Available online at www.sciencedirect.com
ScienceDirect
Polymer 48 (2007) 5688–5695
polymer
www.elsevier.com/locate/polymer

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

Ping Zhao, Ke Wang, Hong Yang, Qin Zhang, Rongni Du, Qiang Fu*

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

Received 28 March 2007; received in revised form 2 June 2007; accepted 10 July 2007
Available online 18 July 2007

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

* Corresponding author. Tel.: +86 28 85405402.
E-mail address: qiangfu@scu.edu.cn (Q. Fu).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.022

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 multi-wall 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 PPCNT*x* (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 PPCNT*x*-d; otherwise the specimen obtained by static packing injection molding is called static sample, and was signed as PPCNT*x*-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