Using Photosensitive Dye To Improve Multi Walled Carbon Nanotubes Dispersion

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Abstract.

As already well-known, the outstanding mechanical and electrical properties of carbon nanotubes (CNT) are partially lost when CNT aggregate. The fact that CNT tend to aggregate makes difficult to put them into a host matrix, for example. Until now, achieving stable dispersions of CNT is still a challenge. In the present work, we show that the addition of an azobenzene derivative, Disperse Orange 3 (DO3) to dispersions of multi walled carbon nanotubes (MWCNT) in the organic solvent tetrahydrofuran (THF) efficiently helps debundling MWCNT and makes dispersions stable for days. We report UV-Vis optical absorption experiments that suggest an interaction between MWCNT and DO3 molecules following the behavior qualitatively observed. Dispersions with MWCNT and DO3 in THF were observed qualitatively over time. Successful suspensions (for the higher DO3 concentrations studied) were stable for several days. Also, we prepared polymeric films doped with MWCNT non-covalent functionalized with DO3 in one of the proper DO3/MWCNT weight relation where stable supensions were obtained. In this study we show preliminary results where the optical response of these samples was also measured.

1. Introduction

Carbon nanotubes (CNT) are unique one-dimensional structures in terms of their structural and electronic properties. In order to obtain better dispersions of CNT into polymer matrices, several methods have been developed. The non-covalent functionalization of CNT is widely used to improve CNT solubility due to the weaker modification of the intrinsic properties of carbon nanotubes [1]. Non-covalent functionalization includes polymer wrapping [2, 3], the use of biocompatible surfactants [4] the encapsulation by supramolecular systems of small molecules, like surfactant micelles [5] and the π-stacking by rigid, conjugated macromolecules. These attemps with non-covalent functionalization have their basis in the sp^2 molecular structure of carbon nanotubes, which in fact can be seen as an extended π system. Figure 1 shows schematically the p_z atomic orbitals that are present in a typical ring molecular geometry that leads to the characteristic electron clouds on both sides of the ring. The electrons that are in those orbitals are known as π electrons. In a theoretical frame, molecules with aromatic rings such as benzene or anthracene can interact with the sidewalls of carbon nanotubes [6] via π-π stacking interactions. In these interactions, both π electron systems of both systems are combined leading to minor changes in the electronic structure of the nanotubes [1]. In the

past few years, several works studied the dispersion of carbon nanotubes. Particularly, it has been demonstrated that a diazo dye molecule, Congo Red, efficiently improves the dispersion of MWCNT in water [7] without damaging the molecular characteristics of carbon nanotubes and thus preserving their properties. In order to go further in the understanding of solubility of carbon nanotubes, Zhang et al. [8] recently studied the effect of methyl substitutes of organic dyes in the dispersion of MWCNT.

DO3 is an azobenzene derivative with an amine and a nitro group. Its molecular structure is shown in Figure 2. According to what it was previously said, it could interact with carbon nanotubes via π-π stacking interactions, thus helping to achieve stable dispersions in THF. In addition, the fact that DO3 has a terminal amine group could be helpful for a covalent bonding with an epoxy resin. One of the main characteristics of azobenzene, as well as its derivatives, is that they can undergo a photoisomerization process. When illuminated with a linear polarized beam of the proper wavelength, the molecule undergoes cycles *trans-cis-trans*. These cycles will happen whenever the dipole moment of the molecule has a component in the direction of the polarization of light. This characteristic process implies that anisotropy could be induced in a host material doped with azobenzene derivatives since the photoisomerization process will end up only when all molecules have their dipole moment aligned perpendicularly to the polarization axis of light. In this sense, the addition of carbon nanotubes with DO3 to polymers could lead to potential applications in the development of optical data storage devices.

In other respects, one of the applications of carbon nanotubes is to introduce them in a polymer [9, 10, 11, 12]. In particular, in epoxy matrices MWCNT are used in order to obtain certain degree of electrical conductivity without modifying their mechanical properties. The most frequently used solvent in epoxy resins, which are not water soluble, is tethrahydrofuran (THF). For this reason, it is relevant to find proper mechanisms to disperse carbon nanotubes in THF.

Taking into account this kind of application, in this work we pay our attention to the MWCNT dispersion and interaction with DO3 in THF to effectively disperse the nanotubes in epoxy resins to go on further in the development of new optoelectronic devices. Additionally, we show our preliminary results in measuring the induced anisotropy of epoxy resin films containing MWCNT functionalized with DO3 molecules.
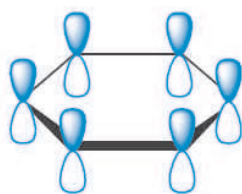

Figure 1. Scheme of the p_z atomic orbitals that are present in a typical ring molecular geometry.
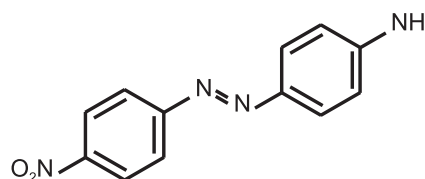

Figure 2. Molecular structure of Disperse Orange 3.

In this work, we show that the addition of DO3 to dispersions of MWCNT in THF in specific quantities efficiently helps to debundle MWCNT making dispersions stable for several days. We report optical absorption experiments that suggest an interaction between MWCNT and DO3 molecules that would explain the stability observed in the suspensions observed.

2. Experimental Methods

We worked with commercial MWCNT from NANOCYL (NC3100). Their length is about 1,5 μm and their diameter is around 20-40 nm as observed by field emission scanning electron

microscopy. MWCNT were dried in a vacuum oven at 120 C during 3 h (in order to remove adsorbed water) and were left in vacuum at room temperature until used.

We used DO3, 4-(4-Nitrophenylazo)aniline $O_2NC_6H_4N=NC_6H_4NH_2$ as received from Sigma-Aldrich.

We employed as solvent tetrahydrofuran, from Sintorgan (HPLC analytical grade). In this study, we present the results for two different set of samples employed: 1) samples in which only DO3 was dissolved in THF at different concentrations (reference samples) and 2) samples in which a fixed amount, 10 μg/mL, of MWCNT was added to each reference sample. The concentrations of DO3 for the reference samples were 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 μg/mL. All the obtained results for the samples containing MWCNT and DO3 were compared to the corresponding reference sample. Three different set of reference samples and samples with MWCNT added were prepared in order to ensure the results were repetitive. Other MWCNT concentrations (6 μg/mL, 0.1 mg/mL and 1 mg/mL) were also studied in order to test our results to a certain extent. All samples containing MWCNT were sonicated during four periods of 15 minutes each one. Stability of the dispersion in samples with MWCNT was qualitatively evaluated by capturing images at different times. Images were taken with a commercial Sony DSC-W120 camera.

Interactions between MWCNT and DO3 were studied by comparing the UV visible spectra of reference samples to those containing MWCNT and DO3. UV-vis spectra were measured with a HP 8453 spectrometer (wavelength resolution: 1 nm). All the absorption spectra were obtained at room temperature.

Films of epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) and MWCNT with DO3 were prepared by the spin coating technique onto properly cleaned cover glasses. Films were made with MWCNT 0,05 % wt. and a DO3/MWCNT weight relation of 2.

The anisotropy in the material was induced by using a linearly polarized beam of light from a 473 nm, 50 mW, laser. The induced anisotropy was measured with a normally incident 632.8 nm, He-Ne laser. The epoxy resin film was in between two crossed polarizers. The intensity of the He-Ne beam was measured after passing through this array. The excitation beam polarization was set to 45° with respect to the crossed polarizers [13]. The experimental optical setup is shown in the inset of Figure 8.

3. Results and Discussion

We qualitatively followed the stability of the dispersions containing 6 μg/mL, 10 μg/mL, 0.1 mg/mL and 1 mg/mL MWCNT and DO3 at different concentrations for several days. From direct observation, two different behaviors were observed when progressively increasing DO3 concentration to MWCNT in THF: one for the lower DO3 concentrations and other for the higher DO3 concentrations. All these samples were followed for at least 45 days. For low DO3 concentrations, MWCNT still aggregated but in a different way as they did in THF. For high DO3 concentrations, there was no MWCNT aggregation. Effective dispersion of MWCNT would suggest an interaction with a large number of DO3 molecules. This effect could be attributed to π-π stacking interactions between MWCNT and DO3 molecules.
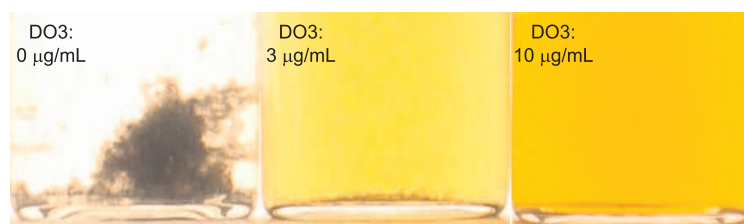

Figure 3. Enlarged image of the bottom of the containers having samples with MWCNT 6 μg/mL after 45 days of being sonicated.

As an example, we show in Figure 3 a picture taken after 45 days of the preparation of the samples. A zoom of the area of interest is shown in order to clarify the extent of aggregation. It is worth to note that even for a low DO3 concentration, 3 μg/mL there was a significant change in the way MWCNT started to aggregate. When MWCNT were in THF, they created very large bundles that decanted within the first hours. On the contrary, when DO3 was added in low concentrations, MWCNT aggregation still happened but in an absolutely different way. MWCNT did aggregate and finally decanted but in smaller aggregates as if they were *little rocks*. This fact suggests the existence of interactions between DO3 molecules and MWCNT. Similar results were evidenced when samples with MWCNT were settled for days. MWCNT started to aggregate within the first hours when dispersed in THF and also a certain degree of aggregation was noticed for the lower DO3 concentrations (from 1 to 5 μg/mL). The non-aggregation was only achieved when DO3 concentration was higher than 6 μg/mL. Similar observations showed the efficience of DO3 as dispersing agent of MWCNT until MWCNT concentrations of 1 mg/mL.

The UV-vis absorbance spectra of the reference samples for all the different concentrations are shown in Figure 4. There are two absorption bands: at 276 nm and at 443 nm. They correspond to π-π* and n-π* transitions. The π-π* transition at 276 nm is associated to the benzene ring. The one at 443 nm corresponds to the stronger π-π* electronic transition overlapped with an n-π* transition of the azo group. Both electronic transitions overlapped, π-π* and n-π*, are associated to the *trans-cis* and to the *cis-trans* photoisomerization process respectively. Thus, irradiating a material doped with DO3 at a wavelength near this absorption band will induce the cycle *trans-cis-trans* and hence anisotropy.

In Figure 5 the absorbance spectra of samples containing 10 μg/mL MWCNT are shown. From bottom to top, the curves corresponding to 1, 2, 4, 5, 6, 7, 8, 9, 10, 11 and 12 μg/mL of DO3. The inset show a typical absorption spectrum of MWCNT in THF at the same MWCNT concentration, 10 μg/mL. As can be seen, no absorption band appeared in the UV-vis range for MWCNT in THF. Recently, Lidorikis and co workers [14] reported the energy values of the π plasmon absorption of MWCNT of varying diameters. They found π plasmon absorption of MWCNT to be centered around 4.5 eV, UV range. The fact that no absorption band was observed in the MWCNT spectra is a consequence of their aggregation of the MWCNT. Taking into account that larger surface area of MWCNT leads to higher absorbance, it would be expected that a more efficient dispersion will produce an increment in absorption.

In Figure 6 we show the absorbance at 276 nm for the reference samples and those containing MWCNT 10 μg/mL. The absorbance of samples with MWCNT was corrected by subtraction of the MWCNT absorbance in THF. For the absorbance band at 276 nm the influence of the MWCNT was clearly evident as this band was higher than that for the reference samples. For those samples with MWCNT, the results in absorbance at 276 nm have two characteristic features. First, there exist a fixed DO3 concentration beyond which absorbance at 276 nm increases keeping a high linear correlation and second, the displacement in absorbance corresponds to a certain quantity greater than the statistical error.

In Figure 7 the maxima of the absorbance band at 443 nm for the different kinds of samples are plotted against DO3 concentration. Absorbance of samples with MWCNT was again corrected subtraction of MWCNT absorbance at the same wavelength. Absorbance maxima at 443 nm of the reference samples grew linearly with concentration, thus indicating it followed Beer's law. Also for samples with MWCNT, no significant changes did appear in the maxima at 443 nm though there were some differences for the higher DO3 concentrations tested. This could be attributed to the appearance of the characteristic absorption bands of carbon nanotubes in this wavelength range [15, 16]. These bands, that are present only when the nanotubes are dispersed, could eventually make absorbance stronger for the higher DO3 concentrations. As can be seen below, the concentrations for which there is a subtle difference in absorbance around 443 nm are the same concentrations for which dispersion by DO3 is effective.
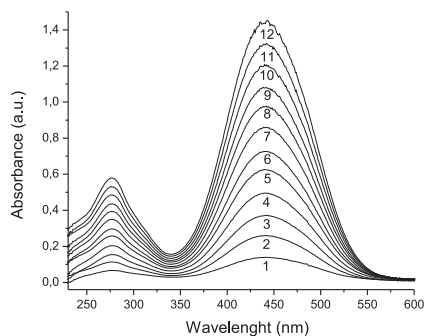
Figure 4. Absorption spectra of reference samples. Numbers against each curve refer to the DO3 concentration of the sample. From bottom to top, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12 μg/mL.
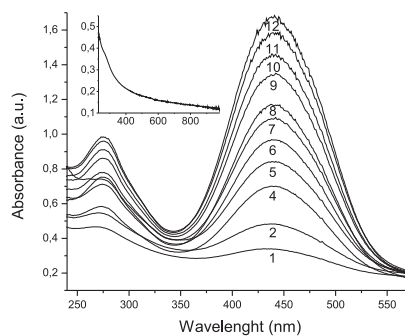
Figure 5. Absorption spectra for samples with MWCNT 10 μg/mL and different DO3 concentrations. Numbers against each curve refer to DO3 concentration in μg/mL. Inset: MWCNT absorption in THF.

The same characteristic features shown here in Figures 6 and 7 were also found for the other MWCNT concentrations studied (6 μg/mL, 0.1 mg/mL and 1 mg/mL).
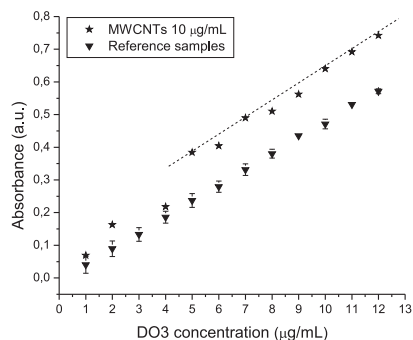

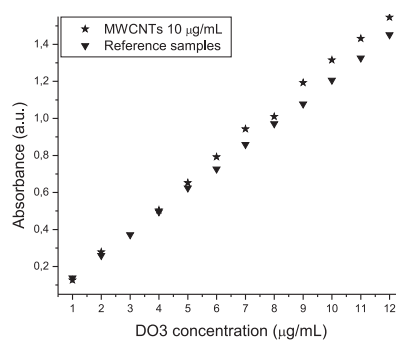**Figure 6.** Absorbance at 276 nm for the reference samples and samples with MWCNT at 10 μg/mL.

Figure 7. Absorbance at 443 nm for the reference samples and samples with MWCNT at 10 μg/mL.

When compared UV-vis results with the direct observation of the samples, there existed a good correlation. At low concentrations, DO3 interacted with MWCNT by modifying the way they aggregated suggesting the existence of interactions. However, these interactions are so weak that they can not be distinguished by analysing an UV-vis absorption spectrum. But as DO3 was added, the interactions became more important as MWCNT were better dispersed and thus the exposed area increased. As already mentioned, MWCNT have an absorption band around 4.5 eV (around 274 nm). This band is associated to MWCNT π plasmon electronic transition and it becomes stronger when MWCNT have better dispersion as the superficial area increases. Our results are conclusive and reveal that π-π stackings interaction between the benzene rings of DO3 molecules and MWCNT sidewalls do exist. These interactions lead to stable dispersions

of the nanotubes for days.

Figure 8 shows a typical induced, relaxation normalized birefringence. In the plot, there are two different curves superimposed. One belongs to an epoxy resin film with MWCNT and DO3, and the other to a film with DO3 only. In both cases the samples contained 5 wt% of DO3. Birefringence was induced in the material during the first 20 minutes while the exciting beam was on. At 20 minutes, the exciting beam was turned off and the relaxion of birefringence occured making the azo molecules return to their random arrangement. At 25 minutes the exciting beam was turned on again, thus inducing the molecules recover their anisotropy. The inset in Figure 8 shows the optical architecture used to carry out the measurements as already mentioned in the Experimental Methods section. There are two aspects that are interesting to note about these preliminary tests in epoxy resin films with WMCNT and DO3. First, that the rate of induced birefringence is reduced for the film containing MWCNT. And second, that the relaxation losses achieve 40% for the MWCNT case while the 80% is almost reached for the film with DO3 only. The fact that the rate of birefringence was slower for the film with MWCNT could be attributed to the obstruction that the molecules are non-covalent attached to the MWCNT find to make the photoisomerization. The relaxation process, started when the the exciting beam is turned off, is related to the free volume in the polymer matrix [17]. The free volume in the matrix was obviously changed when MWCNT were added. There exist several parameters to take into account when trying to improve the efficience in photoorientation, or the losses in birefringence. However, when thinking about the polymer matrix, there is a compromise between flexibility and rigidity: the flexibility, necessary to reach high levels of birefringence, and the rigidity, necessary to avoid losses in relaxation. In this sense, these preliminary results would suggest that the rigidity in the polymer film, that would be enhaced by the addition of MWCNT, though alters the rate of birefringence also avoids losses in the birefringence at room temperatures.

We undoubtedly consider further work is needed related to this new optical nanomaterials, notwithstanding we find these preliminary results very promising.
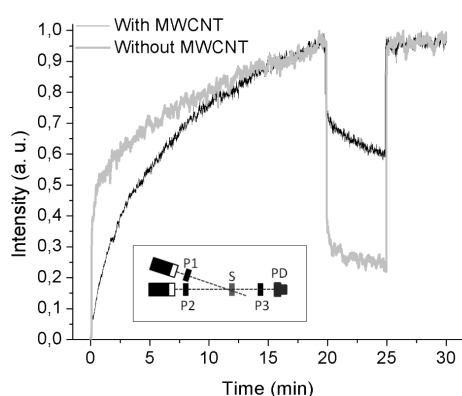

Figure 8. Induced-relaxation cycle for a film with DO3 and a film with MWCNT non-covalent functionalized with DO3. Inset: optical arrangement used. P1, P2 and P3, polarizers; S, sample and PD photodetector.

4. Conclusions

We studied the interactions between DO3 and MWCNT. Stable dispersions of MWCNT and DO3 in THF were achieved during at least 45 days for weight ratios of DO3/MWCNT higher than 2/3. The UV-vis absorption spectroscopy results indicated that interactions between MWCNT and DO3 molecules do exist. These interactions were noticeable in the absorption band around 276 nm associated to the benzene ring of the DO3 molecules. This fact suggested a successful non-covalent functionalization of the MWCNT by π-π interactions with DO3. In contrast to the changes in the absorption band of the benzene ring, the electronic transitions of the azo

group were almost unaffected. Taking into account these results altogether, we conclude that π-π stacking interactions existing between DO3 molecules and MWCNT are high enough to obtain stable dispersions of the nanotubes for several days. The possibility of having well dispersed MWCNT non-covelent functionalized with DO3 allowed us to put them into an epoxy resin matrix. Efficient birefringence could be induced in those films containing MWCNT with DO3. In films with MWCNT lower losses were achieved by relaxation at room temperature in comparison to films without MWCNT. We do not find these last preliminary results as conclusive, but promising. Future study will be done associated to these materials with the aim of developing novel optical nanoarchitectures.

Acknowledgments

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