

Unusual thermal diffusion of carbon nanotubes in a thermoplastic polymer

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ABSTRACT

The dispersion of agglomerated carbon nanotubes in polymers is a major challenge. We find that when annealing, the agglomerated tubes disperse spontaneously in a highly viscous thermoplastic polymer. We attribute the thermal diffusion induced dispersion to the difference in the dielectric properties of the nanotubes and the polymer matrix. Strong infrared absorption of the nanotubes leads to selective heating of the nanotubes. The formation of a temperature gradient between the nanotubes and polymer matrix enhances diffusion at the tube surface and along the tube axis. As a result annealing disperses the carbon nanotubes efficiently in a viscous thermoplastic polymer. Transmission electron microscopy, Raman spectral maps and *insitu* optical microscopy studies show the formation of a uniform diffusion layer.

Keywords: carbon nanotubes, thermoplastic polymer, TEM, Raman, dispersion

1 INTRODUCTION

Using carbon nanotubes (CNT) in a thermoplastic polymer, the electrical conducting properties of CNTs are combined with the solvent resistant properties of the polymer to improve the electromagnetic shielding properties of thermoplastics for their application in aeronautics industry. The high aspect ratio and small diameter of CNTs reduces the filling factor making it possible to observe percolation of the nanotube network in the range of 0.1-1.0 w% [1]. We use here as a thermoplastic polymer Poly(ether ether ketone) (PEEK) [2]. The major challenge of using CNTs in composites is in controlling the dispersion in the polymer matrix. Carbon nanotubes are highly polarizable and hence inherently agglomerate. Agglomerated tubes reduce percolation and do not show the same record breaking properties of individual tubes. The use of surfactants to disperse the tubes is not useful because they increase the contact resistance and reduce the electrical conductivity of the percolating CNT network [6]. Yet, to improve the electrical conductivity, agglomeration of tubes at a smaller degree, is beneficial for the formation of conductive network of CNTs in bundles and complex secondary structures depending on their diameter and length distribution. The presence of other forms of disordered carbons can also influence agglomeration. CNTs have so far been dispersed in thermoplastic polymers by mixing the powder with carbon nanotubes solutions followed by hot pressing or using twin screw extruders [3].

First electron microscopy images and Raman maps show that a substantial fraction of the nanotubes remain agglomerated. To have a better insight of the wetting properties of the CNTs with PEEK we have dispersed nanotubes on the polymer substrate and heated the polymer above the melting temperature.

It has been reported that diffusion of polyethylene is 30% larger along the tube axis than perpendicular to the tube axis in a polymer SWNT composite above the glass transition temperature [4]. The higher diffusion rate along the tubes has been attributed to Brownian motion of the nanotubes in the polymer matrix leading to a larger excluded volume at higher temperature. We have observed that small molecules such as methanol can form uniform shells around CNTs [5]. We expect that larger diffusion of polymer molecules along the tube axis influences CNT agglomeration.

2 EXPERIMENTAL

Multi wall carbon nanotubes (MWNT) were used from Arkema (density 50-150kg/m³, 5-15 layers, average diameter 15 nm, average length 2-10 μm, carbon purity of 90%). We use PEEK as supplied by Victrex, UK (Victrex® PEEK™ 90P high flow unfilled powder). To form a polymer film, PEEK powder was mixed with acetone and several droplets were deposited on a glass slide and backed after evaporation of the solvent at 380°C (PEEK melting temperature 343°C) for 10 minutes in argon atmosphere. Dispersions of carbon nanotubes was prepared by sonication using acetone. The CNTs were deposited on the PEEK film by placing droplets and annealed at 380°C for 10 min in argon atmosphere. The temperature in the oven was monitored separately by using a thermo couple. To analyze the tube distribution the thin films were placed in an epoxy matrix and cut with Ultratome equipped with a diamond knife, in a direction perpendicular to the film interface. Multispectral Raman maps were obtained on a Xplora (Horiba Inc.) spectrometer using the 785 nm excitation wavelength and using a piezoelectric XY table. Transmission electron microscopy (TEM) has been performed on a Phillips CM30 microscope operating at 150 kV. We used a TEM thermal heating stage to heat up to 450°C on a JEOL 2010 at 160kV to observe *in situ* the melting, diffusion of the polymer and the formation of the CNT nano composite layer. We also used a cryostat with a heating element to study the *in situ* annealing in vacuum at 380°C in combination with a optical video microscope.

3 RESULTS

Figure 1.a) shows an optical image of the interface with a surface layer with uniform contrast with sharp interfaces with PEEK and the epoxy cap layer. Figure 1.b) shows a Raman line scan across the surface layer in the spectral range of the Raman G and D band. The uniform intensity of the two Raman spectral lines across the diffusion layer shows that the nanotube distribution is uniform at scales comparable to the size of the focal spot (700 nm). In figure 1.c) we plot the intensity of the Raman D and G band and the subtracted background signal across the diffusion layer. The Raman bands have a uniform intensity across the diffusion layer showing uniform distribution of the CNTs. The background signal is due to luminescence in PEEK.

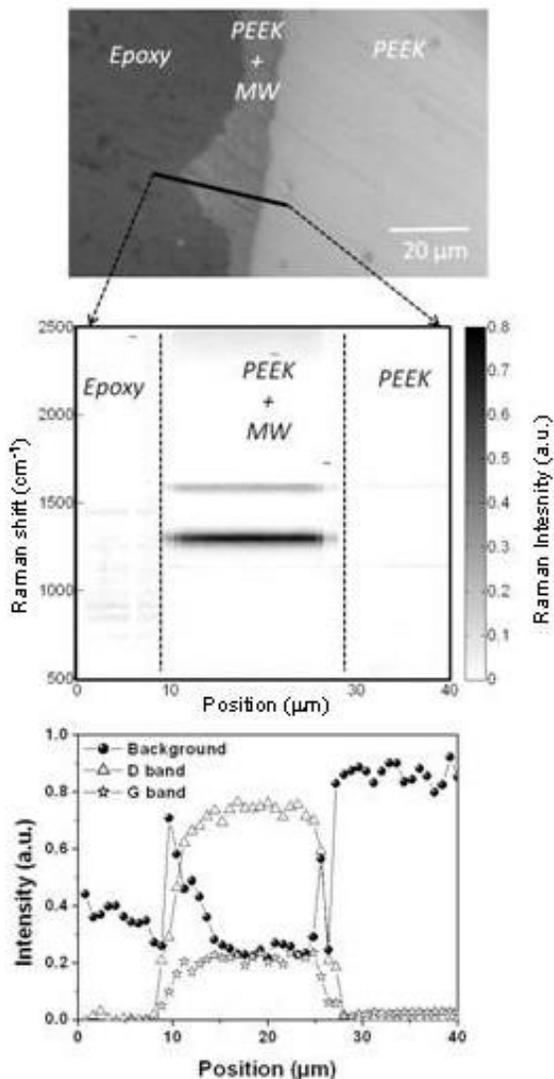


Figure 1. a) Optical cross section image of the diffusion layer of MWCNTs in PEEK, b) Raman spectral line scan across the diffusion layer, c) Raman intensity of G band, D band and luminescent background signal.

The reduction of the background signal can be explained by the quenching of photo generated charge carriers by the presence of the CNTs. It is surprising to observe a uniform tube distribution across the layer and sharp interfaces. The interface shows though a roughness which is stronger on the side of the epoxy.

Figure 2 shows a TEM cross section at the interface between the diffusion layer and the PEEK matrix. The MWs are found to be uniformly distributed and the interface is well defined down to scales of 100 nm, the average distance between tubes in the image plane. No large agglomerations are observed. Interestingly no concentration changes are observed in the vicinity of the diffusion layer or at scales larger than the mean distance between the tubes. The formation of a uniform diffusion layer from highly agglomerated multi wall tubes is unexpected and needs a better understanding of the diffusion of the polymer matrix molecules in the presence of nanotubes.

In general the diffusion of nanoparticles in a polymer matrix depends on size and shape of the nanoparticle. While the diameter of carbon nanotubes is comparable or smaller than the chain length of the polymer, the tube length is several orders of magnitude larger. For individual nanotubes with a mobility depending on diameter and length, one would expect a gradual reduction of the concentration with increasing distance from the surface. However, the fact that the tubes were agglomerated when the solvent evaporated on the surface of the PEEK film, indicates that tubes remain connected in a loose network after annealing acting as a single phase. The TEM images are consistent with what has been observed in the optical image (Figure 1.a) and shows that the diffusion layer is highly uniform.

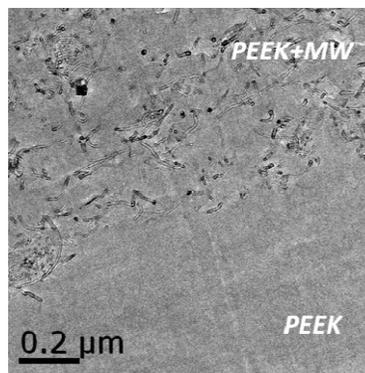


Figure 2. TEM image of the interface between the diffusion layer and the PEEK matrix. The MW distribution is uniform at scales down to 200 nm.

The anisotropy of nanotubes has the effect as mentioned above that polymer diffusion along tubes is larger than perpendicular to the tube axis. The higher diffusion of the

polymer molecules along the tube axis appears to have the effect to break up the tube agglomerations. Figure 3 shows an individual tube inside the PEEK matrix where one tube end is sticking out. The part of the tube which is sticking out is covered with a uniform polymer film. This shows that PEEK is wetting the tubes.

To see the effect of the dispersion of the tubes at larger scales we have annealed (380°C) dispersed tubes on the surface of PEEK in vacuum under a optical microscope. Figure 4. shows a region before (top left, frame 1), during (top left and bottom right, frame 2, 5) and after annealing (bottom right, frame 8). The circle shows a region before and after annealing. The contrast from agglomerated tubes on the surface is reduced after annealing. This is attributed to the diffusion of the tubes into the PEEK substrate. The arrow shows a scratch on the surface before melting which disappears once the PEEK melts.



Figure 3. Individual tube in PEEK with a uniform layer on the part which is sticking out of the layer; scale: 80 nm.

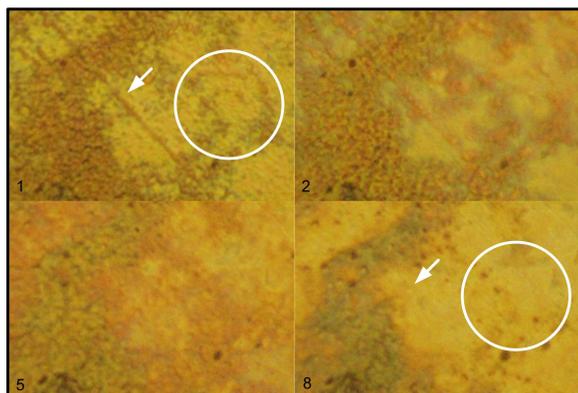


Figure 4. Annealing agglomerated tubes on the surface of PEEK, before (top left, frame 1), during (top right, bottom left, frame 2, 5) and after annealing (bottom right, frame 8); scale: 100x150 micrometers.

3. DISCUSSION

Multiwall CNTs are conductors or small gap semiconductors while the polymer matrix is insulating. As a result, CNTs are excellent absorbers of electromagnetic radiation. The high absorption of electromagnetic radiation at the nanotube leads to the formation of a heat gradient at the polymer nanotube interface. The higher temperature in the proximity of the tubes results in a higher diffusion near the tubes and the higher diffusion along the tube has the effect of separating agglomerated tubes. In short the tube acts as diffusion paths. Differently put, the high infrared absorption of nanotubes compared to the polymer matrix leads to selective heating. Regions with higher concentrations of nanotubes absorb more photons and get heated to a higher temperature, increasing diffusion and forming a more uniform dispersion. By heating preferentially the tubes, the tubes distribution gets at the same time more uniform. The higher temperature of the tubes also increases their Brownian motion which contributes to separate the tubes.

Figure 1.a shows that the interface with PEEK is uniform while the interface with the epoxy is less uniform which can be related to the non-uniform distribution of the agglomerates when depositing on the surface. One expects as a result thicker layers when the tube agglomeration is denser.

Figure 5 shows schematically that the selective heating of the CNT lead to a temperature gradient which has the effect to increase the diffusion at the tube surface along the tube axis leading to a uniform polymer coating of the tubes which separates tubes.

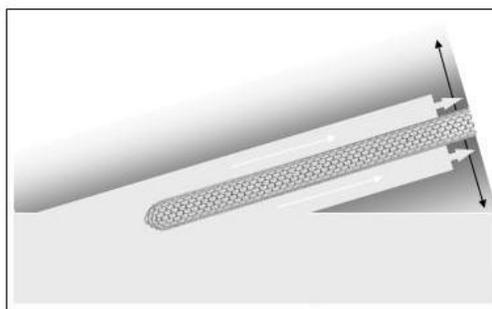


Figure 5. Schematic of the formation of a polymer film on CNTs by preferential infrared absorption of CNTs leading to a temperature gradient (black arrow) having the effect of increasing diffusion of the polymer along the tube axis (white arrow).

While we use here multi walled CNTs we have recently carried out studies using double wall and single wall CNTs [7]. In general the properties of macroscopic amounts of CNTs depend on the diameter distribution, number of layers, tube lengths and the presence of other forms of carbon such as disordered forms of graphene layers. We

find that due to the different length distribution and secondary tube agglomerations but also different infrared absorption properties, the annealing induced dispersion of tubes is less important for double and single wall tubes. Smaller diameter tubes have transition energies in the visible spectral region, having the effect of reducing the heat gradient at the polymer tube interface when annealing.

4. CONCLUSION

We show that annealing a thermoplastic polymer (PEEK) has the effect that agglomerated CNTs on the surface of the polymer are forming a uniform composite layer with highly dispersed CNTs. This is evidenced by using optical microscopy, transmission electron microscopy and multispectral Raman mapping across the composite layer. The unexpected effect of annealing on the dispersion of the CNTs is explained by the different optical absorption properties of CNTs and the matrix polymer. The high optical absorption of CNTs in the infrared spectral region leads to a temperature gradient which increases the diffusion on the polymer CNT interface. Furthermore higher diffusion rates along the tubes favors the formation of a polymer layer at the surface of the CNTs. This has the effect of separating agglomerated tubes efficiently. The selective absorption has in addition the effect that larger agglomerates of tubes increase optical absorption resulting in higher uniformity of the CNT dispersion in the polymer. A decrease of the photoluminescent background signal in the composite layer indicates that the tubes are still forming a percolation network. We are currently studying the electronic transport properties of the composite layer to confirm these results.

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