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Complete CNT disentanglement–dispersion–functionalisation in a pulsating micro-structured reactor

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HIGHLIGHTS

- ► CNT disentanglement–dispersion–distribution is fully attained by a micro-reactor.
- ► Also, functionalisation, leading to homogenised reinforcement, is complete.
- ► Disentanglement–functionalisation are attained with negligible CNT attrition.
- ► The reactor generates an extensional-shear-spiralling flow and is easy up-scalable.

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ABSTRACT

Disentanglement, dispersion of CNTs without attrition and efficient interfacial interaction with polymer chains are a major challenge in developing CNT/polymer composites. In the present device the mixture of highly viscous polyphosphoric acid (PPA) and entangled MWCNTs fills a hollow cylinder where a perforated piston, encasing micro-grids, is axially translating, oscillating and simultaneously rotating. This generates an extensional-shear-spiralling flow, magnified in the entrance/exit zone of the grid micro-openings, the smallest having diameter of 40 μm. The reciprocating action forces the agglomerates to cross the grid many times, while the oscillation reduces effectively the clogging of the grid. Flow micro-splitting and recombination, across millions of micro-openings in a time dependent regime, facilitated erosion and collision mechanisms to prevail, leading to a gradual CNT deagglomeration–dispersion without CNT attrition. The resulting high multi-directional-rotational flow generated the conditions for efficient functionalisation.

1. Introduction

A significant challenge in developing high performance polymer/CNT composites is the introduction of individual CNTs in a polymer matrix fully dispersed, functionalised, aligned and straightened (Hilding et al., 2003). This is a prerequisite for strong interfacial interactions and therefore load transfer across the CNT–matrix interface. However, as-supplied CNTs ($\sim 3.66 \times 10^{12}\ \mathrm{mm}^{-3}$) are initially entangled and form agglomerates held together by steric interactions as well as by Van der Waals forces. The extraordinary surface-to-volume ratio of as-supplied CNTs ($\sim 140\ \mathrm{m}^2/\mathrm{cm}^3$) make their disentanglement and dispersion extremely difficult (Delsman et al., 2005), particularly when one aims at eliminating attrition as well.

Using CNTs as a reinforcing component in polymer composites requires the ability to modify the nature of CNT's walls in order to control the interfacial interactions between the CNT and the polymer chains. These interactions govern the load-transfer efficiency from the polymer to CNT and the optimum procedure is to introduce covalent attachment of functional groups of the polymer to the CNT wall. Molecular dynamics simulations indicate that if only 1% of the carbon atoms of the CNTs form reactive bridges with a polymer matrix, a significant improvement in mechanical properties of the polymer–CNT composite can be observed (Frankland et al., 2002). In addition, the covalent CNT functionalisation is an effective way to prevent re-aggregation of separated CNTs.

Stirring and ultrasonication are used extensively for CNT disentanglement, dispersion and functionalisation. Both techniques develop flow patterns non-homogeneously distributed in the mixture. Stirring is characterised by a shear flow, which in many applications is not achieving sufficient mixing, it is time consuming and when it becomes intense turbulence develops only along peripheral zones, which may impart structural damage to CNTs depending on exposure time and power level (Hilding et al., 2003; Suslick 1990; Sutherland and Tan, 1970). Ultrasonic waves develop

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low shear forces and are associated with violent (microsecond time scale) collapse of cavitation bubbles, generating high local temperature and high pressure (500 Atm) (Suslick 1990). Depending on the conditions, ultrasonic treatment of CNTs in methylene chloride causes a considerable amount of defects, including buckling, bending and dislocations (Lu et al., 1996).

CNT melt-mixing with polymers is more problematic since melt viscosity is several orders of magnitude higher than solution viscosity and residence time is limited by polymer degradation and operational concerns. Recently, an accurate method to determine CNT attrition, during melt mixing with polycarbonate, confirmed shortening of CNTs up to 30% for the products Nanocyl NC7000 and Baytubes C150HP (Krause et al., 2011). Three-roll calendering was reported to achieve homogeneous dispersion of CNTs in epoxy matrix but recent examination (Fu et al., 2009) of the CNTs length revealed severe reduction from ~15 μm to ~1.5 μm. The same extent of CNT length reduction (from ~10 μm to ~0.5 μm) was measured when CNT was melt mixed with polyamide 6 (PA6) in a Brabender mixing machine with optimum blade geometry for the application (Logakis et al., 2009). Kasaliwal et al. (2010) carried out an analysis of agglomerate dispersion mechanism of CNTs during melt mixing in polycarbonate using a microcompounder (conical, corotating twin extruder) and concluded that no complete dispersion of the nanotubes could be achieved.

Recently, flow in micro-channels was proposed to promote the mixing process, in which the mixing of the reactants usually occurs in 10–500 μm wide channels (Luo et al., 2006). The small channel dimensions lead to a large surface area-to-volume ratio and also to increased driving forces for mass transport and heat. The sudden fluid flow expansion/contraction at the entrance/exit of microchannels and micro-orifices can generate adequate and controllable shear/extensional stresses, capable to reduce the mixing time to reach milliseconds (Kumar et al., 2011). However, the narrow flow channels limit the flow rate and an efficient process to scale up to mass production has not yet been achieved.

In the present work, the development and validation of a microstructured, active, reactor-mixer is presented. Operating around the principles of a time dependent pressure disturbance and the imposition of rotation address the unique requirements for successful CNT disentanglements, dispersion, distribution and functionalisation. The reactor, which is easily upscalable, relies on a controlled combination of flow micro-splitting–twisting–folding–recombination in a time dependent chaotic regime and it is especially suited for highly viscous fluids.

2. Materials

The NC7000 multi-wall CNTs (purity 90%) were supplied by Nanocyl (Sambreville, Belgium) with average diameter 9.5 nm, average length 1.5 μm and bulk density ~66 kg/m^3. The CNTs are physically entangled (entwined, interwoven, Fig. 1), chemically entangled (surface-to-surface attraction) and are forming agglomerates of several hundreds of microns. The extremely high CNT aspect ratio (usually ranging from 100 to 1000) in combination with their high flexibility dramatically increase the formation of loops between them, while the molecular attraction to each other increases further the dispersion difficulty. Small aggregates are often connected by relatively weaker adhesion and electrostatic forces and deagglomeration starts usually from them.

In the present work polyphosphoric acid (PPA 117%) was selected to disentangle–disperse CNTs at room temperature (high viscosity) and then to functionalise them at 130 °C (much lower viscosity). PPA was supplied by Panreac (Barcelona, Spain) with total P_2O_5 84.4%, density (ρ) 2.06 g/cm^3, kinematic viscosity (ν) in shear 13,400 cSt (therefore viscosity $\mu=\rho\nu=26.8$ Pa s) at room temperature and about 680 cSt ($\mu=\rho\nu=1.36$ Pa s) at 130 °C. PPA was selected since it is a mild, less-destructive reaction medium for CNT functionalisation (Baek and Tan, 2003), its moderate acidic nature promotes CNTs deagglomeration and its viscous character impedes reaggregation. The CNT agglomerates absorb extensively PPA and become flexible and permeable three-dimensional structures, flowing in a PPA fluid suspension. The addition of 1 wt% of CNTs in PPA at room temperature increases the PPA suspension viscosity before dispersion about 11%.

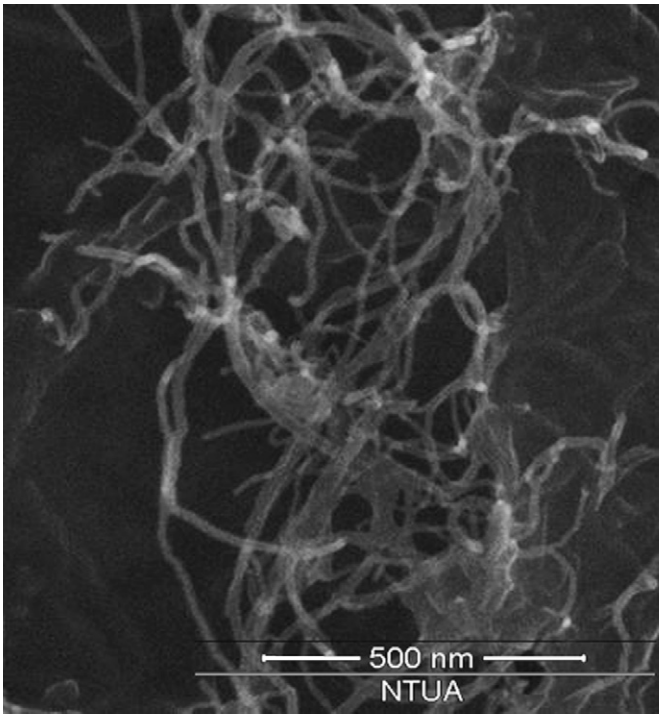

Fig. 1. Entangled CNTs, as received.

2.1. CNT disentanglement–deagglomeration and dispersion considerations

The process of deagglomeration of CNTs depends on the balance of hydrodynamic shearing-extensional forces applied on the agglomerate to "break" it and on the cohesive forces acting within the agglomerate to resist separation. Since CNT breakage should be avoided the de-agglomeration process should be limited to an erosion mechanism (a continuous CNTs detachment from the outer surface of the agglomerate) and to a collision one, where agglomerates collide with each other and with the reactor walls.

It has been known, for some time, that extensional flow is more efficient than shear for both distributive and dispersive mixing in highly viscous fluids. Distributive mixing, which involves distribution of a minor component throughout a major fluid component, is greatly enhanced in shear flow by introduction of obstacles that interrupt the flow and reorientate interfacial area (Rauwendaal, 1991; Tadmor and Gogos, 2006). Dispersive mixing, which involves breakup of liquid drops or agglomerates, is easier in extensional flow than in shear. This was demonstrated by the design-construction of an extensional flow mixer (Luciani and Ultracki, 1996), facilitating the hydrodynamic mixing in melt phase systems (polymer blends, filled systems) by flowing through a series of convergent/divergent regions. Also, the Kao and Mason (1975) studies indicated that the extensional flow is