

Long-Range, Entangled Carbon Nanotube Networks in Polycarbonate**

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A method is presented for dispersing ropes or bundles of single-walled carbon nanotubes (RCNTs) in a polycarbonate (PC) matrix. Films of PC/RCNT composites are produced, with thicknesses ranging from 10 to 60 μm , and containing small concentrations (0.06–0.25 wt.-%) of RCNT. Our process is based on a unique method of hot casting, annealing, and drying from dichlorobenzene solution. A wet annealing prior to complete drying yields a uniform and transparent film. Despite the low RCNT loading, scanning electron microscopy (SEM) analysis of the films after fracture reveals that the RCNTs form an entangled network throughout the film, which is a key requirement for enhanced properties. An increase of up to 30 % in the Young's modulus, as compared to PC, results with this method of composite fabrication.

1. Introduction

An ideal high-performance polymer or polymer composite is a lightweight material with a high Young's modulus (Y), which exhibits little or no deformation under applied load and has high strength without sacrificing ductility. Theoretically, Y of a single-walled carbon nanotube (CNT) is predicted to be at least an order of magnitude larger than any known polymer matrix.^[1] CNTs are flexible,^[2] of low density,^[3] with a modulus in the range of 0.2–1 TPa^[1] and strength between 200 and 900 MPa.^[4] Hence, it is expected that incorporating CNTs into polymeric materials would promote both high strength and a high Young's modulus. However, the Y of CNT/polymer composites reported to date shows only a moderate increase compared to the virgin polymer.^[5] Generally, this can be ascribed to insufficient load transfer from the polymer to the nanotube, as indicated by microscopic examination of the fractured composite surface. The CNTs appear to be stretched out^[6] or aggregated,^[7] and the true benefits for the mechanical properties are as yet unclear. The requirements for favorable polymer reinforcement are uniform dispersion of the CNTs in the polymer matrix and a compatible interface between the two components. We report the formation of a CNT network within a polycarbonate (PC) matrix using a simple scalable technique. Whereas previous emphasis has been placed on aligning CNTs during fabrication of the composite to enhance properties, our method takes advantage of the naturally occurring entanglements between the nanotubes. We present a procedure, based on high-temperature PC/CNT solution casting, whereby thin

(10–60 μm) films with areas of at least 50 cm^2 are produced. These macroscopic film specimens are suitable for (conventional) mechanical tensile testing. The CNT loading in these films is small, ranging from 0.06 to 0.25 wt.-%, resulting in optically transparent films. Even at these small CNT concentrations it was revealed, after mechanical fracture of the PC/CNT composite above the glass transition temperature, that the CNTs formed an entangled network structure throughout the specimen. This is a desirable feature for future development of PC/CNT composites with enhanced electrical and thermal properties, as well as for any improvements to mechanical strength and toughness to be derived from the CNTs. We also investigate the effect of the CNT loading on the Young's modulus of the composite.

It is known that pure CNTs are notoriously difficult to manipulate. Strong inter-tube van der Waals forces promote bundling rather than homogeneous dispersion, and the inert CNT surface is incompatible with most polymer systems. Several groups are focussing efforts on chemically tailoring the CNT surface and/or blending techniques (high shear mixing, ultrasonication, melt blending, etc.). Using polyvinyl alcohol (PVA) and poly (9-vinylcarbazole) (PVK), Cadec et al.^[5] found that Y increased from 7 to 12.5 GPa using 1 wt.-% CNT in the PVA system, and from 2 to 6 GPa using 8 wt.-% CNT in the PVK system. The interfacial bonding was found to be better with PVA than PVK. Although both are vinyl polymers, the latter has a bulky side group as compared to PVA. In the present study, we use polycarbonate, which has phenyl groups on the backbone.

2. Results and Discussion

The CNTs purchased from CarboLex are prepared from the electric-arc discharge technique to produce single-walled nanotubes (SWNT) of 1.4 nm diameter. These tend to bundle into ropes (RCNTs) with an average final diameter of 30 nm, as measured from scanning electron microscopy (SEM) micrographs from the supplier.^[8] The final average RCNT length

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and diameter did not change after our purification steps as measured by SEM (Fig. 1).

The measured lengths of these RCNTs ranged from 1 to 2 μ m in the dry state. However, we note that the actual lengths may be considerably greater, since upon SEM sample preparation,

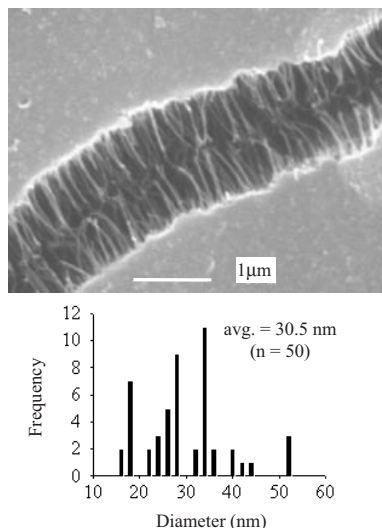


Fig. 1. SEM image used to estimate the size distribution of purified RCNTs, as shown. The average length of the nanotubes bridging the flake is 2 μ m.

the bulk of the RCNTs are trapped within large flakes, so the entire length is not resolved.

Films prepared by hot-casting suspensions of PC/CNT in 1,2-dichlorobenzene (DCB) were opaque, with a thickness of ca. 10 μ m, and an estimated CNT content of \sim 0.06 wt.-% (see Experimental). Most areas of the films prepared in this manner started developing cracks as the drying proceeded, with small transparent regions. The glass-transition temperature of PC did not change, and additional transitions were not observed, as in the case of PVK.^[5] Even with small loading of the CNT, phase separation seems to have occurred. The mechanical properties of this film were also tested (see Experimental) and showed that the sample stretched by 7 % of its original length before breaking at room temperature for the above composite. The elongation was 20 % for pure polycarbonate under the same conditions.

Since the transparency of the film is a requirement for most applications, another approach was taken to improve the transparency over the entire region of the film. The films were first hot-cast onto a non-stick surface using the above method. After initial drying at 120 $^{\circ}$ C for 3 h, but while the film is still tacky, the temperature was increased to 150 $^{\circ}$ C, about 5 $^{\circ}$ C higher than the T_g of the PC, for subsequent drying. This resulted in a highly transparent film, with very little phase separation (i.e., little opacity). This final technique was used to successfully produce transparent films of between 0.06 and 0.25 wt.-% RCNTs. Manual stretching at 150 $^{\circ}$ C resulted in fracture at an elongation of 30 %. Figure 2 shows images of this fractured film sample, and a sample of pure PC subject to identical fabrication and fracture methods. SEM of both samples show that the film thickness had been reduced from ca. 10 μ m

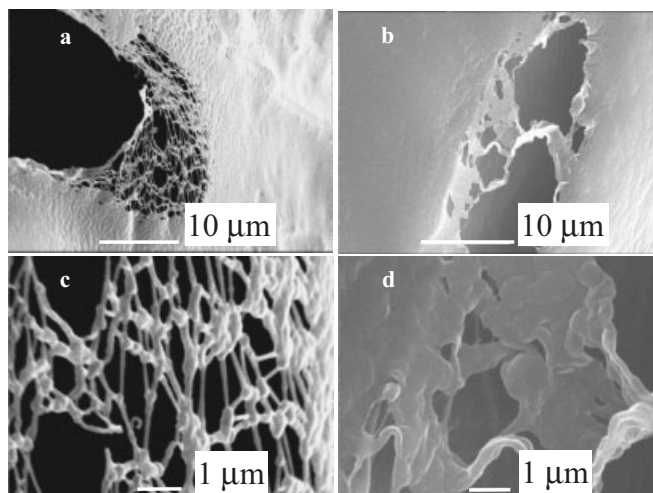


Fig. 2. SEM image the fractured surface: a) low magnification of CNT/PC (0.06 wt.-%) showing a large region of the fractured edge; b) low magnification of pure PC under the same electron beam current as (a) showing a large region of the fractured edge starting to deform; c) higher magnification of (a) showing the exposed PC/CNT network bridging the fracture; d) higher magnification of (b) showing the pure PC fracture morphology.

to \ll 1 μ m at the fracture edge. However, a strikingly high density of interlaced microfibrils is revealed at the fractured edge of the CNT reinforced film (compare Figs. 2a,b). It is this phenomenon that is the focus of the remainder of this article.

The average diameter of the linear portion of the microfibrils revealed in the CNT/PC fracture is 130 nm. Based on a diameter of 30 nm for the RCNTs after purification, the larger diameter suggests that these fibrils contain CNTs that are well coated with PC. At higher magnification, Figure 2c, these fibrils are seen to be joined by nodules spaced approximately 1 μ m apart, which is similar to the measured average length of the RCNTs after purification. However, these fibrils are not pulled out of the polymer matrix, as commonly noted with room-temperature composite fractures.^[9,10] They appear fully extended without any deformation between nodules, and bridge the entire fracture region. This bridging phenomenon is a desirable mechanism for enhanced toughness of the composite, and is known to be an effective route for load transfer that is necessary for CNT composites.^[10–12] Additional evidence of CNT reinforcement of the fibrils is the response of this sample upon increasing the SEM electron beam current, from 0.007 nA to 17.07 nA. The purified CNTs are stable under these beam conditions but the average diameter of these fibrils gradually decreases to about 110 nm, and then remains stable after prolonged irradiation.

In comparison, the sample of the pure PC is much less robust than the composite and readily deforms under an electron beam current of 0.007 nA, followed by degradation after irradiation at 17.07 nA. Figure 2d shows that the virgin PC sample lacks the extensive bridging mechanism enabled by entanglement of CNTs. Finally, Figure 3 shows the room-temperature fracture surface of a CNT/PC film formed with a manual stretcher. The network remains embedded within the film. The lengths of the few nanotubes that are exposed are slightly less than those of the purified RCNTs. These images are compar-

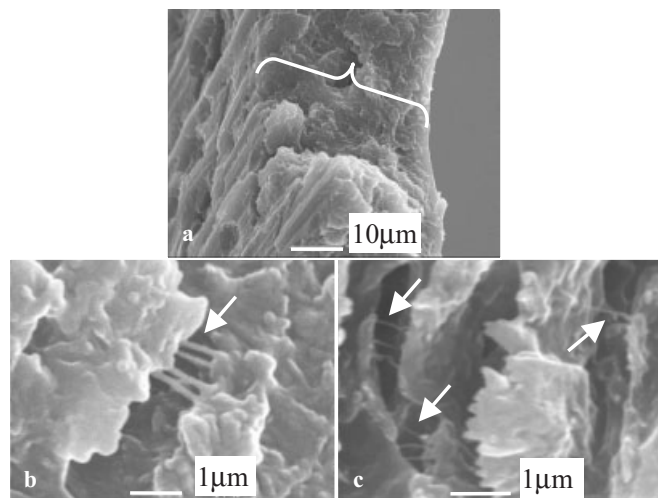


Fig. 3. SEM images of CNT/PC room temperature fracture: a) low magnification showing the whole fractured cross-section surface of thickness ca. 20 μm ; b,c) close-up of embedded RCNTs indicated by arrows, aligned by the stretching process.

able to previous studies of room-temperature fracture surfaces of polymer/CNT composites.^[12]

Although previous studies used much higher concentrations of CNT in composites, none of them suggested the formation of networks.^[11,13] A concentration of 20 wt.-% CNTs (considerably above the CNT percolation threshold) in a melt-blended PC/CNT composite showed the formation of a randomly oriented interconnected lattice of CNTs within the polymer.^[13] In an ultrasonically dispersed multi-walled CNT/epoxy resin composite containing 5 wt.-% CNTs, the nanotubes remain curved and interwoven, essentially forming a network again above the percolation limit.^[10] Our method as described above generated a CNT network with $\ll 1$ wt.-% loading. This network may have formed from a critical amount of CNT entanglements generated at the water/DCB phase boundary when dispersing CNTs (see Experimental). Some entanglement points may even be retained from the purification process after the CNTs sediment was extracted from a highly concentrated supernatant phase. These nanotube–nanotube interactions in solution are stable and cause connectivity between tubes.^[13]

CNTs of a critical length naturally form inter-tube entanglements that have been compared to the critical entanglement length associated with polymer chains.^[14] The energetics of formation of a random CNT network structure within the PC matrix may be considered to be more favorable than incorporating aligned CNTs over the same macroscopic scale, since the more randomly dispersed system is entropically more favorable. Pre-existing entanglements may even act as “nucleation sites” where further entanglements become trapped during the mechanics of hot casting and kinetics of slow evaporation of the solvent (120 °C for 3 h, see Experimental). The measured diameter of the networked fibrils is 3–4 times that of the pure RCNTs, suggesting a thick adsorbed layer of PC. Stretching above the T_g of the polymer may have enhanced this adsorption since there may be sufficient (reptation) motion along the polycarbonate backbone to wet the RCNT surface. Figure 4

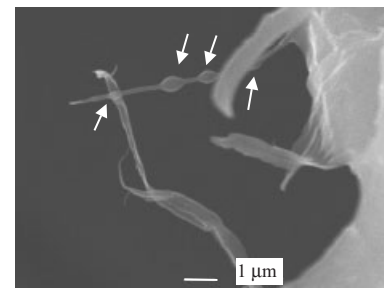


Fig. 4. RCNTs extending from high-temperature fracture. Arrows indicate droplets of PC adhering to RCNT.

shows more evidence of wetting in which the RCNTs extend from the fracture after hot stretching and support multiple droplets of polymer. This indicates that the simple method described here for preparing films yields the same intimate polymer/CNT contact when compared to more intricate techniques reported previously by various authors. The morphology is thus dependent upon the method of composite preparation. The formation of a network of entangled CNTs in a fracture surface, as we have shown here, is markedly different than the morphology of conventional polymer/CNT fracture surfaces reported to date.

The nodules that seem to connect the fibrils (Figs. 2,4) have not been previously reported. We believe that these are junction points where the RCNTs have crossed or bundled together. The nature of the adhesion between PC and the RCNT is difficult to characterize. The outer surface of the RCNTs may contain debris from oxidized SWNTs^[15] and, after acid reflux, the surface of the RCNT may have COOH groups,^[16] which all aid the PC/CNT interaction.

As mentioned above, the films that were dried at 150 °C were transparent. This indicates a good dispersion of the CNTs in the matrix. Drying the films above the T_g of the matrix perhaps facilitates the interaction between the PC and the CNT. The previous studies on PVA and PVK involved vinyl polymers, the preferred conformation of which is either an extended chain or a tightly wound helical form.^[17] However, PC can form a range of energetically favorable conformations, from an extended zigzag to flat helical conformations, with a large radius.^[18] An example of an amylose chain (with a flat helical conformation) wrapping around a CNT was reported recently.^[19] Whether such wrapping of the CNT by PC chains occurs in the present study is not confirmed. However, drying at a temperature slightly above the T_g of the matrix does seem to improve the compatibility.

This improved compatibility is shown as a moderate (29 %) increase in the Young's modulus for a loading of 0.06 wt.-% CNTs when compared to the pure “wet annealed” PC as shown in Figure 5. This very low CNT concentration was calculated to be the minimum requirement in which a three-dimensional (3D) network may occur within a given volume of PC, based on the average dry length and diameter of the RCNT starting material. In this geometric approximation, we assumed that the CNT length is the same in each direction of the 3D network and the density of the RCNTs is the same as SWNTs. By idea-

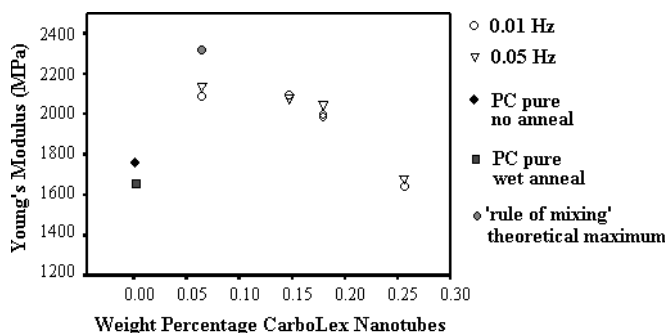


Fig. 5. Young's modulus of wet-annealed films, both pure PC and CNT/PC, measured using a thermal mechanical analyzer. The theoretical maximum is indicated for 0.06 wt.-% CNT/PC calculated using the "rule of mixing" ($Y_{\text{CNT}} = 1 \text{ TPa}$, $Y_{\text{PCpure}} = 1662 \text{ MPa}$, and converting wt.-% to volume using densities of $\text{PC} = 1.20 \text{ g cm}^{-3}$ and $\text{CNT} = 1.34 \text{ g cm}^{-3}$).

lizing the network as a cubic lattice of RCNTs, with the cube side equal to the average RCNT length, it was found that 0.06 wt.-% is the approximate minimum CNT loading required for network formation. Figure 5 shows that Young's modulus decreases as the concentration of CNTs increases above this minimum requirement, as is the case with most filler reinforced polymer composites. Of note is a rather significant increase in Y (29 %) given the small amount (0.06 wt.-%) of RCNT added. Yet, the decrease in modulus beyond this amount suggests that there is a limit to the stiffness increases that the RCNTs can impart on the PC matrix. For comparison, the filled circle in Figure 5 shows the theoretical Y for a PC matrix containing 0.06 wt.-% CNT, based on a simple "rule of mixtures" estimate.^[20] The rule of mixtures value is an upper bound expected in the ideal case of perfect dispersion and alignment of the RCNTs, and perfect bonding at the PC/CNT interface. It is clear that in the 0.06 wt.-% composite, the entangled RCNTs are providing 85 % of this theoretical improvement to Y .

3. Conclusion

In summary, for an improvement in mechanical properties we propose that the entangled geometry of a CNT network is intrinsically favorable to formation, and may lead to a material with high toughness through crack bridging when using a minimum CNT concentration. Additionally, the CNT network formed at the lowest concentration reported to date. Young's modulus improvements were considerable for this small concentration of RCNTs, but demonstrated that the stiffness improvements could not be indefinitely increased; there is an optimal CNT concentration of only 0.06 wt.-%, beyond which Y decreases with added CNT.

4. Experimental

Polycarbonate was purchased from Aldrich and used as received ($M_w = 64 \text{ kg mol}^{-1}$ and $T_g = 147^\circ\text{C}$). The CNTs were purchased from CarboLex (Batch CLAP8333). They were electric-arc generated and purified using procedures previously reported for small-scale batches of CNTs [21]. These RCNTs

were oxidatively purified using HNO_3 (35 %, reflux, 24 h), repetitively washed with distilled water, and then centrifuged until a neutral supernatant solution was obtained ($15000 \times g$ for 35 min intervals). Thus, the residual catalyst, oxides, and carbon species were removed. SEM showed that all supernatant solutions contain a high concentration of CNTs (amorphous carbon or carbon nanoparticles are removed with acid reflux but are not resolved with SEM). The final neutral supernatant solution was used in further experiments to prepare films of the composite. This supernatant suspension shows no sedimentation or aggregation to date [21].

Exchange of water for an organic solvent suitable for dissolving polycarbonate and keeping the CNTs suspended [22] was performed by slowly adding 500 mL of supernatant solution to a small amount of 1,2-dichlorobenzene (DCB; Caledon, laboratory grade) vigorously stirred at 100°C for 3 h. Solvent exchange between the water of the supernatant solution and DCB resulted in a pale brown solution. The hot DCB/CNT suspension was added to a polycarbonate/DCB solution ($\sim 0.5 \text{ g}$ in 5 mL) at 100°C . The resulting hot solution was then poured onto a silanized aluminum plate maintained at 120°C , and an aluminum draw bar was used to spread a film across the hot Al surface. The resulting film was left at 120°C for approximately 3 h, and then vacuum dried for 48 h at 120°C . This yielded an opaque film of thickness ca. $10 \mu\text{m}$ and with an estimated [CNT] $\sim 0.06 \text{ wt.-%}$ based on the dry mass of solids in the supernatant.

Calorimetry was performed using a DuPont 990 DSC calibrated for temperature and area using indium. Glass transition temperatures were obtained using $7\text{--}10 \text{ mg}$ of sample and a heating rate of $10^\circ\text{C min}^{-1}$ under a nitrogen flow ($50\text{--}70 \text{ mL min}^{-1}$). Samples were prepared for SEM (JEOL 800) by mounting on carbon tape and sputter coating with 60:40 Au/Pd. Manual mechanical stretching of films was accomplished as follows; a $2.5 \text{ cm} \times 1.5 \text{ cm}$ transparent section of the film was clamped in a manual stretching device capable of 1.55 mm per load cycle. The sample was slowly stretched at a low strain rate, $< 2\%$ strain for each load cycle until fracture. For high temperature fractures (Fig. 2) the manual stretching device was maintained in an oven set to 150°C , and care was taken to equilibrate the sample before each load cycle. Young's moduli of all the films were measured at room temperature using a Seiko SSC 5200 thermal mechanical analyzer. Rectangular strips of the film were cut ($10 \text{ mm} \times 2 \text{ mm}$, thickness $0.010\text{--}0.06 \text{ mm}$) and mounted between two chucks. Operating parameters were set at: offset load = 75 g , load amplitude = 50 g , initial tension = 5 g , and cycling frequency 0.01 or 0.05 Hz . Young's modulus was obtained from the slope of the linear portion of the stress-strain plot.

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