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Fracture behavior of nanotube–polymer composites: Insights on surface roughness and failure mechanism

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ABSTRACT

The utilization of highly branched polymer (e.g., epoxy resins) in engineering applications is often limited by their brittle nature (low fracture toughness). Loading the polymer matrix by fillers such as individual nanotubes is a promising alternative to enhance fracture toughness without compromising other mechanical properties. However, to fully understand the nanotubes toughening role and correctly characterize the nanocomposite failure mechanisms, a complete exfoliation of the nanotubes aggregates into individual nanotubes is essential. In this work, we embed only individual nanotubes in the polymer matrix using a novel dispersion method. The individual nanotube concentration in the composite is accurately determined. We achieve a record fracture toughness enhancement and, for the first time, demonstrate a coherent quantitative correlation between the fracture toughness and the surface roughness. Finally, comprehensive statistical investigation of the nanotube failure mechanisms shows that carbon nanotubes fail via fracture mechanism, while tungsten di-sulfide nanotubes via pullout mechanism. The failure mechanism could be predicted by the slope of the surface roughness vs. fracture toughness curve.

1. Introduction

Epoxy resins are widely used in various industrial applications due to their superior properties such as resistance to corrosion, thermal and mechanical shocks, superior electrical insulation, light weight, and ease of processing [1]. However, the usefulness of some epoxy resins is often limited by their brittle nature (low fracture toughness (FT)), stemming from heavy crosslinking. Indeed, the addition of traditional fillers such as rubber particles has been shown to toughen the epoxy resins [2], but often at the expense of other mechanical properties (e.g., elastic modulus, strength, strain, and thermal properties) as a result of local stress concentrations and microcracking. Individual nanotube (**NT**) fillers such as carbon or tungsten di-sulfide nanotubes (**CNT** and **WS_2NT**) with exceptional mechanical properties [3,4] and large surface area [5] represent a promising alternative to increase the epoxy's FT without compromising other properties [6–8]. The nanometric size of the NT prevents stress concentration and their large surface area increase the interaction with the polymer matrix, enhancing the stress-transfer mechanism. Although beneficial to stress-transfer, the large surface area of the NT induces excessive aggregation [9–14] due to fairly strong interfacial interaction by van der Waals forces. NT aggregation negates any benefit associated with their nanoscale dimension and impairs the stress-transfer due to limited surface area. Therefore, the NT aggregates behave in some cases as microscopic defects. It is clear from the above that for any type of NT fillers it is essential to develop dispersion methods yielding individual NTs (isolated NT or small aggregates, up to ~4 tubes [15]) and yet applicable through macroscopic processing. Suppression of NT aggregation can be achieved by controlling the NT surface forming either electrostatic or steric repulsion. There are two main approaches to achieve that: (i) covalently attaching hydrophilic groups to the NT surface (chemical functionalization) [16] (ii) non-covalently adsorbing dispersing molecules (dispersants) [6,17–19]. Although approach (i) may improve interfacial adhesion between the resin and the NT, it usually results in structural defects in the NTs, reducing their strength, stiffness and surface area available for stress-transfer. While approach (ii) drastically reduces NT structural defects, it comes with a number of technological disadvantages: The NTs are dispersed in a solvent that needs to be evaporated from the polymer matrix, which calls for low boiling point solvents. Moreover, the low concentration of exfoliated NTs (<1 wt.%) in dispersions requires evaporation of a large volume of

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Abbreviations: CNT, carbon nanotubes; FT, fracture toughness; NCM, nanocomposite materials; NT, nanotube; SR, surface roughness; SWLIM, scanning white light interference microscopy; WS_2NT, tungsten disulfide nanotubes.

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solvent, some of which remains in the matrix and may result in inferior properties. The above arguments make the scaling-up of approach (ii) to industrial application impractical. Another approach to overcome NTs aggregation is by applying high energy to break the dispersant-free NTs aggregates. This can be done by mechanical methods (iii) such as ultrasonication, high shear mixing in a solvent, calendering and ball milling, as well as a combination of these methods in series or parallel [6,20–22]. However, this approach is usually the less effective since it results in structural defects [23] in the NTs, and in NTs' re-aggregation due to the absence of stabilizing agents.

The above dispersion approaches usually result only in partial NTs exfoliation. Thus, only part of the initial NTs is actually exfoliated and contributes to properties enhancement (namely, **effective** NTs concentration), while the rest (NT aggregates) impairs the properties of the nanocomposite materials (**NCM**). Therefore, only when we use the precisely measured effective NTs concentration (after removing the NT aggregates) in the investigation of NT failure mechanisms we are able to evaluate the NTs toughening true effect.

Previous studies [24–27] on the failure mechanisms of NCMs suggested that NTs fail by two basic mechanisms: pull-out or fracture. The failure mechanism is dictated by NT length and NT–polymer interfacial adhesion. During crack propagation, the NTs tend to be fractured in systems with strong filler–matrix interfacial adhesion; otherwise they are pulled-out of the matrix. The determination of the failure mechanism is based in most cases only on imaging of fractured surface by transmission electron microscopy (TEM) [28,29] or scanning electron microscopy (SEM) [8,26].

In this paper we develop a dispersion method that yields mostly individual NTs (carbon or WS_2), and measure their **effective** concentration by our recently developed nanoparticles concentration determination method [30]. Implementing these two methods eliminates the complex contribution of NT aggregates to the mechanical properties of epoxy matrix, and results in a record fracture toughness enhancement. Furthermore, for the first time we demonstrate a coherent correlation between the fracture toughness and the surface roughness of the fractured specimen, and clarify the failure mechanisms of nanocomposite materials.

2. Materials and methods

2.1. Materials

An epoxy resin, diglycidyl ether of bisphenol A (EPON 828, Momentive), polyether triamine hardener (JEFFAMINE® T-403, Momentive), pristine Multi-Wall Carbon Nanotubes (**CNTs,** Nanocyl (NC7000)), tungsten disulfide inorganic nanotubes (**WS_2NTs**, Nanomaterials), β-Lactoglobulin (**BLAC**, Sigma–Aldrich) and pluronic F-127 (**F127,** Sigma–Aldrich) were used as received.

2.2. Specimens preparation

2.2.1. NT dispersion

NTs were mixed with a pre-prepared solution of dispersant in deionized water, as indicated in Table 1. These NT-based dispersions were then sonicated. Two sonication methods were used: Bath sonication (BS) was performed in an Elma sonic bath (model S10; 30 W, 37 kHz, Singen). The water level in the bath was kept constant and the vial (20 mL) was placed in the center of the bath. Tip sonication (TS) was performed in a VCX 400 instrument (400 W, 20 kHz, µtip, Sonics & Materials Inc.) at 38% intensity. The dispersion temperature was kept at 0 °C. Following sonication the dispersion was centrifuged (Megafuge 1.0, Heraues, 20 min at 4000g) to accelerate precipitation. We found that longer centrifugation does not change the NT concentration. Following sonication and centrifugation, a phase separation of exfoliated (supernatant) and aggregated (precipitate) NTs was performed by decantation.

2.2.2. NCM preparation

Following decantation, the aqueous dispersions of NT (plastic flasks 40 mL, diameter = 3 cm) were frozen by liquid nitrogen and placed in a lyophilizer (Labconco Freezone 4.5) for 48 h. The lyophilized NTs were added into the epoxy resin and then manually mixed with a spatula for 5 min. Epoxy hardener was then added (1 g resin: 0.38 g hardener) to the NT/epoxy resin and the resulting NCM was manually mixed with a spatula and degassed for 10 min at 80 °C vacuum oven ($P = 10$ mbar). The NCM mixture was cast into variously-shaped silicone molds, and cured for 12 h at 80 °C. A similar preparation procedure was used for pure (reference) epoxy specimens (without filler addition and sonication/mixing steps).

2.3. Specimens characterization

2.3.1. Concentration determination [30]

Both supernatant and precipitate phases were filtered (using 0.22 µm pore size filter membranes (MF-Milipore)), washed (to remove excess dispersant and to enhance thermogravimetric analysis (TGA) accuracy) and dried (120 °C for 1 h). The exact weights of the dried precipitate and dried supernatant phases were determined by weighing the respective loaded filter membranes (and subtracting the filter membranes weight). The NTs and dispersant weight percentages were then calculated from the thermograms (Mettler Toledo Star System, TGA/STDA85, 50 mL/min N_2, 100 µL aluminum crucibles).

2.3.2. UV–vis spectroscopy

The supernatant-phase adsorption was measured by a double-beam UV–vis spectrophotometer (JascoV-630, 350–700 nm range, plastic cuvettes (10 mm width)).

2.3.3. Electron microscopy of dispersions [31]

NTs dispersions were characterized by Transmission Electron Microscopy (TEM) or cryogenic TEM (cryo-TEM) (FEI Tecnai 12 G2 TWIN TEM, 120 kV).

2.3.4. Mechanical characterization

Fracture toughness (FT) of the NCM was measured using (at least seven) small compact tension specimens (LRX, LLOYD instruments, 1 mm/min deformation rate, ASTM D 5045-91), which allows plane-strain conditions with relatively small specimens. The specimens were pre-cracked by tapping a razor blade into the root of a machined notch. The presence of a sharp starter crack means that no energy contribution for crack initiation is included in the measurement of FT.

Table 1
Initial concentration of NTs and dispersants in sonicated dispersions.

NT type	Dispersant type	Dispersant concentration (mg/mL)	NT concentration (mg/mL)	Sonication procedure and (energy) (J)
CNT	F127	1.5	2.0	Tip sonication (5040)
WS_2NT	BLAC	2.0	6.0	Bath sonication (540)