

A latex-based concept for obtaining carbon nanotube-polymer nanocomposites

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ABSTRACT

By using a latex-based technology, it is possible to homogeneously disperse single and multi wall carbon nanotubes (NTs) within most of the polymers that are produced by emulsion polymerization, or that can be brought into the form of an emulsion. The first step of the process consists of exfoliating NTs in an aqueous surfactant solution. This step can be monitored by UV-Vis spectroscopy. Four experimental techniques have been developed in order to determine the minimum amount of surfactant, which is necessary to reach the highest degree of exfoliation of the NTs. The key step of this latex-based process is mixing a stable dispersion of NTs, covered by surfactant molecules, with a polymer latex. The use of this technology results in conductive nanocomposites with a low percolation threshold. Several procedures were explored in order to improve the properties of the materials, like tuning the characteristics of the polymer matrix.

Keywords: latex, carbon nanotube, conductive nanocomposites, wetting, dispersion.

Several methods have been developed over the last few years to achieve the incorporation of carbon nanotubes (NTs) into a polymer in order to obtain conductive nanocomposites.[1] The key factors for the making of this type of composites remain the quality of the wetting between the filler and the polymer matrix, as well as the quality of dispersion of the NTs throughout the matrix. The final target is manufacturing easily-processable “conductive plastics” that would be able in the future to supplant metals in applications for which these are still preferred. The direct mixing of the NTs with the polymer appears to be the simplest method to achieve the effective incorporation of NTs into polymer matrices. Unluckily, the final dispersion of the NTs is, most of the time, relatively inhomogeneous. The modification of either the walls of the NTs by functionalization or the use of matrix-forming polymers able to interact with the NT walls by π - π stacking are also

possible. Even if the NT-polymer wetting is improved in this way, the circulation of the electrons along the NT walls is disturbed, which might result in a lowering of the conductivity of the nanocomposites obtained. Our strategy is based on the use of a third component, most of the time a surfactant. The main step of the process consists of mixing two colloids, which are a dispersion of NTs coated by surfactant, and a polymer latex, i.e. polymer particles also coated by surfactant molecules. Subsequently the water is removed and the resulting powder is compression molded into a nanocomposite film. This process is extremely attractive as it is a simple, reproducible and efficient method that allows the homogeneous dispersion of NTs into a polymer matrix. Furthermore, this ‘latex-based’ concept is extremely versatile since it enables to disperse single or multi-wall nanotubes (SWNTs or MWNTs) into most of the polymers produced by emulsion polymerization or artificially brought into a latex form.[2-4]

The conductivity behavior of (nano)composites made of conductive fillers, such as NTs, dispersed in insulating polymers, is strongly dependent on the concentration of fillers dispersed in the polymer matrix.[5] In the region of low filler concentration, the filler is distributed homogeneously in the volume of the polymer host. No contact is possible between adjacent fillers. As a result, the conductivity of the system remains very close to the one of the insulating matrix. With increasing filler concentration, some agglomerates begin to form. From a specific filler concentration, the so-called percolation threshold, the conductivity increases drastically upon very little further addition of filler particles. This raise in conductivity corresponds to the formation of a connected network of filler particles in the polymer matrix. The shape of the filler has a tremendous influence on the value of the percolation threshold. It has been demonstrated that the use of rod-like conductive fibers helps to significantly decrease the value of the percolation threshold, compared to spherical fillers. Moreover, at similar states of filler orientation, the higher the aspect ratio of these fibers (ratio length over diameter) is, the lower the value of the percolation threshold becomes.[6,7] Since NTs have a very high aspect ratio in the range of 500-1000, combined with excellent electrical

properties, they appear to be very promising candidates for the making of conductive nanocomposites.

As-produced NTs are either held together in thick bundles by very strong van der Waals interactions in the case of single-wall nanotubes (SWNTs), or are highly entangled in the case of multi-wall nanotubes (MWNTs). NT dissolution in water is very commonly achieved with the help of surfactant. The method basically consists of mixing NTs with an aqueous surfactant solution and of sonicating the mixture: the sonication provides enough energy to “break” the NT bundles, whereas at the same time surfactant molecules adsorb on the NT walls and introduce electrostatic and/or steric repulsions, which lead to the production of stable colloidal suspensions. The first step of the latex-based process consists thus of a surfactant-assisted exfoliation of NTs in water in order to obtain a stable colloidal dispersion of NTs covered by surfactant molecules. A typical surfactant is sodium dodecyl sulfate (SDS). The achievement of this first step is crucial: in order to get conductive films with a filler loading as low as possible, it is imperative to achieve a good dispersion of the NTs into the polymer matrix; consequently it is highly important to control and monitor the NT exfoliation during the first step of the process, even if it does not guarantee a good exfoliation of the NTs in the final composite.

This sonication-driven exfoliation of the NTs can be monitored by UV-Vis spectroscopy.[8-10] All kinds of individual NTs are active in the UV-Vis region. Nevertheless, NTs bundles are hardly active the wavelength region between 200 and 1200nm, whereas dispersed NTs exhibit characteristic bands corresponding to adsorption due to van Hove singularities.[11,12] As a result, the peeling of the SWNT bundles, or the debundling of the MWNTs during sonication, results in an increase of the concentration of individual NTs, and finally in an increase of the UV-Vis signal recorded. In other words, a leveling off of the UV-Vis absorption, and/or the total ultrasonic energy supplied to the system, recorded as a function of time, indicates that the maximum degree of exfoliation has been achieved and that accordingly further energy input can be stopped in order to prevent unnecessary damaging of the NTs.[13] Scanning Electron Microscopy, as well as cryogenic Transmission Electron Microscopy pictures, confirm that the leveling off of the absorbance corresponds to well-exfoliated CNTs.

Four different experimental techniques, based on UV-Vis spectroscopy, surface tension measurements, thermogravimetry and a modified version of the Maron’s titration, were developed in order to determine the minimum amount of surfactant, which is necessary to reach the highest degree of exfoliation of the nanotubes.[14] All these experimental techniques appeared to be reproducible and equivalent to each other. The results obtained enabled us to estimate a lower boundary for the specific surface area

of exfoliated HiPCO SWNTs, as well as an estimation of the packing of the adsorbed SDS molecules at the surface of the NT walls.⁷ It is worth noticing that these procedures are in principle applicable to a large range of surfactant-particle systems.

After a mild centrifugation, the NT-SDS dispersion obtained is mixed with a polymer latex. The mixture obtained is finally freeze-dried and compression-molded.

In the nanocomposite films obtained, the NTs are homogeneously dispersed in the polymer, and form a network of preponderantly individualized NTs (see Figure 1).[15]

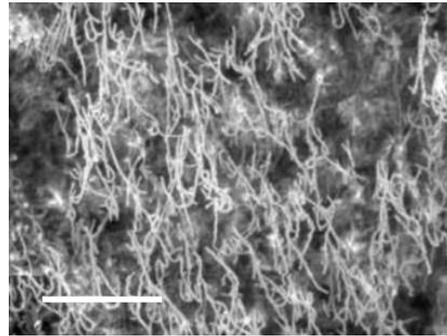


Figure 1: SEM image visualizing the SWNT network in the PS matrix at the surface of the nanocomposite. The scale bar corresponds to a length of 1 μ m.

This leads to electrically conductive nanocomposites with a percolation threshold of about 0.3wt% for HiPCO SWNTs in a high molecular weight polystyrene (PS), produced by free radical emulsion polymerization, as shown in Figure 2.

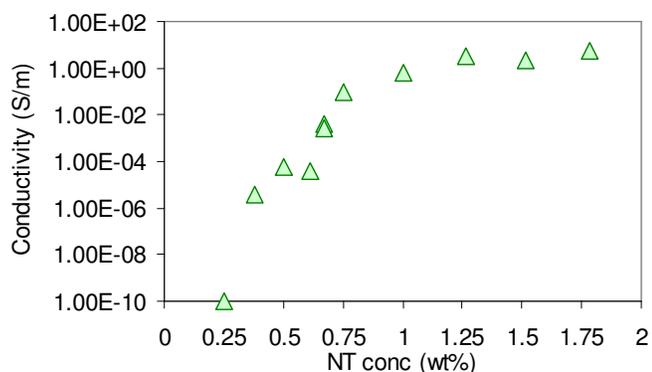


Figure 2 Conductivity of a HiPCO SWNT-PS nanocomposite plotted in function of the concentration of NTs in wt%.

A few procedures were explored in order to improve the properties of the materials, in other words: to lower the percolation threshold, to increase the conductivity, and/or to improve the filler-matrix interface. We demonstrated that tuning the characteristics of the polymer matrix (molecular weight and particle size distribution) is a promising way to achieve this objective. For instance, we have shown that, in a polystyrene matrix, the presence of polymer chains having a molar mass of the same order of magnitude as SDS favors the NT-matrix wetting, leading to higher glass transition values.[16,17] We believe that, during the processing of the materials, a fraction of the polymeric chains of the PS matrix that have a molecular weight of the same order of magnitude as SDS can compete with the surfactant for the adsorption on the NT walls: a fraction of these chains certainly adsorb on the surface of the NTs, leading to a partial desorption of the SDS molecules from the NT surface. Besides, the presence of low molecular weight PS in the polymer matrix also results in a considerable enhancement of the conductivity of the nanocomposite.

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