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A methodology to orient carbon nanotubes in a thermosetting matrix

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ABSTRACT

A new procedure for the alignment of carbon nanotubes in a thermosetting matrix is proposed in this study. The two-step approach is based on (i) the alignment of carbon nanotubes (CNTs) in thermoplastic fibres by electrospinning and (ii) the transfer of these nanocompositefibres into a reactive thermosetting resin, in which they are easily soluble. After fibre dissolution, the CNTs remain aligned in the cured thermosetting matrix.

The proof of concept is demonstrated by producing electrospunpolymethyl methacrylate (PMMA) fibres filled with single wall carbon nanotubes (SWCNTs) in the form of unidirectional tape, which are then solubilised into a vinylester (VE) matrix. The PMMA is easily dissolved by the styrene present in the VE resin, leaving SWCNTs aligned in the cured VE network, as confirmed by Raman spectroscopy studies. A 50% increase in elastic modulus (SWCNT 1.3 wt.%) has been obtained by dynamic mechanical analysis carried out in tensile mode at 1 Hz. Thanks to its ability to orient carbon nanotubes in a thermosetting matrix, the proposed method can be exploited also to transfer oriented nanofillers into continuous fibre composites, thus obtaining multiscale or hierarchical composites.

1. Introduction

The intrinsic outstanding mechanical, electrical and thermal properties of carbon nanotubes (CNTs) have stimulated over the past decade intensive investigations aimed at developing nanostructured composites [1–8]. Considering that the diameter of the single-wall carbon nanotubes (SWCNTs) is on the same scale of the polymer chains, SWCNTs are expected to reinforce the matrix at the molecular scale. The introduction of CNTs into conventional fibre-reinforced polymer composites leads to multiscale (or hierarchical or three phases) composites, characterized by a reinforcement structure which is able to significantly enhance the composite performances mainly improving the matrix dominated properties [2]. The most suitable matrices for multiscale nanocomposites seem to be the thermosetting resins, already widely used in the developments of several kinds of polymer nanocomposites [9–11]. So far, an extensive use of CNTs in the manufacturing of multiscale composites has been hindered by their poor dispersion in the polymer matrix and by an unacceptable increase of resin viscosity even at low concentrations. Currently, only small amounts of CNTs, mostly randomly dispersed in polymers, are used. However, this leads to marginal improvements in mechanical properties [12,13], which are still well below the theoretical calculations and expectations [5] and make often inefficient the use of CNTs.

The most straightforward processes for manufacturing multiscale or hierarchical composites are based on resin transfer moulding (RTM) and vacuum-assisted resin transfer moulding (VARTM), where the mixing of CNTs into the resin is followed by a conventional infusion/impregnation of the CNT-modified resin into the fibre assembly [2,7,14]. The recent literature proves that to take full advantage of the extraordinary properties of CNTs (and other nanofillers), they should be characterized by a high aspect ratio [15–17] and by a proper alignment in the polymer matrix [18–20], as better explained in Section 2. Both RTM and VARTM could benefit from using pre-aligned CNTs since in this case a nanoreinforced matrix can be obtained by filling the mould with a low viscosity unfilled resin [21].

Different techniques for orienting CNTs in a polymer have been reported in literature, mainly based on the application of electric fields [22–24], magnetic fields [25] and shear flows [26,27], although these methods cannot be easily implemented with the production of continuous fibre reinforced composites. Nanotube alignment in hierarchical composites was attempted by Garcia

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et al. [1] who propose to transfer CNTs, grown in a aligned fashion on a catalyst, at the interface of two prepregs, maintaining CNT alignment in the through-thickness direction.

In particular, the orientation of CNTs in a polymer fibre, i.e. 1D solids, has been successfully obtained by spinning processes such as melt spinning [28–30], gel spinning [31] and electrospinning [32–35]. Among the methods allowing to fabricate CNT-filled fibres, electrospinning is likely the most versatile process, able to form continuous fibres with diameter ranging from nano- to microscale, which can be filled with aligned nanotubes thanks to the high extension of the electrospun jet [36,37]. Both single-walled carbon nanotubes (SWCNTs) [38,39] and multi-walled carbon nanotubes (MWCNTs) [40–42] can be used as fillers in electrospun fibres.

The new approach proposed in this work stems from the need to both overcoming the mentioned limitations associated to the manufacturing of multiscale composites and facing the challenge of CNT alignment. First, carbon nanotubes (CNTs) are aligned in thermoplastic fibres by means of electrospinning. The nanofilled polymer fibres are then transferred into a reactive thermosetting resin, in which they are easily soluble. After fibre dissolution, the CNTs remain aligned in the cured thermosetting matrix. The proposed approach can be properly adapted to RTM and VARTM manufacturing processes, where pre-aligned CNTs in thermoplastic fibres and conventional continuous fibres could be impregnated by an unfilled thermosetting resin.

In order to demonstrate the feasibility of this approach, nanocomposites have been realized by dissolving an array of aligned electrospunfibres of poly(methyl methacrylate) (PMMA) filled with single-wall nanotubes (SWCNTs) into an uncured vinylester (VE) resin. Raman spectroscopy has been used to get information on the orientation of SWCNTs in the PMMA fibre after electrospinning and to verify whether SWCNTs remain aligned in the thermosetting matrix after dissolution of the PMMA fibres. Mechanical and viscoelastic properties changes induced by the oriented SWCNTs have been examined by dynamic mechanical analysis (DMA).

2. Young modulus of continuous carbon fibre and carbon nanotube composites

Micromechanic of composite materials teaches that to achieve an effective reinforcement, CNTs must be well aligned in the polymer matrix. This results by the application of Halpin–Tsai equations [43,44] to the calculation of the longitudinal modulus E_1, parallel to perfectly oriented CNTs:

$$E_1 = \frac{1 + 2\left(\frac{l}{d}\right)\eta_L \Phi}{1 - \eta_L \Phi} E_m \tag{1}$$

where l/d is the aspect ratio, i.e. the ratio between length and diameter of the nanofiller, Φ is the volume fraction of the nanofiller, E_m the modulus of the matrix and η_L is given by:

$$\eta_L = \frac{\left(\frac{E_f}{E_m}\right) - 1}{\left(\frac{E_f}{E_m}\right) + 2\left(\frac{l}{d}\right)} \tag{2}$$

where E_f represents the Young's modulus of the nanofiller.

Eq. (1) holds for an oriented fibre reinforcement. When dealing with 3D random oriented and quasi-isotropic nanocomposites, the lamination theory [45] leads to the calculation of a single modulus from:

$$E_{3D} \cong \frac{1}{5}E_1 + \frac{4}{5}E_2 \tag{3}$$

where E_1 and E_2 are calculated from Eqs. (1) and (2) assuming for E_2 an aspect ratio $l/d = 2$.

The modulus of a quasi isotropic continuous fibre laminate with unidirectional plies randomly oriented in 2D is given by:

$$E_{2D} \cong \frac{3}{8}E_1 + \frac{5}{8}E_2 \tag{4}$$

where again E_1 and E_2 are calculated from Eqs. (1) and (2) assuming for E_2 an aspect ratio $l/d = 2$ and for E_1 an aspect ratio $l/d = \infty$.

Applying these equations, the stiffness of CNT filled nanocomposites, unidirectionally or randomly oriented (Eqs. (1) and (2)), can be obtained and compared with that of continuous carbon fibre composites (Eqs. (1), (2) and (4)) as a function of volume fraction, as reported in Fig. 1. Assuming a Young modulus of a typical thermosetting matrix equal to 3.5 GPa, it can be increased up to about 9.2 GPa when the resin is reinforced by a 5% by volume of 2D random SWCNTs, assuming a nominal Young modulus value of 1.2 TPa [46,47] and an aspect ratio l/d of 50 (dashed line 1 in Fig. 1). It should be underlined that the above reported models are based on idealized two-phase composites with perfectly straight tubes, perfect CNT-matrix bonding and maximum theoretical CNT properties. A modulus of about 9 GPa is obtained for a quasi isotropic laminate reinforced with intermediate modulus carbon fibres (E_f = 280 GPa and 5% fibres by volume). Using the same volume fraction with the same matrix and CNTs but in an unidirectional composite, micromechanics predicts a modulus of 17.7 GPa. Keeping the same properties, if the aspect ratio of CNTs is increased to 500 and they are arranged in a unidirectional way, the modulus increases up to 48.7 GPa.

Comparing the modulus increase expected according to the classic micromechanical approach, it is clear that only oriented CNTs can lead to a reasonable increase of matrix properties, taking also into account a practical maximum volume content of CNTs that hardly can be reach 5%. Furthermore, the volume content of continuous carbon fibres reinforcement typically reaches 60% leading to a modulus for a quasi isotropic laminate of about 76.8 GPa. This value can be reached using a randomly dispersed CNT with l/d = 50 at a volume fraction of about 44% (intersection of the dashed lines 2 and 3 in Fig. 1), that cannot be reached in any practical application.

On the other hand, when CNTs are aligned, the much higher modulus increase with a low CNT content (<5%) could be exploited in hierarchical composites to improve the matrix dominated properties, considering that this value is more than the double of the maximum modulus of a high performance composite matrix. Only

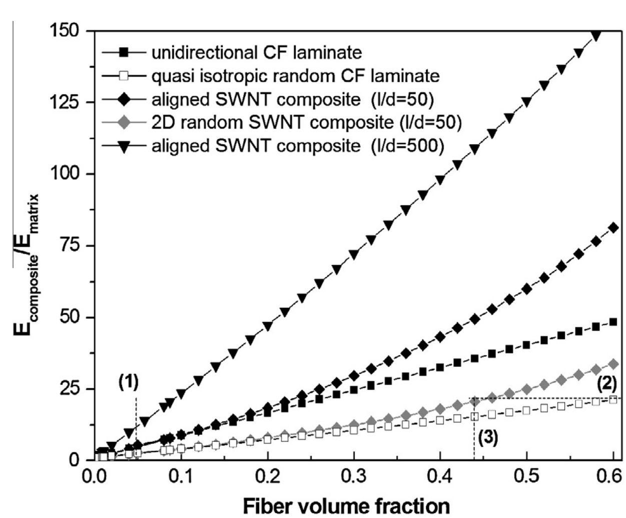

Fig. 1. Comparison among modulus improvements obtained in carbon fibre (CF) epoxy laminates and SWNT filled epoxy, either assuming unidirectional and random orientation of the reinforcement.