sample; (C) dynamic PC/PE sample; (D) dynamic CNT filled PC/PE sample.

Table 1
Mechanical properties of the materials obtained in this study

Sample	Tensile strength (MPa)	Elastic modulus (MPa)	Failure strain (%)	Toughness (kJ/m^2)
PC/PE	22.8	772.8	1117.4	1.3
D-PC/PE	72.4	1797.5	42.3	3.5
CNT/PC/PE	26.0	876.7	209.7	1.5
D-CNT/PC/PE	81.4	2302.0	35.3	4.4

Note: PC/PE, static PC/PE sample; D-PC/PE, dynamic PC/PE sample; CNT/PC/PE, CNT filled static PC/PE sample; D-CNT/PC/PE, CNT filled dynamic PC/PE sample.

increment in mechanical properties suggests that molecular chain orientation plays an important role. A high level molecular orientation was obtained as a result of DIPM processing, and is the primary reason for the improved tensile strength of dynamic samples in comparison with static samples. Unfortunately, these increases in strength and modulus are on sacrifice of ductility (failure strain) of composites. Besides, generation of higher proportion and more fine PC fibers by shear while packing have further promoted their tensile properties of the dynamic samples.

The orientation of microfibril was also evaluated by small angle X-ray scattering (SAXS) measurement. The selected 2D SAXS patterns are shown in the inset of Fig. 2(a) and (b), which indicates high molecule orientation in the dynamic sample. The orientation parameters of dynamic CNT filled PC/PE sample, dynamic PC/PE sample and all static samples are 0.68, 0.61, and 0, respectively. It is once again convinced that there does have been strong molecular orientation in dynamic samples, with respect to static samples. The orientation of chains would also benefit the alignment of CNTs in PC dispersed phase, which are probably due to strong interaction between CNTs and PC fibers. On the other hand, 0.5 wt% of CNTs can bring out an increment of about 9.0 MPa (from 72.4 to 81.4 MPa) and about 500 MPa (from 1797.5 to 2302.0 MPa) in tensile strength and Young's modulus for dynamic samples compared to 3.2 MPa (from 22.8 to 26 MPa) and 100 MPa (from 772.8 to 876.7 MPa) for static samples, respectively, which once again testify that dynamic shearing can favor orientation of CNT in PC fibers to impress its unique anisotropic properties [11]. Meanwhile, the strength, modulus, and toughness (before strain of about 35%) of CNT filled samples including static and dynamic ones are constantly higher than those free of CNT. These enhancements of CNT filled samples are due to effective load transfer from microfibrils to CNT through strong interfacial bonding between nanotubes and EVA matrix, and between EVA and PC, and between PC microfibrils and PE matrix where EVA acts as a successful compatilizer, which could help more strain energy absorption before fracture.

Fully agreeing with our previous study [18], static samples here also exhibited double yielding behavior, as shown in Fig. 3. In the beginning, the common yielding occurs after the necking of PE matrix, where the necked material is not sufficient to counteract the reduction in the cross-sectional area

of the necked region, leading to a reduction in load. The stress first drops quickly, while the strain continues to increase substantially. Then, it is frictional force in the interface between PC microfibrils and PE matrix and effect of EVA compatibilization that transferred strain energy from PE matrix to PC fibers. When higher energy causes PC yielding, the stress starts to drop rapidly again, indicating a second yielding [18]. More attractively, one could notice that a small amount of CNTs in PC dispersed phase would strengthen double yielding behavior. We suppose this is related to enhancement of PC melt strength in the presence of CNTs, which would stabilize structure of microfibrils during processing, and tend to generate more and finer CNT/PC fibers. The fact that the CNTs favor forming of PC microfibrils was also evidenced by SEM micrographs (not shown here). In contrast, the dynamic samples with limited elongation always fractured before PC fibers yielded. Therefore, no double yielding behavior is observed in all dynamic samples.

4. Conclusion

In summary, DIPM is a successful approach to preparing alignment of CNT in polymer composites to effectively utilize nanotubes as an ideal reinforcement for advanced composite. In this material, the dispersed phase can generate in situ numerous and oriented microfibrils, and the CNTs predominantly localized in the microfibrils, and also aligned along the microfibrils. Such a structure can simultaneously increase strength, modulus, and toughness of polymers. Moreover, these unique CNTs filled microfibrils form a sheath-core structure, which offers the potential for exciting applications such as ultrastrong wires, and new type nanocomposite materials, etc.

Acknowledgements

The authors gratefully acknowledge the financial support of this work by the Nature Science Foundation of China (Grant no.: 50527301) and Ying Tung Fok Education Foundation (Grant no.: 101045).

References

[1] Zeng HL, Gao C, Wang YP, Watts PCP, Kong H, Cui XW, et al. Polymer 2006;47:113.
[2] Zhao CG, Hu GJ, Justice R, Schaefer DW, Zhang SM, Yang MS, et al. Polymer 2005;46:5125.
[3] Ruan SL, Gao P, Yang XG, Yu TX. Polymer 2003;44:5643.
[4] Wang M, Pramoda KP, Goh SH. Polymer 2006;45:11510.
[5] Shieh YT, Liu GL, Hwang KC, Chen CC. Polymer 2006;45:10945.
[6] McNally T, Pvtschke P, Halley P, Murphy M, Martin D, Bell SEJ, et al. Polymer 2006;45:8222.
[7] Koerner H, Liu WD, Alexander M, Mirau P, Dowty H, Vaia RA. Polymer 2005;46:4405.
[8] Meincke O, Kaempfer D, Weickmann H, Friedrich C, Vathauer M, Warth H. Polymer 2004;45:739.
[9] Sen R, Zhao B, Perea D, Itkis ME, Hu H, Love J, et al. Nano Lett 2004;4:459.
[10] Terrones M, Grobert N, Olivares J, Zhang JP, Terrones H, Kordatos K, et al. Nature 1997;388:52.
[11] Dror Y, Salalha W, Khalfin RL, Cohen Y, Yarin AL, Zussman E. Langmuir 2003;19:7012.
[12] Li ZM, Li SN, Yang MB, Huang R. Carbon 2005;43:2413.
[13] Kalay G, Bevis MJ. J Polym Sci, B 1997;30:241.
[14] Li ZM, Yang W, Xie BH, Shen KZ, Huang R, Yang MB. Macromol Mater Eng 2004;289:349.
[15] Chen LM, Shen KZ. J Appl Polym Sci 2000;78:1906.
[16] Li LB, de Jeu WH. Macromolecules 2003;36:4862.
[17] Li SN, Li ZM, Yang MB, Hu ZQ, Xu XB, Huang R. Mater Lett 2004;58:3967.
[18] Li ZM, Huang CG, Yang W, Yang MB, Huang R. Macromol Mater Eng 2004;289:1004.