

Conductive Carbon-Nanotube/Polymer Composites: Spectroscopic Monitoring of the Exfoliation Process in Water and the Crucial Role of Wetting

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ABSTRACT

A versatile, latex-based concept for efficiently dispersing Single Wall Carbon Nanotubes (SWNTs) in a highly viscous polystyrene matrix is described

Crucial for the entire process is the ultrasound-driven exfoliation of the as produced SWNT bundles in water. The energy input must be sufficiently high to achieve the desired individualization, but at this stage sonication should be stopped to avoid damaging the SWNTs, which would reduce both electrical conductivity and strength. With UV/VIS spectroscopy the unraveling of the NT bundles can easily be monitored, a process which was simultaneously visualized with cryo-TEM and SEM images. These images were in agreement with the collected UV/VIS data.

Depending on the molar mass distribution of the PS matrix, the well-dispersed SWNTs significantly raise the T_g of the PS. A low molar mass PS fraction, probably acting as a wetting agent for the SWNTs, seems to be required for an improved PS/SWNT interaction.

Keywords: polystyrene-swnt nanocomposites, latex, uv/vis spectroscopy, thermal analysis

1 INTRODUCTION

Single wall carbon nanotubes (SWNTs) exhibit high strength, high stiffness and good electrical conductivity. Because of their high aspect ratio (length/diameter ratio), these NTs are very interesting fillers for polymers [1, 2], since property enhancement, usually related to percolation, can already be expected at very low loadings. SWNTs usually agglomerate in bundles, driven by Van der Waals interactions [3], and therefore exfoliation of the nanotube bundles and the incorporation of NTs as individuals or very thin bundles into a highly viscous polymer matrix remains a challenge. The key issues for making technically interesting NT-polymer nanocomposites are the full exfoliation of the NTs and the subsequent efficient dispersion of the

individual NTs in the polymer matrix [4], as well as controlling the interfacial interaction between the filler and the polymer matrix. If well dispersed, the filler-matrix interface area is huge, and a perfect control of the interfacial interaction is crucial for obtaining optimal physical properties.

The present paper deals with both these crucial issues, *viz.* the exfoliation of the NT bundles, the first step towards technically interesting polymer-NT nanocomposites, and the interfacial interaction. We report on an extremely simple UV/VIS method for monitoring the exfoliation of SWNTs in water [5], and in addition present preliminary results on the influence of the molar mass distribution of the polymer matrix on the interfacial interaction. This latter phenomenon is studied by Differential Scanning Calorimetry.

2 EXPERIMENTAL

2.1 Materials

In this work two types of SWNTs have been studied, namely Carbolex NTs provided by Carbolex Inc. and HiPCO NTs from Carbon Nanotechnology Inc. Carbolex NTs (Batch number CLAP 8510) are produced by arc-discharge technology and contain about 30 wt% of impurities composed of both carbon impurities and Nickel and/or Yttrium catalyst particles. HiPCO NTs have been produced by a modified gas process based on chemical vapour deposition. The batch (PO 257) contained around 10-15 wt% of impurities, composed, according to the manufacturer, of 5 wt% of small iron catalyst particles encased in carbon shells and, in some cases, also in the NTs themselves. The surfactant used for the dispersion of the NTs in water is sodium dodecyl sulfate (SDS, 90%) provided by the Merck Chemical Co. All experiments were carried out with demineralized water.

2.2 Methods and Procedures

The molecular weights of the different PS latexes used were analyzed at 40°C by Gel Permeation Chromatography (GPC) using a Waters Model 510 pump system with mixed packed columns preceded by a guard column PLgel mixC. Injections were done by a Waters Model WISP 712 auto-injector. Tetrahydrofurane (THF) was used as an eluent at a flow rate of 1.0mL/min. The measurements themselves were carried out with a refractive index detector Waters Model 410, and a Model 486 UV detector (at 254nm), and the data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software. The calibration was done by using PS standards supplied by Polymer Laboratories, Inc.

All sonication processes were carried out with a horn sonicator Sonic Vibracell VC750 with a cylindrical tip (10 mm end cap diameter). The frequency was fixed at 20 kHz +/-200Hz. UV/VIS absorption spectra were recorded by a Hewlett Packard 8453 spectrometer operating between 200 and 1100 nm.

For each UV/VIS experiment, 0.5 wt% of SWNTs was mixed with 20 mL of an aqueous solution containing 1 wt% of SDS. The resulting mixture was then sonicated for different times under mild conditions, i.e. at a power of 20 W. Samples were taken regularly during the sonicating process, diluted by a factor of 30, resulting in NT contents of 0.0167 wt%, and UV/VIS spectra were recorded. Quartz cuvettes were employed and the blank used as reference for the measurements was a 1 wt% SDS solution diluted by a factor of 30, under the same conditions as the samples themselves.

For the preparation of the nanocomposites, SWNTs were directly mixed with a solution containing 1 wt% of SDS, sonicated at 20W for 15min in order to exfoliate the nanotubes, and then centrifuged at 4000rpm for 30min (Heraeus Sepatech Varifuge RF). The remaining SWNT supernatant solution was then mixed with the polymer latex and freeze dried (Chris Alpha 2-4). The resulting powder was processed into films by compression molding at 180°C (Collin Press 300G).

Modulated Temperature Differential Scanning Calorimetry (MTDSC) measurements have been performed using a helium-purged TA Instruments 2920 DSC with MDSC option, equipped with a refrigerated cooling system (RCS). Temperature and heat capacity calibration were performed using indium and poly(methyl methacrylate) standards, respectively. Measurements were performed at a rate of 2.5°C/min, with an applied temperature modulation of $\pm 0.5^\circ/60s$.

Two-point conductivity measurements were carried out using a Keithley 6512 Programmable Electrometer. Measurements were performed directly on the film surface of the films. The contact between the sample and the measuring device was improved by the use of a colloidal graphite paste (Cat#12660) provided by Electron Microscopy Science.

3 RESULTS AND DISCUSSION

Sonicated aqueous dispersions of Carbolex and HiPCO SWNTs were examined with UV/VIS spectroscopy according to the procedure described in the experimental section. The UV/VIS spectra recorded for these Carbolex and HiPCO SWNT dispersions are given in Figure 1.

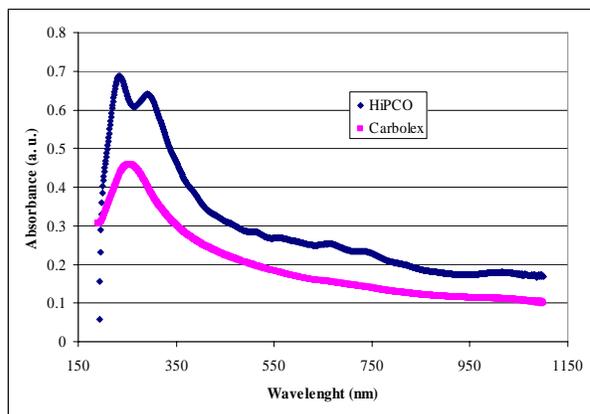


Figure 1: UV/VIS spectra of Carbolex NT (lower curve) and HiPCO NT (upper curve) solutions in water. For both solutions a solution containing 0.5wt% SWNT and 1wt% of SDS was diluted 30 times. Energy input for Carbolex ca. 1,500 J, for HiPCO ca. 140,000 J.

Figure 1 shows that the UV/VIS spectra obtained are specific for the NT type studied. This is not surprising, since the Carbolex and HiPCO NTs studied have different characteristics in terms of chirality and diameter, two parameters which directly determine the shape of the UV/VIS spectrum. For both the Carbolex and the HiPCO SWNTs, the absorbance gradually decreases from UV to near-IR, in agreement with the absorption spectrum reported by Jiang et al. [6]. This is partly due to scattering, especially in the lower wavelength range.

During the sonication procedure, the increasing amount of exfoliated NTs gives rise to an increasing area below the lines representing the absorbance. It was verified that the relative evolution of the area under the spectrum during the sonication process is proportional to the relative evolution of the absorbance value at a specific wavelength. Therefore, we decided to determine the absorbance maximum at one specific wavelength, namely at 237 nm for the HiPCO solutions and at 250 nm for the Carbolex solutions, and to plot these respective value as a function of the total energy supplied to the solutions.

As the sonication power is constant throughout the experiments, a direct relationship exists between a specific sonication time and the energy delivered to the sample during this same time interval. Therefore it doesn't make any difference whether the absorbance at a certain wavelength is plotted, either versus the time of sonication or versus the energy supplied to the solution. Figure 2 shows the absorbance at 237 nm as a function of the energy

supplied to the aqueous HiPCO/SDS solution. The recorded UV/VIS absorbance is directly proportional to the amount of individualized SWNTs.

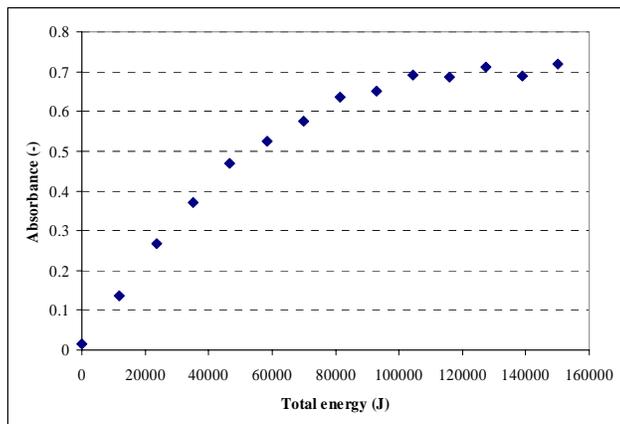


Figure 2: Evolution of the height of the peak located at 237nm for an aqueous 0.5wt% HiPCO NT solution, containing 1wt% of SDS, diluted 30 times. Please note that the dilution factor (30 times) has been chosen to ensure that all the UV absorption values stay below 1 so that the error implied by the measurement itself is reduced. The error induced by the sampling and the accuracy of the measurements of the UV spectra is about 0.03 a.u. (value of the standard deviation).

The shape of the curve representing the UV/VIS absorbance at 250 nm versus total energy-input, obtained for aqueous Carbolex/SDS solutions (not shown), is very similar to the HiPCO curve, given in Figure 2. For both SWNT dispersions, for relatively low energy input values the absorption strongly increases with increasing energy input, but later on in the sonicating process the value of the absorbance levels off, and a plateau value is reached, namely after an energy input of ca. 5,000 J for the Carbolex SWNTs and ca 100,000 J for the HiPCO SWNTs. This is in agreement with what can be expected: the absorbance increases at the beginning of the sonicating process, when the exfoliation is in progress. The levelling off and the ultimate highest limit of the absorbance correspond to the maximum achievable degree of individualization or dispersion of the NTs. Although no cryo-TEM, nor SEM pictures are shown in this paper, these were made and confirmed incomplete exfoliation of the SWNTs at the stage at which the UV/VIS absorbance is still increasing, and nearly complete dispersion at the stage where the absorbance levels off.

Note that although the shape of the UV absorbance versus total energy input curves, as well as the plateau value, for the Carbolex and HiPCO systems are very similar, there is an important and interesting difference: HiPCO NTs exfoliate at a much lower rate than Carbolex NTs. Obviously, 100,000 J are necessary to reach the

maximum degree of exfoliation of the HiPCO bundles (see Figure 2), whereas only 5,000 J are required for Carbolex NTs to achieve the same level of individualization. This result implies that in the HiPCO NT bundles the Van der Waals attraction is stronger. This different behaviour might partly be ascribed to the fact that Carbolex NTs contain more impurities. Moreover, Carbolex NTs are interconnected via catalyst particles. These particles, as well as other carbon impurities can be present between the NTs in the bundles, decreasing the contact area between NTs in comparison with “cleaner” HiPCO NTs. This implies a weaker interaction between the NTs in the Carbolex bundles, and accordingly should lead to a faster exfoliation.

A second crucial issue in the process of making polymer nanocomposites with satisfactory physical properties is the control of the interaction between the nanotubes and the polymer matrix. Interestingly, we found that the molar mass distribution of the polystyrene latex plays a crucial role for establishing this favorable interaction. One way to study the interaction between the nanofillers and the polymer matrix is performing a differential scanning calorimetry analysis. If the polymer adheres well to the filler, the inherent restricted mobility of the adsorbed polymer chains will result in a raise of the glass transition temperature (T_g). For a first examined polystyrene latex (PS1) the peak molar mass was around 1,500,000 g/mol, and the molar mass distribution was extremely broad, with significant amounts of extremely low molar mass oligomers present. The presence of these oligomers resulted in a T_g of ca. 90 °C for neat, unfilled PS1. This T_g value is significantly lower than the value of high molecular weight PS, being ca. 100 °C. The addition of 2.5 wt% of SWNTs to this polymer, by the technique described in the experimental section, yielded a T_g of ca. 107 °C, which is even higher than the 100 °C observed for high molar mass PS, and which points to a strong interaction between filler and matrix. Applying a second PS latex (PS2), not containing a low molar mass fraction and having a peak molar mass of ca. 1,000,000 g/mol and a relatively narrow molar mass distribution, afforded a T_g of ca. 97 °C after mixing with 2.5 wt% SWNTs, which is lower than the T_g observed for the unfilled PS2, being 100 °C, as expected for high molar mass PS. The observed difference is striking, and we believe that it is most probably related to the presence of low molar mass PS oligomers in latex PS1, which act as a kind of wetting agent, indispensable for establishing intimate contact between the SWNTs and the PS matrix. The observation that nanocomposites based on PS2, in which no low molar mass PS wetting agent is present, exhibit a lower T_g than the T_g of the neat PS2, is most probably due to the presence of significant amounts of SDS, acting as a plasticizing agent for the PS, and to the absence of intimate contact between matrix and filler material, which might imply an increased free volume, lowering the glass transition temperature.

For PS1-based nanocomposites the conductivity was determined as described in the experimental section. These data have been published before [5], and therefore we just mention that the percolation threshold proved to be around 0.3 wt% SWNTs and that a maximum conductivity of ca. 0.1-1 S/m was obtained for SWNT loadings of 0.5 wt% and higher. These values are very promising for applications as antistatic materials, for EMI shielding and even for applications in the transistor industry.

4 CONCLUSIONS

This paper demonstrates that the sonication-driven exfoliation of aggregates and bundles of single wall carbon nanotubes (SWNTs) in an aqueous surfactant solution can be easily monitored by UV/VIS spectroscopy. The different stages of the exfoliation process were directly visualized by cryo-TEM (not shown in this paper), showing an excellent correspondence with the spectroscopic data: the maximum achievable exfoliation (which does not mean that 100% of the NTs are effectively exfoliated) corresponds to the maximum UV/VIS absorbance of the NT solution.

This paper also demonstrates that it is possible to control the interaction between the polymer matrix and the nanofillers by adjusting the molar mass distribution of the polymer latex, applied for the preparation of polymer nanocomposites. The good electrical conductivity of PS/SWNT nanocomposites with a carefully designed polymer matrix opens the way to numerous applications in the electrical and electronics industry, like antistatic materials, materials for EMI shielding and even parts for transistors.

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