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Importance of the morphology and structure of the primary aggregates for the dispersibility of carbon nanotubes in polymer melts ☆

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ABSTRACT

The dispersibility of unfunctionalized multi-walled carbon nanotubes in a polymer matrix is studied focusing on the role of the morphology and structure of the primary aggregates. The particles, synthesized by fluidized bed catalytic chemical vapor deposition and purified through a scalable one-pot method, are dispersed in polystyrene by melt mixing. The filler percolation threshold, assessed through rheological analyses and dielectric spectroscopy, is one order of magnitude lower than that of commercially available nanotubes with similar features. This is ascribed to the hierarchical structure of the primary aggregates, which facilitates both the infiltration of the polymer in the earlier stages of mixing and the pulling out of the nanotubes required for their individualization. The high dispersibility is not achieved to the detriment of the nanotube integrity, and the nanocomposites exhibit enhanced thermal stability and dynamic mechanical properties at low amounts of filler.

1. Introduction

The extremely high stiffness, electrical and thermal conductivity make carbon nanotubes (CNTs) an ideal candidate as filler for polymer nanocomposites (PNCs) of technological interest. The large-scale synthesis of CNTs usually results into bundles of hundreds of microns formed by thousands of individual nanotubes held together by physical entanglements and Van der Waals forces. This prevents an efficient transfer of the CNT superior properties to the nanocomposite. Therefore, the commercial breakthrough of CNT-based nanocomposites requires the overcoming of the difficulties related to the de-agglomeration and dispersion of the primary aggregates during the mixing with the polymer. A good nanoscale dispersion is often related to a low percolation threshold, Φ_c. The latter, however, may hide nanotube breakage that compromises the macroscopic properties of the PNC [1]. On the other hand, higher Φ_c are not necessarily coupled with low performances, the PNC properties being the result of a complex interplay among various features of the nanotubes [2].

Basically, the dispersion of CNTs inside polymer melts starts with the infiltration of polymer chains into the aggregates, which crack and erode, and it ends with the pulling out of single nanotubes in the late stages of the process [3]. To expedite the dispersion, the surface of the nanotubes can be functionalized via a chemical reaction that enhances the affinity with the host polymer and/or reduces the tube-tube attractive forces [4]. On the other hand, dealing with unfunctionalized nanotubes that are themselves easy to disperse would be preferred for a large-scale production of CNT-based nanocomposites [5]. To reach this goal, understanding the influence of the morphological features of the nanotubes and their aggregates in the dispersion process is of crucial importance. Numerous studies have compared the properties of PNCs based on nanotubes prepared through different synthesis methods [6], having different aspect ratios [7,8] and different morphology of the primary aggregates [2,9,10]. A series of focused papers by Pötschke and co-workers ultimately correlated the ease of dispersion of CNTs in polymer melts to a low bulk density of the initial aggregates [11–13]. The relationship, however, is not univocal, the bulk density being only one of many parameters which play a role in determining the actual dispersibility of CNTs [14]. Among others, in this paper we focus on the morphology and structure of the primary aggregate, interpreted as the space arrangement of the nanotubes over various length scales, from the texture of the grain down to the entanglements among the CNTs. More in detail, unfunctionalized multi-walled carbon nanotubes (MWCNTs) have been synthesized by fluidized bed catalytic chemical vapor deposition (FBCCVD) and purified by means of a novel, potentially up-scalable three-step process. The dispersibility in polystyrene (PS) of the resulting powder, whose grains exhibit a

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peculiar hierarchical structure, has been compared to that of commercially available nanotubes with similar features but differently arranged in the primary aggregates. PS was deliberately selected as its high chain stiffness is known to hinder the infiltration process within the pristine aggregates [3]. PNCs at different particle loading have been prepared through a deliberately mild masterbatch melt mixing route. The state of dispersion of the two kinds of CNTs has been investigated through rheological analyses, dielectric spectroscopy and transmission electron microscopy (TEM). The high dispersibility of the synthesized nanotubes is proved by a very low filler percolation threshold, comparable with those attainable through much more intensive mixing procedures. The PNCs also exhibit high thermal stability and dynamic mechanical strength at low filler content, which means that the ease of dispersion is achieved preserving the structural integrity of the nanotubes. Our results demonstrate that the synthesis of easily dispersible CNTs represents a viable route for the large-scale production of PNCs of technological interest.

2. Experimental

2.1. Materials

The polymer matrix is atactic polystyrene (PS, Polimeri Europa, Italy) with average molecular weight $M_w = 125$ KDa, polydispersity index $M_w/M_n = 2$, zero-shear rate viscosity $\eta_0 = 1.7 \times 10^3$ Pa s at temperature $T = 200$ °C and glass transition temperature $T_g = 100$ °C. Unfunctionalized MWCNTs are produced by FBCCVD and then purified via a novel three-step process entirely carried out in a single device (details are given in the next section). Commercial grade MWCNTs (Baytubes® C150P, Bayer MaterialScience, Germany), produced by chemical vapor deposition using a metal catalyst, are used as reference material. The main features of the synthesized and commercial nanotubes are summarized in Table 1.

2.2. Synthesis of the nanotubes and preparation of the nanocomposites

Unfunctionalized MWCNTs were synthesized in a large scale (500 g/batch) fluidized bed reactor (diameter 15 cm, height 100 cm) using a γ-alumina substrate impregnated with iron as catalyst [17], ethylene as carbon source, hydrogen and nitrogen as fluidizing agents. The reaction was carried out at $T = 600$ °C and at atmospheric pressure. The reaction was monitored by an on-line gas-chromatograph (Double Channel MicroGC 3000 Agilent) to evaluate in real-time the ethylene conversion and the yield of the reaction; the average duration of the synthesis was about 120 min. Then, the pristine MWCNTs were purified in a three phase slurry bubble vessel through a three-step liquid phase acid treatment: (i) refluxing sulfuric acid solution to dissolve catalyst particles; (ii) water washing to remove the amount of acid; (iii) drying to remove the remaining water. PNCs at different filler content (Φ) were prepared by a two-step melt mixing route. First, a masterbatch at $\Phi \sim 6$ wt.% of MWCNTs was produced using a co-rotating conical twin-screw micro-compounder (Xplore, DSM). The resulting sample was then diluted by melt mixing with neat PS to adjust

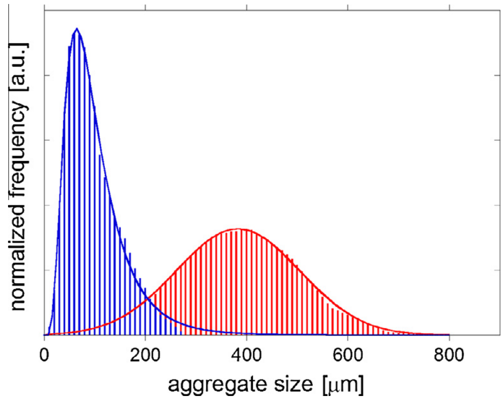

Fig. 1. Normalized size distribution functions of synthesized (blue) and commercial (red) CNT aggregates. Solid lines are Lognormal and Gaussian fittings, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

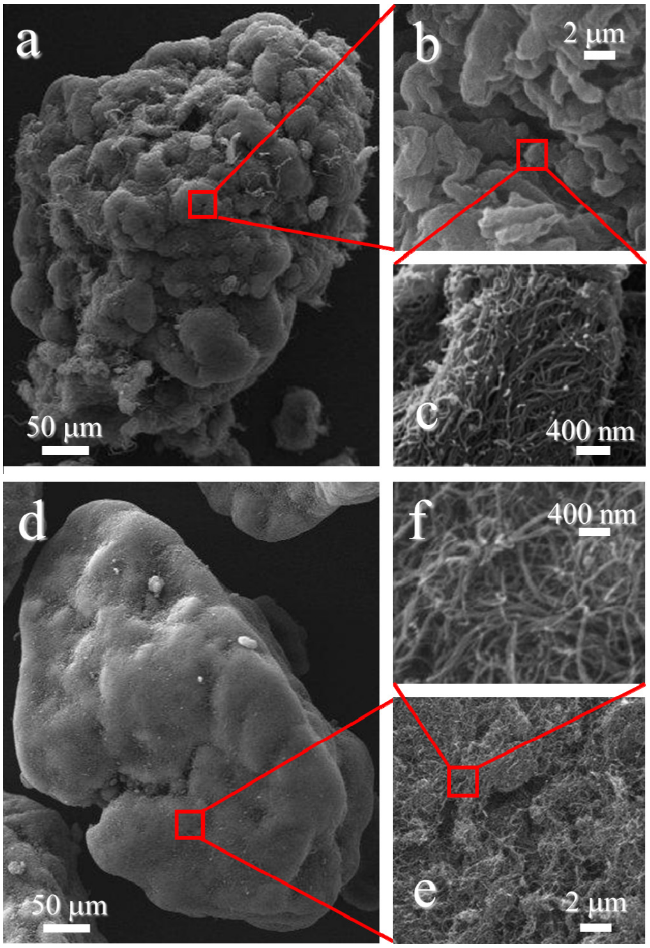

Fig. 2. SEM micrographs of the primary aggregates of the (a–c) synthesized and (d–f) commercial CNTs on different length scales.

Table 1
Main features of the two kinds of MWCNTs.

Property	Synthesized MWCNTs	Commercial MWCNTs
Carbon purity	>99%[a]	⩾95%[b]
Outer mean diameter	~10 nm[c]	~10.5 nm[d]
Mean length	~720 nm[e]	~770 nm[d]
I_D/I_G ratio[f]	1.21 ± 0.15	1.22 ± 0.04
Aggregates average size	103 ± 63 μm[g]	382 ± 122 μm[g]
Bulk density	90–120 Kg m^{-3}[h]	130–150 Kg m^{-3}[b]

[a] From TGA analyses.

[b] Taken from Ref. [15].

[c] From image analysis of TEM micrographs.

[d] Taken from Ref. [2].

[e] From image analysis of TEM micrographs following the same procedure as described in Ref. [16].

[f] Ratio between the intensity of the D (1280–1350 cm^{-1}) and G (1580–1600 cm^{-1}) bands as deduced through Raman spectroscopy.

[g] From particles size analysis.

[h] According to EN ISO 60 norm.