Composite Structures 174 (2017) 12–18

Contents lists available at ScienceDirect

Composite Structures

journal homepage: www.elsevier.com/locate/compstruct

Experimental evaluations and modeling of the tensile behavior of polypropylene/single-walled carbon nanotubes fibers

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ARTICLE INFO

Article history:
Received 28 February 2017
Revised 27 March 2017
Accepted 20 April 2017
Available online 22 April 2017

Keywords:
Nonlocal effects
Polypropylene
Carbon nanotubes
Small-scale parameter
Two-phase constitutive mixture

ABSTRACT

Polypropylene fibers containing up to 0.2 vol% of single-wall carbon nanotubes, prepared by melt-spinning, are analyzed in terms of both experimental mechanical properties and numerical nonlocal models. In particular, fibers of a commercial polypropylene (PP) resin are compared with composite fibers, based on the same matrix, reinforced with 0.1 and 0.2 vol% of carbon nanotubes (CNT). Experimental findings shows that, although the applied processing conditions are such that the inclusion of carbon nanotubes does not alter the crystalline structure and the degree of crystallinity of the hosting matrix, tensile properties of nanocomposite fibers vary significantly with the filler content. Specifically, Young modulus, yield strength and ductility show a linear dependence upon the nanotube content over the range of compositions explored; in particular with respect to neat PP fibers filaments containing 0.2 vol% of single wall carbon nanotubes show increases of approximately 16% and 6% in the modulus and the yield strength, respectively, while the ductility decreases of about 65%.

Moreover, the analysis of the elastic behavior performed by means of a nonlocal modeling approach based on the two-phase constitutive mixture allows us to identify the values of the small-scale parameter for the considered PP-CNT microrods.

1. Introduction

In the last decades composite systems based on the combination of polymer matrices and fillers have gained a huge interest for their interesting functional and/or structural performances. In this frame, carbon nanotubes (CNTs), since their discovery in 1991 by Iijima [1], have attracted a vast attention as fillers given their very high aspect ratios (typically in the range of several thousand), a extremely high moduli (of the order TPa), relevant thermal and electrical conductivity, and so on. Depending on the synthesis conditions, nanotubes can be single-walled or multi-walled as well as may show different architecture of the wrapped graphene layer.

Potential applications of polymer/CNTs composites are in aerospace, automobile, electronics, packaging, adhesives and coatings. Actually, despite the benefits theoretically expected from the use of nanocomposite systems, the true potential of nanosized fillers have not yet been realized by Kearns and Shambaugh [2] for the technological challenges commonly faced to obtain adequate dispersions of fillers in hosting polymer matrices and to ensure a satisfactory adhesion at the nanoparticles-polymer interface to allow load transfers from the matrix to the filler [3–5]. Among the technologies conventionally employed to disperse nanosized fillers in a polymer matrix (in-situ polymerization, solution blending, melt compounding) undoubtedly the melt compounding remains the most versatile and industrial valuable procedure also from the environmental point of view.

Thostenson and Chou [6] studied the alignment of multi-walled nanotubes (MWNTs) in a polystyrene matrix. They produced aligned nanocomposite films by shear mixing of the nanotubes in a micro-scale twin-screw extruder. A fivefold increase in storage modulus was found in the aligned system compared with the randomly oriented one. Haggenmueller et al. [7] investigated the alignment of single-walled nanotubes (SWNTs) in poly(methyl methacrylate) (PMMA) via melt spinning which resulted in composites with enhanced mechanical and electrical properties. The elastic modulus of fibers increased with the increase of the nanotubes content. The effect of shear force parameters on the align-

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http://dx.doi.org/10.1016/j.compstruct.2017.04.049
0263-8223/

ment of nanotubes, both SWNTs and MWNTs, in polycarbonate (PC) was analyzed by Sennett at al. [8].

Melt-spinning is the most common method for producing polymer fibers. The stresses applied during spinning can align the nanotubes along the fiber axis giving rise to very strong polymer fibers.

Polypropylene (PP) is a commodity polymer, with a wide range of well-established applications in a variety of forms including fibers. Thus, the enhancement of PP properties by inclusion of carbon nanotubes, despite already reported by several authors [9–19], might still be of significant interest.

Lopez Mancanhado et al. [20] studied compounds prepared by melt mixing of small amounts of SWNTs into isotactic polypropylene. They observed a significant increase of the modulus from 0.85 GPa to 1.19 GPa at 0.75 wt% and an increase of the strength from 31 MPa to 36 MPa by including 0.5 wt% of SWNTs. Both properties were observed to be reduced at higher loading levels.

Patti et al. [21] investigated the effect of multi-walled carbon nanotubes content on the flexural properties of polypropylene based composites by experimental tests and nonlocal modeling.

Nonlocal and gradient elasticity continuum theories are widely used for modeling micro-scale structures and a characteristic length at a lower scale influences the response at a given scale, see e.g. [22–35].

Applications to nano-actuators modelled as Euler–Bernoulli beams with the differential constitutive law consequent to the strain-driven integral model proposed by Eringen [22] have highlighted drawbacks of nonlocal elasticity theories. In fact, the solution of the equilibrium problem for the nonlocal model coincides with the local solution for given loading conditions [36–37].

According to Romano et al. [38], the Eringen integral nonlocal elastic law [22] with the exponential kernel is equivalent to a differential equation and two constitutive boundary conditions. Such constitutive boundary conditions are, however, in contrast with equilibrium requirements for all structures of applicative interest, see Romano and Barretta [39]. Accordingly, no paradox occurs since the nonlocal solution does not exist.

Since the nonlocal constitutive theory of Eringen type cannot be adopted in order to study size phenomena in nanorods, a two-phase constitutive mixture, introduced in Eringen [40,41] and successfully resorted to in [42–45], is exploited in this paper.

Advantages of nonlocal models are based on the definition of an internal length into the constitutive equations considered as a material parameter providing information about atomic forces and interactions. Nevertheless, nonlocal material parameters are difficult to be determined due to the small size of CNTs.

Hence, we explore the possibility to apply a two-phase constitutive mixture to nanocomposite microrods PP-SWNT where the small-scale effects due to the interaction between matrix and CNTs are active at the nanoscale. The proposed approach consists in adopting a two-phase nonlocal law for microrods under axial pin loads described by a differential equation with two constitutive boundary conditions. The Young modulus obtained from mechanical tests is implemented in the nonlocal model and the small-scale parameter is chosen in order to match the experimental axial elongation of the tip of the nanorod under the considered load level.

2. Experimental

2.1. Materials

The polypropylene used for this study was a film extrusion grade homopolymer (PP 524P by SABIC) with a melt flow rate of 2 g/10 min at 230 °C and 2.16 kg.

Mass-produced single wall carbon nanotubes (TUBALL by OCSiAl), with an outer diameter of about 1.5 nm and an average length greater than 5 μm, were used as filler with concentrations of 0.1 and 0.2 vol%.

In order to limit the thermal degradation of the polypropylene during the mixing process at relatively high temperature, an antioxidant (IRGANOX 1010 by CIBA), with a concentration of about 0.1 wt% with respect to PP, was added to the systems.

The materials were blended using an internal mixer (Plastograph EC by Brabender GmbH & Co. KG) operating at 220 °C, with a screw speed of 50 rpm and a processing time of 20 min. The mixtures were subsequently made into pellets and fed to the fiber-line.

2.2. Fiber preparation

Melt-drawn fibers were prepared using a laboratory twin-screw micro-compounder (DSM Xplore MC15), operated at 200 °C, equipped with single spinneret hole (diameter $D_0 = 1.00$ mm). The extruded fibers were air-cooled and collected by a spool located about 50 cm from the spinneret. The collected fibers were post drawn (at 50 °C) to a final diameter of approximately $D = 260$ μm. The draw ratio, DR, calculated as $DR = (D_0/D)^2$, assumed a value of about 15 for all our systems.

2.3. Characterization techniques

Differential scanning calorimetry (DSC) measurements were carried out on a Mettler Toledo instrument (model DSC 30). Non-isothermal scans were performed according to the following procedure: i) samples of about 10 mg were heated from 50 to 210 °C at a rate of 10 °C/min and held for 10 min to erase the influence of previous thermal and mechanical treatments; ii) the samples were cooled to 50 °C at a rate of 5 °C/min; iii) the samples were heated up again to 210 °C at a rate of 5 °C/min. Crystallization and melting processes were monitored during the second and third steps, respectively, in order to obtain information about the enthalpy of fusion (ΔH_c), the melting (T_m) and crystallization (T_c) temperatures. Each test was repeated using 5 different specimens and results are presented in terms of averages.

Tensile properties of the fibers were measured, at room temperature, using a universal testing machine (Alpha Technologies mod. 2020) equipped with a 100 N load cell. The fibers were fixed on paper frames with a gage length of 45 mm and tested with a deformation rate of 27 mm/min. Fibers diameters were measured with an optical microscope (Leica DM2700) equipped with a 10× magnification objective. For each sample at least 5 specimens were analyzed while the specimens that broke in the jaws or within 3 mm of the edge of the jaws were discarded.

2.4. Modeling approach

A nonlocal elastic law for microrods is usually formulated by expressing the axial force N_c in terms of the axial strain ε by means of the integral convolution law proposed by Eringen [46]

$$N_c(x) = \int_0^L \phi(x-y,c)EA\varepsilon(y)dy \tag{1}$$

with L beam length, A cross-sectional area and E Young modulus. The smoothing *special kernel* ϕ depends on a small-scale parameter $c > 0$ and is defined in the following form:

$$\phi(x,c) = \frac{1}{2c}e^{-\frac{|x|}{c}}. \tag{2}$$

The special kernel fulfils symmetry, positivity and impulsivity. A critical discussion of the Eringen nonlocal constitutive law is provided in Romano et al. [38].

A representation of the special kernel $\phi(x-y,c)$ in the interval [0,5] mm, centred at the midpoint point $x = 2.5$ mm, is reported in