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Embedded carbon nanotubes on surface of thermoplastic poly(ether ether ketone)

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The conductivity of thermoplastic polymers can be effectively enhanced by using conductive fillers on surfaces. Carbon nanotubes are incorporated in thermoplastic poly(ether ether ketone) polymer, a polymer that is used extensively in aerospace applications, by annealing of uniform carbon nanotubes thin films on the polymer surface. Multiwall carbon nanotubes thin films of 2 cm² area was obtained by nanotube suspensions in methanol placed on water surface and then transferred on polymer surface. Single and multiple layers of nanotubes were deposited. The 200 nm thick composite layers so formed, showed an electrical conductivity up to 8 S/cm. Strong variations in the electronic transport was observed at 2.8 vol% of carbon nanotubes. The distribution of individual carbon nanotubes in the composite layer was studied by transmission electron microscopy. The amount of carbon nanotubes in the surface composite falling in the range of 2-12 vol% were determined through optical transmission measurements.

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The electrical conductivity or mechanical properties of polymers can be significantly modified by introducing even small amounts of carbon nanotubes (CNT) into the polymer matrix. The high aspect ratio of CNT leads to a low percolation threshold and allows to maintain the intrinsic mechanical properties of the polymer. However, to take advantage of the small size and exceptional electrical and mechanical properties of CNT, it is important to disperse them well, which has proven to be a major challenge despite much effort. Our previous experiments have shown that for applications using thermoplastic polymers, significant improvements in conductivity can be obtained just by changing the electrical conductivity on its surface.¹ We have shown that this can be achieved by incorporating conductive nano-particles such as CNT on the polymer surface, which offers a number of advantages in terms of cost and processing. Although this concept has significant application potential, the effective incorporation of CNT on a polymer surface has remained mostly unexplored, even though such approaches have been investigated for gas or strain sensor applications^{2,3}. An added benefit of dispersing multi walled (MW) CNT on the surface of a polymer is the improved wear resistance.³ Combining wear resistance and strain sensitivity, composites formed on the surface are also promising for artificial skins in robotics. Recently, it was reported that the addition of polysulfones improves the electrical conductivity.⁴ In addition, the observation of dynamical percolation⁵ or hierarchical conductivity⁶ open new aspects in improving polymer composites.

PEEK⁷ is suitable to replace steel, aluminum or titanium in aerospace technology and its bio compatibility makes it attractive for biomedical applications⁸ or fuel cells⁹. But for aerospace applications it is important that PEEK is conductive¹⁰ to evacuate static charges and reduce the impact of lightning strikes. Laminates of single wall (SW) CNT and thin PEEK films (structure thickness: 50 μm) have been fabricated through hot pressing¹¹ to improve the mechanical, electrical and thermal properties of PEEK. PEEK infiltrated the SWCNT thin film (thickness: 10 μm) resulting in a composite with regions with high concentrations of SWCNTs. The high melting temperature of PEEK compared to other thermoplastic polymers makes it more difficult to process PEEK and this might have had the effect that there has been limited progress in the last decades in the large scale fabrication and application of PEEK-CNT composite. The incorporation of CNTs on surfaces represents an important alternative.

We have previously observed that agglomerated multiwalled CNT (MWCNT) on PEEK are spontaneously incorporated into the surface by diffusion of PEEK through annealing at the melting temperature of PEEK.¹ The compatibility of PEEK with the CNT surface promotes diffusion and

separates the tube bundles. Lack of uniformity of CNT deposition on PEEK surface over larger distances (> 0.1 mm) resulted in limited control of composite layer thickness. We attributed this to the drying process when depositing CNT suspensions which caused the CNTs to agglomerate resulting in non-uniformity of the CNT films. In this work, we show that CNTs can be effectively incorporated on a large surface area on PEEK. We have characterised the electrical conductivity of the resulting composite materials as a function of the CNT content and annealing time.

The experimental details are as follows. MWCNT from Arkema corporation (graphistrength C100) with on average 12 walls and outer mean diameter of 12 nm and length of approximately 1-5 μm were used. MWCNT were first dispersed in methanol by sonication. The suspension was then injected on to the water surface with the help of a syringe to form a uniform layer of MWCNT on the water. The MWCNT layer, which was as large as 2×2 cm^2 , was then transferred onto the PEEK (VICTREX APTIV 2000) substrate by placing the substrate under the CNT layer and lifting it up.¹² PEEK was used as received. The thermal history of the PEEK was the same for all the systems studied. In the final step, the PEEK substrate with MWCNT were heated in vacuum at a rate of 1 $^{\circ}\text{C}/\text{min}$ up to 360 $^{\circ}\text{C}$ for various time intervals from 5 - 60 min and then cooled at the same rate for a first series of samples. To prevent reaction of oxygen with PEEK either vacuum annealing or annealing in nitrogen was used. No differences were found between the two methods. In a second series of experiments, up to 5 layers of MWCNT were deposited and annealed in nitrogen (heating and cooling at a rate of 10 $^{\circ}\text{C}/\text{min}$) on which silver pads, 2 mm wide, were deposited for electrical resistance measurements. Mixing occurs by melting of PEEK and diffusion of PEEK into the CNT deposit on the surface without presence of water. Important in the annealing process is that the atmosphere is inert. Optical transmission was measured to quantify the CNT content. The optical transmission measurement was carried out using a laser (Ar, 532 nm), collimator, objective lens, aperture (diameter 2mm) and a large area photodiode. A large detector surface was used directly behind the PEEK layer and no differences were found for the optical transmission measurements with different amounts of crystallization of PEEK. Cross sectional images of the composite at the surface of PEEK were obtained using transmission electron microscopy (TEM, JEOL 2000, 200kV) and the 200 nm-thick samples of the composite were prepared using the microtome technique.

Fig. 1 shows a TEM cross sectional image of the composite layer after deposition of a single MWCNT layer and annealing. The image shows individual and bundles of MWCNTs. The average thickness of the composite was determined by analyzing the contrast of the image after first

orienting the interface in the horizontal direction. Each line in the image was then analyzed across the composite layer. The pixel standard deviation and mean contrast are shown on the right side. From the two distributions, the average MWCNT layer thickness of $t \approx 200$ nm was estimated. It was observed that the thickness of the composite layer depends on the uniformity of the CNT layer. The thickness is also influenced by the tube diameter distribution.¹

The MWCNT concentration as a function of layer thickness can also be seen. In Fig. 1, it can be seen that the interface on the side of bulk PEEK is well defined and not diffuse. This has been observed previously¹ and is explained to be due to PEEK diffusion into the MWCNT layer. The PEEK polymer has a higher mobility than individual or bundled CNTs. The diffusion of PEEK separates the tubes and the tubes do not diffuse into the bulk, but remain on the surface. In our previous study, we observed that depositing MWCNT dispersed in acetone resulted in non-uniform films with varying thicknesses over larger distances ($> 10 \mu\text{m}$). This was attributed to the reaction of the polymer by acetone is known to affect PEEK¹³ that presumably has the effect that MWCNT penetrating deeper into the polymer. Using methanol for dispersing the MWCNT, the penetration depth of MWCNT after annealing was reduced to 2 - 3 μm .¹⁴

To quantify the amount of MWCNT present in the composite layer, optical transmission measurements were carried out. Applying the Beer's law and using the extinction coefficient for MWCNT, the MWCNT concentration can be extracted. The extinction coefficient of MWCNT was determined from suspensions of MWCNT of known concentration.¹⁵ Using the values of 1.9 kg.L^{-1} for the density of MWCNT¹⁶, 0.90 kg.L^{-1} for very low density polyethylene and 1.32 kg.L^{-1} for PEEK, the concentration of MWCNT (weight or volume) in the polymer were deduced. A plot of the optical density (OD) divided by the sample thickness (t) as a function of volume concentration shows two slopes, one at low concentration corresponding to the good dispersion of $5.7 \mu^{-1}$ and one at medium concentration at $16.9 \mu^{-1}$ which corresponds to less well dispersed MWCNT (Fig. 2). For a well dispersed sample at low concentration $2.8 \mu^{-1}$ is expected.¹⁵

It was found that the amount of MWCNT on the polymer can be controlled by the initial suspension concentration up to a certain limit. To increase the amount of MWCNT furthermore, up to 5 layers were deposited. Laminates were formed either by annealing after each deposition or by annealing only once at the end of 5 depositions. Fig. 3 shows the histograms of TEM images for the 3 types of samples: sample A with only one deposition and annealing step, sample B, 5 depositions and only one annealing step and sample C, 5 cycles of deposition and then annealed.

With one deposition, the thickness of the CNT film is around 200 nm and varies by about 10 %.

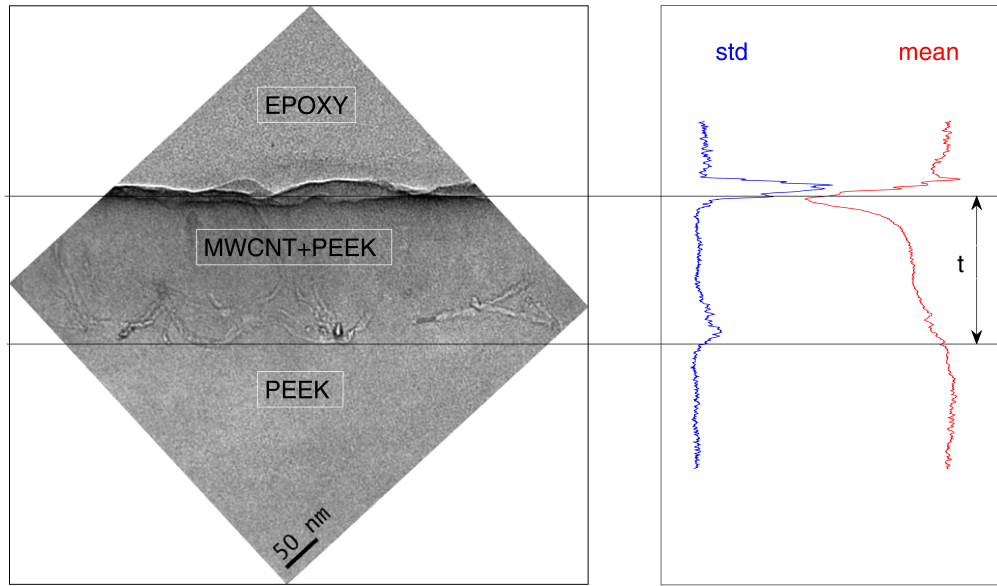


FIG. 1. Rotated TEM image of composite layer on PEEK (left side). The pixel average intensity (mean) across the composite layer as well as the standard deviation (std) of the pixel intensity curve is shown on the right side. The thickness of the composite layer is $t \approx 200$ nm. The CNT density is higher on both interfaces.

Repeated deposition and annealing leads to a thickness of 400 nm while annealing only once leads to a thickness of 280 nm. Both sample B and C are thicker than sample A but less than 5 times the thickness of one layer. That means that the CNT concentration and composite layer thickness can be best increased by adding additional layers and annealing after each deposition. The highest density of tubes is obtained by depositing several CNT layers and annealing only once.

Fig. 4 shows the thickness obtained for samples with only one deposition and annealing step as a function of the annealing time. Increasing annealing time increases the thickness of the surface composite but only by a small amount. This indicates that even so the diffusion is slow due to the high viscosity little difference is observed when extending the annealing time to 30 min.

To correlate the amount of CNT with electrical resistance of the composite, Fig. 2 shows the optical transmission and electrical resistance with various annealing times. By estimating the amount of CNT from the optical transmission measurements it becomes then possible to find the electrical resistivity as a function of CNT concentration.

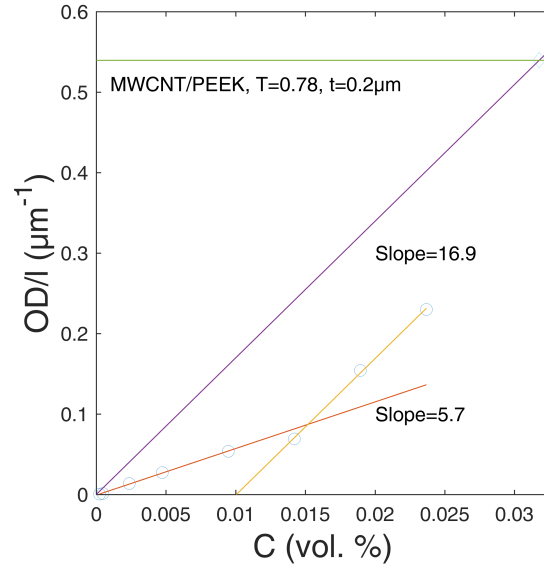


FIG. 2. (left) Law used to find MWCNT concentration from measurements of Combessis *et al*¹⁵. OD is optical density, t is the thickness of the layer, T is the transmission and C the concentration corresponding to the volume fraction. The data points are taken from Combessis *et al.*¹⁵

In Fig. 5, we see that the percolation threshold is observed about at 2.8 vol% of CNT which corresponds to optical transmission of 0.78 and 4.1% in weight of CNTs. This is higher compared to typical literature values where percolation is observed at 1 - 2%.⁷ The higher value found here are attributed to the higher concentration of tubes at the air interface and probably, higher degree of bundling of tubes. Longer annealing time leads to lower electrical conductivity consistent with the fact that prolonged annealing increases the separation of tubes due to diffusion of PEEK, thus reducing percolation. Below percolation, it is observed (fig. 5) that the electrical resistance decreases steeply when reducing CNT concentration. Repeated deposition of CNTs is found to lead to a slight curvature of the PEEK substrate. The curvature is due to a contraction of the upper face (lift of the edges) and linked to the wetting of the CNT network and is along the shorter axis of the rectangular substrate. When accounting for the thickness of the PEEK substrate (0,25mm). The composite layer is strained by approximately 0.1%.

Fig. 6 shows the sensitivity of the measured resistance to temperature in plotting the specific resistance as a function of temperature. In the range between 200 K and 400 K, the relative sensitivity can be described by the following linear expression:

$$S = \frac{\frac{\Delta R}{R}}{\Delta T}$$

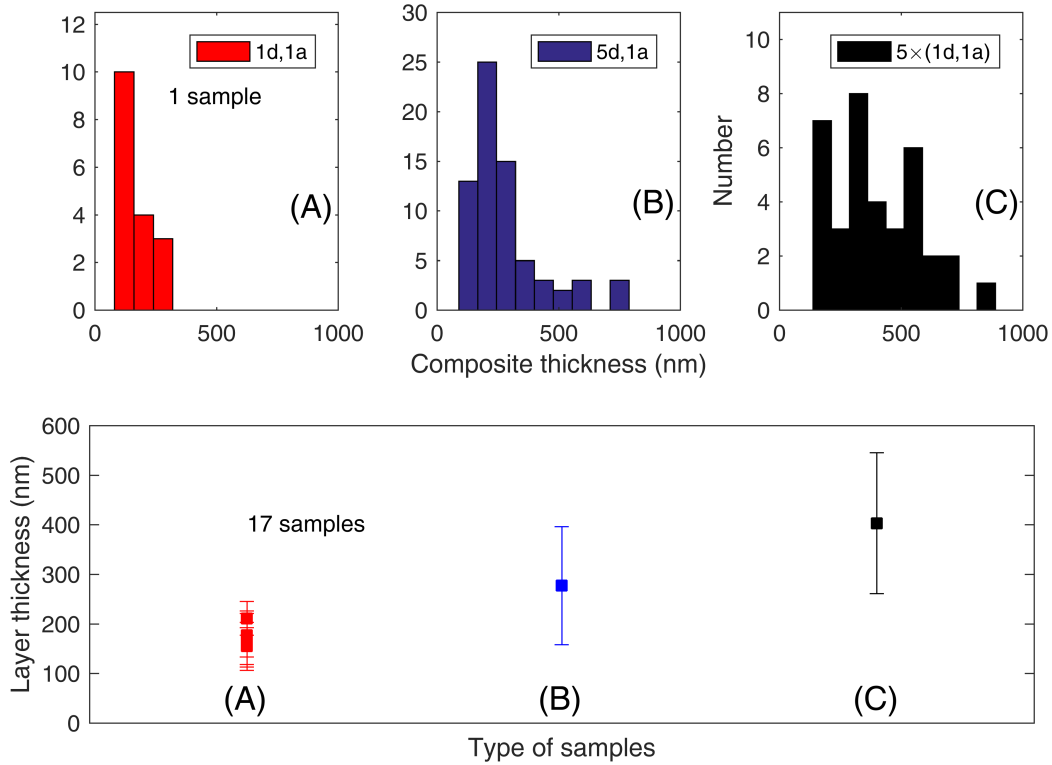


FIG. 3. (top) Histogram of layer thickness determined by TEM of three samples and (bottom) the corresponding average composite thicknesses. The samples are (from left to right): (A) one deposition and one annealing step, (B) 5 depositions and only one annealing step and (C) 5 cycles of deposition and annealing cycles.

Where S is $-0.00059 K^{-1}$. S denotes the average resistance–temperature coefficient of the sample¹⁷, this value is deduced by fitting the data point in Fig. 6 and is sufficient to be able to determine the temperature within 10 K from a given calibration curve but not for higher precision. All the samples shown here are above the threshold percolation (optical transmission $T=0.4$, annealing time 90 min) with only one layer deposited. While we show here results on uniform layers of composites, it is in principle possible to pattern the composite layer using local laser heating.¹⁸ There is also the possibility to repair damaged composites (cracks) by deposition and local laser annealing forming a surface composite which are at least 200 nm thick. A clear change of the resistivity is observed at around 2.8 vol% of MWCNT which corresponds to optical transmission of 0.78 and 4.1% in weight of MWCNT. This value can be considered as percolation

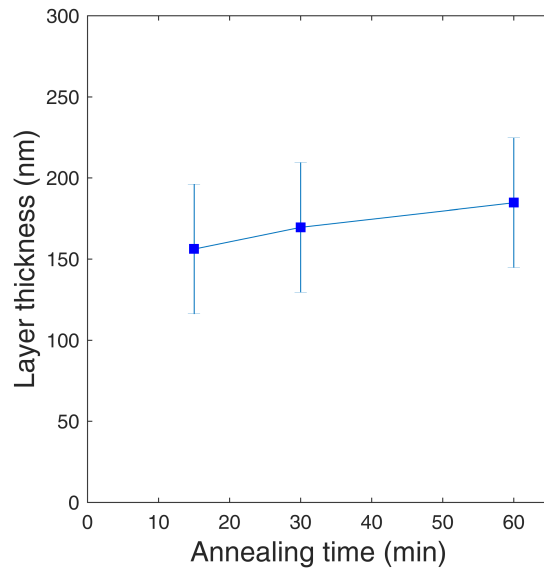


FIG. 4. Typical variation of the thickness of a composite layer for several annealing time.

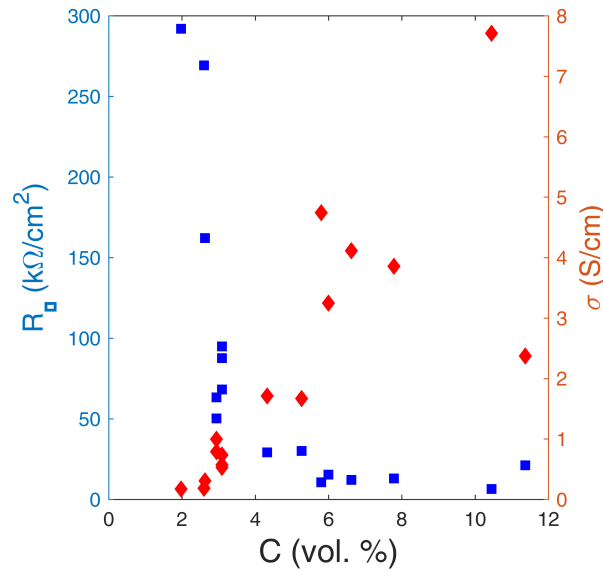


FIG. 5. Resistance square and conductivity as function of MWCNT concentration for a layer thickness of around 200 nm. There is no direct correlation between annealing time and resistance square.

threshold for our poorly dispersed MWCNT. This is a higher but compares well to typical literature values where percolation threshold is observed at 1 - 2% of MWCNT. The error in Fig. 5 depends on numerous parameters starting with the fabrication, annealing, the electrical contact and optical transmission measurements. From the data points an error on average of 20 kOhm/cm²

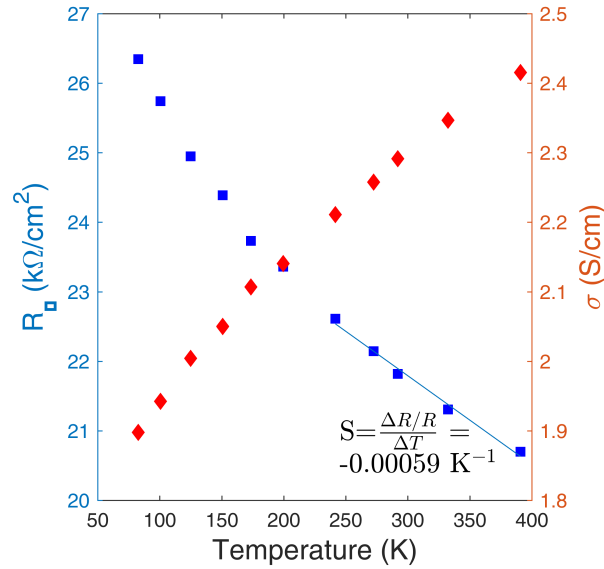


FIG. 6. Resistance variation as a function of the temperature of CNT/PEEK composite layer 200 nm thick.

is estimated. The error in Fig. 6 is considerable smaller (2 kOhm/cm²). The here measured conductivity are several orders of magnitude higher than conductivity reported in literature across 1.4 mm thick films with 8-10% CNTs.¹⁹ This can be attributed to the fact that the CNT film formed on the water surface have a higher connectivity.

We conclude that by depositing large uniform CNT layers on PEEK surface followed by annealing in nitrogen, uniform 200 nm-thick nano-composite laminates can be obtained. TEM observation on microtome thinned samples showed CNTs embedded individually in the polymer at the depth of 200 nm (Fig.1). The electrical conductivity of the composite can be increased by depositing several layers with electrical conductivity as large as 8 S/cm. Repeated annealing leads to thicker composite layers. The temperature dependence of the conductivity of the surface composite is moderate (-0.00059 K^{-1}).¹⁹ Strong variations in conductivity were observed at 2.8 % vol CNT. Depositing CNT layers on polymer surface and converting them into a conductive nano-composite layer (8 S/cm) by annealing, is a straightforward process which represents an attractive alternative for the fabrication of high-performance conductive polymers used in a variety of applications in aerospace technology and for artificial skins.

Data availability statement: The data that supports the findings of this study are available within the article.

ACKNOWLEDGMENTS

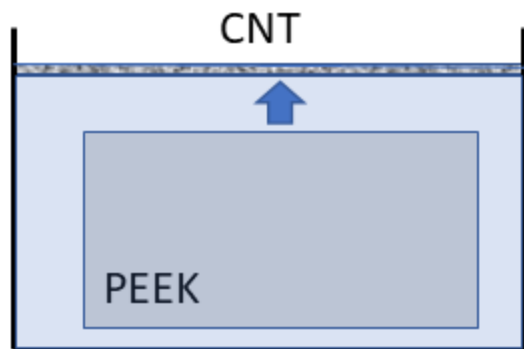
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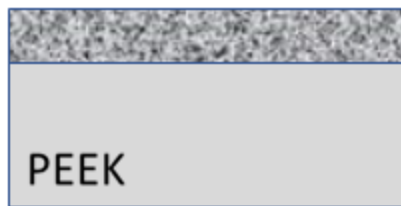
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CNT surface nano-composite



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8 S/cm
@ 10 vol%

↕ 200 nm