

Novel Carbyne Filled Carbon Nanotube – Polymer Nanocomposites

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Abstract

The availability of carbyne in carbon nanotubes (CNTs) induces intrinsic stiffening and strengthening of CNTs, and is exploited for the very first time in this report to process epoxy nanocomposites with improved mechanical and electrical properties. The existence of encapsulated carbyne in double wall CNTs (DWNTs) was confirmed using High Resolution Transmission Electron Microscopy (HR-TEM). The intrinsic stiffening of carbyne reinforced DWNTs (c-DWNTs) in epoxy matrix was visually confirmed by Field Emission Scanning Electron Microscopy (FE-SEM). In comparison to raw DWNTs reinforced epoxy nanocomposites, c-DWNTs imparted modest but improved tensile strength (5.6%), elastic modulus (9.7%), failure strain (9.9%) and fracture toughness (13%) to their respective epoxy nanocomposites. This inaugural study on carbyne-filled polymer composites also reports a minor but distinct increase (an order of magnitude) in the electrical conductivity for c-DWNTs filled epoxy nanocomposites compared to DWNT filled epoxy nanocomposites.

Keywords

Carbyne, Carbon nanotube, Epoxy, Polymer nanocomposite

Introduction

Epoxy nanocomposites filled with variety of super and novel forms of carbon (carbon nanotubes, graphene etc.) presently is one of the most researched topics [1-6]. These combinations have been extensively investigated for the past two decades. Because of the superlative combination of nanotubes' mechanical and electrical properties, a number of applications of carbon nanotube epoxy nanocomposites have been widely investigated, for instance, utilizations in aircraft wings [7], flame retardancy [8], sporting goods [9], fuel cells [10], electromagnetic shielding [11], electronic packaging [12], military devices [13], sensors including biosensors [14, 15], conductive adhesive [16], high speed boats [17], radar absorbing materials [18] and wind turbine blades [19], to name a few. Whilst thorough exploitation and real-time industrial substitution has not reached its mature state, for these hybridizations, we report for the first time, a combination with improved mechanical and electrical properties that has not been formulated nor reported elsewhere.

Reported for the first time back in 1967 by Kasatochkin et al. [20, 21], carbyne is an infinite sp^1 hybridized long linear chain of carbon, where each link is just a single carbon atom [22–26]. On its own, carbyne has also been investigated for applications like mechanical energy harvesting [27], super capacitors [28] and potential batteries [29], but not for any kind of composite materials. To date, carbyne's theoretically modeled and estimated superior strength and elastic modulus have been reported in various studies [30–33], which is much higher than any known material, including other forms of fullerene and even diamond. It is the strongest material in the world with a reported experimental estimation strength of 270 GPa (at 5 K) and 251 GPa (at 77 K), more than twice the strength of graphene (130 GPa) [31]. In another study, carbyne has shown to be about twice stiffer than the stiffest known materials and has an unrivalled specific strength of up to 7.5×10^7 Nm/kg, requiring a force of ~ 10 nN to break a single atomic chain under tensile load [33]. For electrical properties, Shu et al. reported that the band gap of carbyne could vary from 2.26 to 1.81 eV depending on the number of carbon atoms [34]. Such material with this superlative combination of properties is always of great interest for the composites community and this has now allowed foreseeing into new types of composite materials.

The natural/ organic existence of carbyne has been found in meteorites, shock-fused graphite, interstellar dust and various marine sources [35]. However, interests in carbyne will now be heightened because of the recently reported mass production recipe of stable and nearly infinite length of carbon chains (carbyne) inside double walled carbon nanotubes (DWNTs). Carbyne was formed by high temperature high vacuum (HTHV) annealing in DWNTs, housing carbyne in the most stable state without any need for end capping to achieve any further structural stability [36].

In this premier work, we are reporting a new generation of fullerene based nanocomposites, i.e. carbyne reinforced double walled carbon nanotubes (c-DWNTs) filled epoxy nanocomposites and comparing its fundamental mechanical (strength, modulus, failure strain and toughness) and electrical (conductivity) properties with raw/ purified DWNT filled epoxy nanocomposites.

Materials and Methods

c-DWNTs and DWNTs were prepared using high vacuum alcohol Chemical Vapor Deposition (CVD) technique and high temperature high vacuum annealing as elaborated elsewhere [36, 37] with the exception of final steps as carried out by Shi et al. [36] in preparing buckypaper. Briefly, DWNTs were synthesized in high vacuum horizontal tube furnace with the aid of Fe/ MgO powder (nanotube catalyst) Mo/ Al_2O_3 (conditioning catalyst) at 875 °C in an ethanol flow at 60 mbar for 30 minutes. After purification at 430 °C and then with HCl, carbyne growth was carried out using high temperature high vacuum (HTHV) treatment. Purified DWNT powder was annealed at 1475 °C for 30 minutes to synthesize carbyne within DWNTs (i.e. yielding c-DWNTs). The vacuum

pressure was always maintained lower than 6.5×10^{-7} mbar for synthesis of DWNTs as well as during the annealing of purified DWNTs for processing c-DWNTs. For electron microscopic analyses, a batch of DWNTs and c-DWNT was tip-sonicated in Dimethylformamide, DMF [38] for 5 minutes. The supernatant was collected, dried and sprinkled on carbon table for Field Emission Scanning Electron Microscope (FE-SEM, Quanta 50 Series, 10kV). High Resolution Transmission Electron Microscopy (HR-TEM) was carried out on JEOL 2010 (LaB6 filament, 200 kV). Samples for HR-TEM were prepared by tip-ultrasonic treatment in DMF for 2 minutes. A drop of the suspension was dried on the standard TEM sample grid covered with carbon film.

The epoxy resin used in this work was a modified bisphenol-A epoxy resin (EPIKOTE RIMR135/ MGS L135i, low viscosity, resin infusion molding grade) together with an amine-curing agent EPIKURE H137, both supplied by Hexion. DWNTs were mixed with epoxy resin for 10 minutes using a high speed (1000 RPM) mechanical mixer. Three roll calander (Exakt 120S-450 by Exakt Germany) was used for thoroughly dispersing DWNTs and c-DWNTs in epoxy. All nanocomposites were processed using 0.5 wt% of DWNTs and c-DWNTs. The gap size between the ceramic rolls (Al_2O_3) was 5 microns and speed was set to 25RPM (1st roll), 60RPM (2nd roll) and 185 RPM (3rd roll). Dwelling time for the DWNT and epoxy suspensions was around 2 min and 20 seconds. In this dispersion technique, higher shear forces are responsible for homogenous dispersion and de-aggregation of DWNT agglomerates as evidenced by Gojny et al. [4] as well. The calander roll processed suspension was then mechanically stirred at 150 RPM with added hardener (100 parts of resin mixed with 32 parts hardener by weight) for 5 minutes followed by degassing in a vacuum chamber for 30 minutes. The mixtures were then poured in Polytetrafluoroethylene (PTFE) open bath mold (ASTM D1708-13 dog bone shaped). The nanocomposite suspensions were then cured at room temperature for 24 hours and subsequently post-cured for another 24 hours at 70 °C in a conventional oven. The same method was used to prepare c-DWNT filled epoxy nanocomposites for comparison purposes. A batch of epoxy samples without any mixing in the roll calendar was also prepared using the sample processing variables.

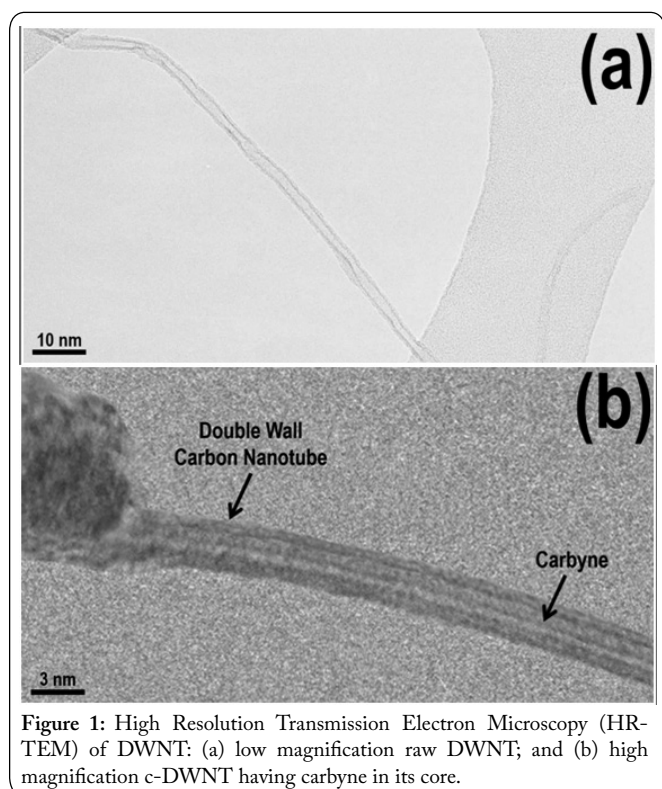
For statistical appropriateness and greater confidence in mechanical and electrical characterizations, at least 10 samples of each composition were examined. All mechanical characterizations (tensile strength, elastic modulus, failure strain and fracture toughness) were carried out using a universal mechanical testing machine, Instron 6025 (a screw-driven universal tensile testing machine; 1 mm/min cross-head speed). The elongation of the specimens during the tests was recorded by using an ultra-sensitive optical distance encoder for monitoring strain in the gauge length area. The elastic moduli were also calculated using modified Halpin Tsai theory [3]. Fracture toughness characterizations were carried out for all samples according to standard ASTM D5045-14 (standard test method for determining fracture toughness of plastic materials) using compact tension (CT) samples.

The deformations of the samples were carefully measured by detecting the crack opening displacements with distance encoder as used for modulus measurements. A sharp incipient crack was made to all CT samples by slowly hammering them with a sharp razor blade into the notch. The load cells used for tensile testing and fracture toughness analysis were 10 kN and 500 N respectively.

The electrical conductivity of the nanocomposite samples was measured at room temperature by two-point method [2, 39] using a highly sensitive digital micro-ohmmeter (Keithley 580). A minimum of 10 samples were analyzed for electrical conductivity measurements. Ultra-low resistivity silver paste was applied on the both ends of the nanocomposite cubes (dimension: 3 mm x 3 mm x 3 mm) which acted as electrodes to ensure good electrical contact.

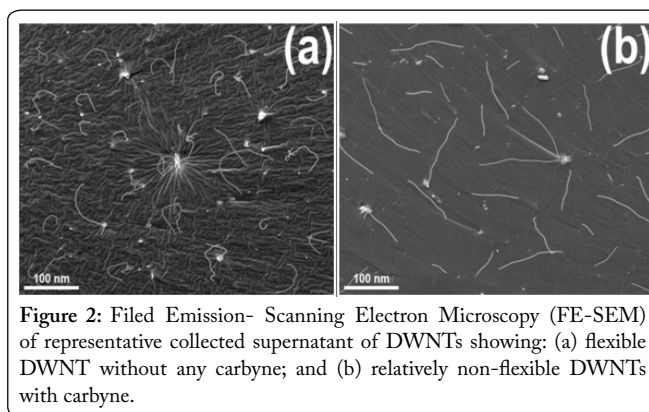
Results and Discussion

Figures 1 and 2 shows the DWNTs (with and without carbyne) using Transmission and Scanning Electron Microscopy, TEM and SEM technologies, respectively. In comparison to figure 1a, the highly magnified image (Figure 1b) confirms the existence of carbyne in the core of DWNTs



as also reported and elaborated elsewhere [36, 37]. The double wall nature, i.e. 2 layers of CNTs, of DWNT can also be confirmed from figure 1b. Carbyne can be seen in the hollow space or core of the DWNT (Figure 1b). The SEM images (Figure 2) of the collected supernatant confirms the relatively non-flexible or stiff geometry of the c-DWNTs induced by the carbyne. This further confirms the presence of carbyne within DWNT in a qualitative manner.

The processed epoxy and nanocomposite compositions



were investigated for their mechanical properties using tensile testing. The intention of these analyses was to understand and compare the effect of addition of carbyne in the core of DWNTs. Figure 3, shows the resulting values of tensile strength, Young's modulus, fracture toughness and fracture strain. An increase of 6.7% and around 10% was observed in the values of strength and Young's modulus respectively due to the incorporation of carbyne in the core of DWNTs (Figures 3). This behavior can be explained by intrinsic strengthening and stiffening of the reinforcing ingredient (i.e. DWNTs) by the strategic embedment of carbyne within DWNTs.

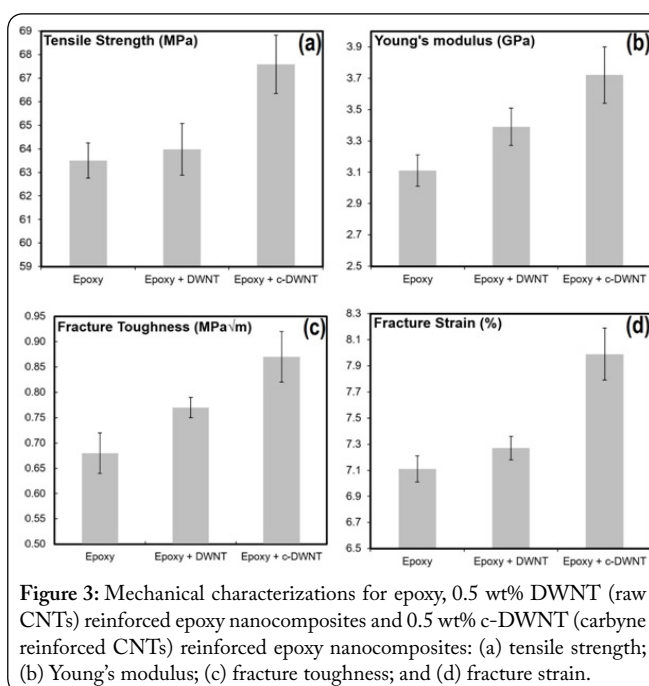


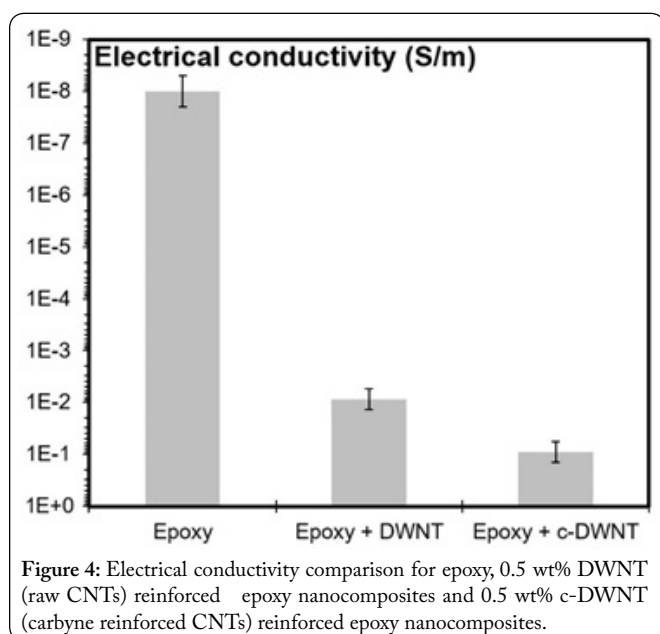
Figure 3: Mechanical characterizations for epoxy, 0.5 wt% DWNT (raw CNTs) reinforced epoxy nanocomposites and 0.5 wt% c-DWNT (carbyne reinforced CNTs) reinforced epoxy nanocomposites: (a) tensile strength; (b) Young's modulus; (c) fracture toughness; and (d) fracture strain.

Figures 3c and 3d show the fracture toughness and strain for the epoxy and nanocomposites. The fracture strain was positively affected using c-DWNTs in comparison to DWNT. The ability of carbyne to possibly enhance strength and stiffness of their respective nanocomposites explains this observed behavior. The versatility of epoxy resins and related brittle polymers in many engineering applications is often limited by their highly fragile and brittle nature. Addition of CNTs in epoxy matrices has proved to be a good practical strategy to reduce brittleness and enhance the fracture toughness and strain of the nanocomposites [4, 40, 41]. The

resultant strengthening and stiffening of DWNT by carbyne (which is the subject of this report) is contributing towards 10% (Figure 3b) and 13% (Figure 3c) enhanced fracture toughness and fracture strain respectively. As widely reported, the associated key failure mechanisms in this mode of fracture toughness analysis are fiber fracture, fiber pull out, fiber/matrix debonding, crack bridging and matrix cracking [3, 6, 42].

The long line chain of carbon (carbyne in figure 1b) in DWNTs should be seen as structural stiffener carrying tensile loads leading to the observed improvement of the strength, Young's modulus, fracture strain and fracture toughness. From the visual analysis (Figure 2), it could also be noted that c-DWNT appears to be straighter, stiffer or non-flexible as compared to DWNTs, which geometrically reduces their capability to make agglomerates. It is also well established in the literature that CNT agglomerates within epoxy lower mechanical and electrical properties for their respective nanocomposites.

Figure 4, reports the electrical conductivities of epoxy and nanocomposites. It is established fact that carbonaceous and conductive fillers increase electrical conductivity when their concentrations within the non-conductive polymer matrix exceeds a critical concentration known as the percolation threshold. The achievement of the percolation threshold occurs when the conductive nanofillers (i.e. DWNTs) physically touch each other or are within close proximity for electron transfer, i.e. a distance of less than 5 nm due to tunneling mechanism [43]. Induced shearing via the calendaring method is also responsible for aligning CNTs as previously reported [4, 40, 44-46]. When the fillers align in one direction, a continuous network of conductive element is formed as confirmed in number of previous studies [40, 44, 46]. An increase in the order of magnitude (i.e. from 0.07 S/m to 0.98 S/m, an increase of 14 times or an order of magnitude) in the electrical conductivity was observed for c-DWNTs filled epoxy nanocomposites compared to DWNT filled epoxy nanocomposites (Figure 4). As observed in figure 2, c-DWNT are relatively non-flexible



or possess stiffer geometry due to the presence of carbyne in its core. The improved electrical conductivity could therefore be explained by the formation of a superior conductive network within c-DWNT reinforced epoxy nanocomposite. Moreover, intrinsic electrical conductivity of c-DWNT improved owing to the incorporation of conductive core in the form of carbyne. An addition of conductive core (carbyne) in the insulating empty space within DWNT reduces the overall electrical resistivity of individual DWNT.

This preliminary paper, which primarily reports an application of a novel DWNT type, is not commenting on the quality of CNT dispersion at this stage. Although, it should be worth mentioning that the advantage of calendaring over other dispersion methods applied is the possibility of scaling-up the capacity without losing the efficiency of the distribution. It is also widely reported that one of the main advantage of this dispersion method is the homogeneous introduction of shear forces over the whole volume of the composite on the rolls, whereas other methods like tip or bath sonication induces energy at a very local level [4].

Conclusion

This is an inaugural paper reporting the utilization of carbyne for manufacturing composite materials. Carbyne reinforced polymer nanocomposites have been successfully processed, characterized and reported for the first time in the study. The natural location of carbyne chain provides an electrically conductive and mechanically reinforced 'spine' for improved electrical conductivity and structural strengthening and stiffening of DWNTs as confirmed from the high resolution visual analysis as well. In comparison to DWNTs reinforced epoxy nanocomposites, c-DWNTs imparted improved tensile strength (5.6%), elastic modulus (9.7%), failure strain (9.9%), fracture toughness (13%) and electrical conductivity (14 times) to their respective epoxy nanocomposites. This inaugural study on carbyne-filled polymer composites also reports a minor but distinct increase (an order of magnitude) in the electrical conductivity for c-DWNTs filled epoxy nanocomposites as compared to DWNT filled epoxy nanocomposites. This inaugural research confirms the improved c-DWNTs filled epoxy nanocomposites present great potential for various applications and will be the subject of substantial research in near future.

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Conflict of Interest

The authors declare no conflict of interest.

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