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Reviews

Toolbox for Dispersing Carbon Nanotubes into Polymers To Get Conductive Nanocomposites

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The three main strategies for dispersing carbon nanotubes (NTs) into a polymer matrix to get conductive nanocomposites are described, and illustrated with some appealing examples. The direct mixing of the NTs and the polymer is the ‘simplest’ concept to achieve this goal. Other approaches concern the modification of either the polymer matrix or the NT walls in order to improve the wetting of the filler with the matrix material, and thus promote the incorporation of the NTs into the polymer matrix. Most promising results seem to be obtained upon the addition of a third component. The basic concept is the generation of a stable colloidal system containing both a suspension of NTs stabilized by surfactant molecules in water, and polymer latex. After removal of the water, the resulting powder can be processed into the desired shape. This versatile and environmentally benign concept offers low percolation thresholds and relatively high conductivity levels.

1. Introduction

Carbon nanotubes (NTs) are the third allotropic carbon form in addition to diamond and graphite and were synthesized for the first time by Iijima in the early 1990s.[1] Single-wall nanotubes (SWNTs) consist of single layers of graphite lattice rolled into perfect cylinders with a diameter usually in the range of 0.7−2 nm, whereas multiwall nanotubes (MWNTs) consist of sets of concentric cylindrical shells, each of which resembles a SWNT, although generally with larger diameters. Relatively recently, selective synthesis of double-wall nanotubes has even been carried out, for example, by Ren and Cheng.[2] The unique structure provides the NTs with exceptional thermal stability and remarkable mechanical, electronic, and structural properties.[3] Therefore, NTs have potential for a vast range of applications, including quantum wires,[4] tips for scanning probe and tunneling microscopy,[5] hydrogen storage application for power generation and vehicles,[6] and molecular diodes.[7] NTs are also expected to provide a circuit fabrication alternative with devices scaled down to a few tens of nanometers in size and smaller.[8]

In general, NTs can be seen as one-dimensional conductors.[9,10] The electronic properties of perfect MWNTs are rather similar to those of perfect SWNTs. However, due to weak coupling between the concentric cylinders of the MWNTs, only the outer shell contributes to the electron transport and thus to the final electronic properties.

The characteristics of NTs, which determine their properties, are strongly influenced by the production method, as well as by the experimental conditions in which the synthesis has been carried out. By choosing appropriate experimental parameters, it is possible to control some properties of the final product, such as the type of NTs synthesized (MWNTs vs SWNTs), the quality of the NTs, the amount and type of impurities, and some structural NT features[11] such as the degree of crystallinity and the tube and wall structure. Three main routes of NT production have already been developed: the arc-discharge (AD) method,[12,13] which implies the arc evaporation of pure or metal-doped carbon electrodes, laser vaporization of metal-doped carbon targets,[14,15] and chemical vapor deposition (CVD),[16,17] which consists of the decomposition of carbon-containing molecules such as ethane, methane, and carbon monoxide on supported nanoparticles of metal that play the role of catalyst for NT growth. Among all reported CVD methods, the so-called high-pressure carbon oxide (HiPCO) process[18] (or modified versions of it) is particularly successful and produces high-quality SWNTs of small diameters and narrow diameter distribution with rather high yields.

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Recently, much attention has been given to the use of NTs in composite materials to harness their exceptional mechanical[19] and electronic[20,21] properties. Even if the market is still in the early stage of product and process development, the projection for NT-filled polymer composite is 160 million Ib by 2009.[22] A large part of these NT-based polymer composites exploit NTs as a conductive dispersed phase in an insulating matrix for applications ranging from electronics to automotive and aerospace sectors, such as electrostatic dissipation,[23] electromagnetic interference (EMI) shielding,[24] multilayer printed circuits,[25] and transparent conductive coatings. (Since the filler size is below the wavelength of visible light, the optimized reinforced polymer may remain transparent.) The aims are to develop easily processed materials for future applications in which metals and/or semiconductors are currently preferred.

Basically, for obtaining conductive NT−polymer composites, the highly electrical conductive NT filler is dispersed into the polymer matrix. Hence, a three-dimensional conductive network of the NTs in the polymer matrix is obtained. The so-called percolation theory[26] is generally used to describe the insulator-to-conductor transition in composites made of conductive filler in an insulating matrix. The electrical conductivity of a composite is strongly dependent on the filler loading. At low filler concentrations, the conductivity remains very close to the conductivity of the pure, electrically insulating polymer matrix since the fillers are dispersed individually or in small clusters in the matrix. When a critical filler volume fraction, the percolation threshold, is reached, the conductivity drastically increases by many orders of magnitude with very little increase in the filler loading. It coincides with the formation of a conductive, three-dimensional network of the filler in the continuous polymer phase. Finally, the conductivity levels off at a certain value, the maximum conductivity of the composite. The composite conductivity σ follows a percolation scaling law of the form of $\sigma \sim (\rho - \rho_c)^t$, where ρ is the volume fraction of filler, ρ_c the percolation threshold, i.e., the critical average concentration to form a conductive network, and t the conductivity exponent, which generally reflects the dimensionality of the system. The values of the latter are typically around 1.3 and 2.0 for two- and three-dimensional filler networks, respectively. Depending on the polymer matrix, the processing technology, and the NT type used, experimental percolation thresholds ranging from 0.025 wt % to more than 10 wt % have been reported for thin films.

It has been shown, both experimentally and theoretically, that the percolation threshold strongly depends on the aspect ratio (length-to-diameter ratio) of the filler particles.[27,28] At similar states of filler orientation, the higher the aspect ratio, the lower the filler concentration necessary to reach the percolation threshold, and to get conductive films. Recently, Foygel and co-workers[29] gave a functional relationship between the aspect ratio and percolation threshold. Based on Monte Carlo simulation, they predicted that an aspect ratio of 10^3 (typical value for NTs) yields a percolation threshold of ca. 10^{-3}. It is found that their results are in excellent agreements with a wealth of SWNT-based composites systems. Munson-McGee[28] used statistical arguments to estimate the critical concentration in a percolating network of an anisotropic, three-dimensional cylinder distribution, which can be considered a schematic representation of an ideal percolating network of NTs into a polymer matrix. The results of his calculations showed that for randomly dispersed cylinders the percolation threshold is strongly influenced by the value of the aspect ratio and can vary from about 12 vol % for an aspect ratio value of 10 to much less than 1 when the aspect ratio is close to 1000. Therefore, fibril-shaped filler particles have been an attractive choice in recent years. Fillers such as carbon black or synthetic graphite, which have aspect ratios varying from 2 to less than 500 on average, require filler concentrations typically ranging from 18 to 2 wt %, respectively, to get conductive materials, depending on the polymer and the level of conductivity needed.[30] Such filler concentrations make the polymer brittle. On the other hand, while using NTs as filler, one gets the same conductivity for 1−3 wt % loading due to their high conductivity, combined with a very high aspect ratio (about 1000). Low filler loadings generally do not significantly affect the other physical properties of the host polymer and usually only result in a minimal increase in melt viscosity, which still allows easy processing. Furthermore, from a commercial point of view, it is highly relevant to take this low required loading into account since NTs are nowadays still very expensive (the price, depending on purity and quality, still ranges from 20 to 1000 Euros/g).[31]

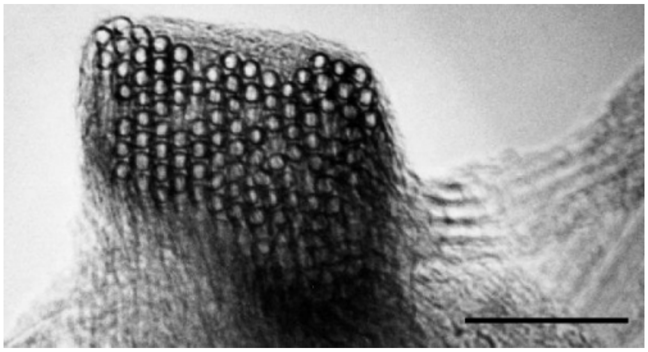

Figure 1. Transmission electron microscopy (TEM) image of a SWNT rope consisting of about 100 SWNTs as it bends through the image plane of the microscope. The diameter of a single tube is typically 1−2 nm. Scale bar: 10 nm. (From ref 15. Reprinted with permission of the American Association for the Advancement of Science.)

1.1. Incorporation of NTs into a Polymer Matrix: A Challenge. The bottleneck for using SWNTs as fillers for polymer-based nanocomposites is that as-produced SWNTs are held together in bundles of 50 to a few hundred individual SWNTs by very strong van der Waals interactions.[15] Figure 1 shows a transmission electron microscopy image of such a SWNT bundle. Baughman et al. proved that bundling results in diminished mechanical and electrical properties as compared to theoretical predictions related to individual SWNTs.[32] The challenge is thus to incorporate exfoliated individual SWNTs, or at least relatively thin SWNT bundles, inside a polymer matrix. In other words, percolation of SWNTs not only is a geometrical problem, dealing with the length and the orientation of the SWNTs but also relates to local improvements in SWNT contacts with the matrix material due to segregation. The key words are the dispersion of the SWNTs into the polymer matrix as well as the quality of the interface filler-matrix.

1.2. Ultrasound as a Tool for SWNT Exfoliation. Since low SWNT loadings and large interface areas are required to optimize the performance of SWNT−polymer nanocomposites, efforts of researchers focus on “breaking” the SWNT bundles, and thus on the incorporation of individual SWNTs, or at least SWNT bundles as thin as possible, in the polymer matrix. Stirring in a solvent or a polymer melt is usually not sufficient to achieve this goal; therefore, ultrasound (bath or horn/tip ultrasonication) is frequently applied.

We briefly summarize the events occurring during sonication of a liquid medium containing bundles of SWNTs.[33] Like any sound wave, ultrasound propagates via a series of compression and rarefaction waves induced in the molecules of the medium through which it passes. This production of shock waves promotes the “peeling off” of individual SWNTs located at the outer part of the SWNT bundles, and thus results in the exfoliation of individualized SWNTs. If the sonication treatment is too aggressive and/or too long, it can lead to localized damage of the SWNT walls, if not to SWNT shortening.[34,35] Localized damage of the NTs deteriorates both electrical and mechanical properties of the composite.

1.3. NT Purification. Another relevant and important issue in integration of NTs in the polymer matrix is the degree of purity of the NTs. It is found that different NT synthesis methods yield NTs with different characteristics, as well as different types and amounts of impurities, (e.g., amorphous carbon and catalyst particles). As a result, it is important to be able to characterize the nature and quantity of the impurities since they are incorporated with the NTs into the polymer matrix, persist throughout the processing, and thus affect the performances of the final composite. Furthermore, it is also essential to obtain the exact amount of impurity-free NTs to enable one to compare experimental results of different studies and theory.

Itkis and co-workers[36] have recently compared different characterization methods, i.e., scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetry (TGA), Raman, and near-infrared (NIR) spectroscopy, to get optimum information on the samples studied. They found that the combination of TGA and Raman spectroscopy is satisfactory. Moreover, Herrera and Resasco[37] reported successful use of in situ temperature-programmed oxidation (TPO) and Raman spectroscopy to reach the same goal.

Several strategies have already been developed over the past decade to purify NTs. Most purification methods include acid treatment such as hydrochloric acid (HCl)[38,39] or nitric acid (HNO_3),[40] or a mixture of HNO_3 and sulfuric (H_2SO_4) acid.[41] First, it is important to note that the properties of NTs are changed upon purification.[11] It has been proven by Monthioux et al.[42] that purification methods based on the use of HNO_3 and H_2SO_4 acid lead to significant oxidation of the NT walls, which results in damage of the structure of the NT walls and even in cutting of the NTs, or reduction of their aspect ratio. In a recent paper Johnston et al. described a purification process, rendering HiPCO NTs with enhanced conductivity with respect to nonpurified tubes.[43]

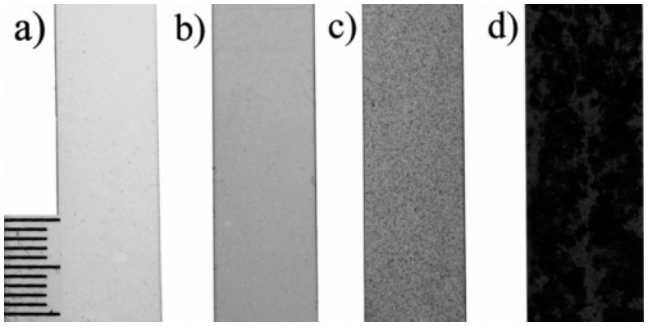

Figure 2. Optical micrographs of NT-epoxy composites: (a) pure epoxy, (b) 0.001 wt %, (c) 0.0025 wt %, and (d) 0.005 wt %. Scale bar (left) is 1 cm and the sample thickness is about 2.2 mm. The formation of small local NT aggregates at a loading fraction of 0.0025 wt % can be seen, which then leads to the macroscopic network of NTs at higher filler contents. (From ref 44. Reprinted with permission of Elsevier.)

2. Methods for Dispersion Individual SWNTs in a Polymer Matrix

Several methods have already been developed in past years to efficiently disperse individual SWNTs in a polymer matrix. The easiest method consists of *directly mixing* the polymer and the filler. One can also either *modify the polymer* to enhance interaction with the π-system of the SWNT wall or *modify the walls of the SWNTs* by functionalization, and thus improve the wetting of the filler, as well as the dispersion in the medium. It is also possible to *use a third component*, such as surfactant molecules, to assist the exfoliation of the NT-bundles and the subsequent incorporation of the NTs into the polymer matrix. All main methods known thus far are briefly discussed below and are illustrated with representative examples. The reader is offered a guided tour through the toolbox for the dispersion of carbon SWNTs into highly viscous polymer matrixes.

2.1. Direct Mixing. Windle and co-workers developed two methods based on the direct mixing of NTs and polymers. The easiest direct mixing procedure[44] consists of dispersing aligned untreated MWNTs, produced by CVD, into an epoxy resin with relatively low viscosity by shear-intensive mechanical stirring, using a dissolver disk. It has to be mentioned that no ultrasonic treatment was required. The formation of the network was not induced by a truly statistical percolation process based on the random distribution of individual high-aspect ratio fillers, but was facilitated by the applied pre-alignment procedure, which explains the low percolation threshold of 0.0025 wt % of NTs. Conductivity values in the range of 1 S/m were recorded around 0.01 wt % of NT loading. Optical micrographs of these composites are shown in Figure 2.

In another direct mixing procedure[45] a solvent is added to lower the viscosity of an epoxy resin and thus favor the dispersion of the filler into the matrix of the composite. In the first step, catalytically grown MWNTs were exfoliated in ethanol under sonication. The resulting suspension was mixed with an epoxy resin under stirring. The low viscosity of the resin was maintained during the mixing by a choice of proper experimental conditions. Once the dispersion of

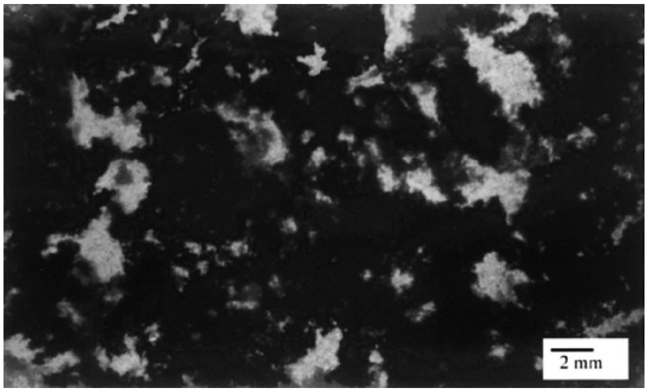

Figure 3. Transmission light photograph of an epoxy resin containing 0.0225 wt % catalytically grown multiwall carbon nanotubes, highlighting the formation of aggregates. The sample thickness was 0.5 cm. (From ref 45. Reprinted with permission of Elsevier.)

the filler was achieved, the solvent was evaporated. Finally, some hardener was added to complete the entrapment of the NTs in the polymer. The distribution of the NTs into the polymer matrix was not uniform because it was impossible to break up all the entanglements of the NT material (Figure 3). An increase of the overall conductivity was achieved, comparable to conductivities achieved for a composite based on the same polymer matrix but filled with carbon black. The percolation threshold was found to be below 0.04 wt % and the conductivity of the nanocomposite was found to be about 10^{-1} S/m.

Bryning et al.[46] uses a similar method based on the use and evaporation of a solvent to incorporate purified (less than 5 wt % of impurities) produced by both laser-oven and HiPCO processes, into an epoxy matrix, to get very low percolation thresholds. As in the first example given in this section,[44] the researchers lower the percolation threshold to an extremely low value by favoring the formation of NT aggregates. A dilute SWNT dispersion of SWNTs in *N*,*N*-dimethylformamide (DMF) was added to an epoxy matrix under sonication, and the DMF was allowed to evaporate. An aliphatic amine cross-linker was finally added under stirring. By controlling the sonication time before curing, the formation of NT aggregates could be favored or inhibited: NT re-aggregation occurred indeed if the sonication was turned off before curing, whereas continuous sonication prior to curing guaranteed a good final dispersion of the NTs into the polymer matrix. The threshold weight percentages were extremely low in the case of the samples for which NT aggregation had been favored: 0.61 wt % for laser-oven NTs and 0.99 wt % for HiPCO NTs, with respective conductivity of about 10^{-2} S/m at 1.2 10^{-1} wt % of laser-oven NTs.

A variant, the so-called "coagulation method",[47] is based on the difference in swellability of polymers in a good and in a poor solvent. In a sonication bath, purified SWNTs produced by a HiPCO process were first mixed with the polymer (poly(methyl methacrylate); PMMA) dissolved in a good solvent (dimethylformamide; DMF). The nanotubes were purified by HCl treatment,[32] which led to the obtaining of a NT sample containing less than 8 wt % of metal residue. Then, still under sonication, water was added to the mixture until the solvent lost its ability to swell the polymer chains. As a result, the polymer coagulated and entrapped the NTs, preventing them from bundling again. The dispersion was comparable to that obtained in the solvent. It was observed that the higher the NT concentration, the more randomly organized the NTs were, certainly due to steric constraints. With change in some experimental parameters, this method should be applicable to a wide range of polymers. The maximum conductivity reached for a SWNT−PMMA nanocomposite was about 10^{-2} S/m and remained approximately at the same level for higher NT loadings. The percolation threshold was reached at a NT loading of 1 wt % for nonaligned NTs.

2.2. Modification of NTs or of the Polymer. The second approach implies either a modification of the NTs by functionalization of their walls or a modification of the polymer matrix in order to improve the interactions at the interface polymer−filler, and accordingly promote the dispersion of the NTs.

2.2.1. Modification of the NT Walls. Many researchers have tried to solubilize NTs through various functionalization routes, e.g., fluorination,[48] or grafting of CN groups on the surface of the NT wall.[49] These cyanide-modified NTs can be used as precursors for, e.g., the preparation of nylon SWNT composites.

A remarkable route to nanoscopically disperse MWNTs in a poly(methyl methacrylate) (PMMA) matrix by directly grafting PMMA chains on the surface of the NT walls was reported,[50,51] which enhances the compatibility between the filler and the matrix. MWNTs synthesized by a thermal CVD method were first purified and oxidized by two sequential acid treatments (nitric acid and then hydrochloric acid), which introduced hydroxylic functional groups on the NT wall surface, but unfortunately shortened the NTs (Figure 4a). The oxidized NTs were then mixed in liquid methyl methacrylate (MMA) monomer under sonication. Finally, an in situ radical polymerization with α,α' azobis(isobutyronitrile) (AIBN) as initiator was performed under sonication. The acid treatment of the NT actually favors the availability of π-bonds on the NT surface, triggering thus the initiation of radical polymerization on the NT walls and the grafting of polymer chains onto the tubes. The composites prepared by Sung and co-workers[50] contain 1−5 wt % MWNTs with conductivity between 10^{-4} and 10^{-2} S/m, respectively. A transparent PMMA−NT film with a uniform MWNTs distribution is shown in Figure 4b.

Shaffer and Koziol[52] followed the same route for grafting polystyrene (PS) onto the walls of MWNTs synthesized by a CVD technique, and purified by a concentrated sulfuric−nitric acid-based treatment. MWNTs coated by a thin polymer layer of typically 5−10 nm were obtained (Figure 5). Depending on the initiator used (benzoyl peroxide or potassium persulfate), from 0.5 to 18 wt % of the total polymer synthesized could be grafted on the surface of more than 50% of the MWNTs present in the reactor during the polymerization. No results concerning the conductivity behavior of the material obtained were given.

NT dispersion into a polymer matrix via functionalization, to improve the electrical properties of the polymer, has not proven to be extremely successful yet. Most publications in

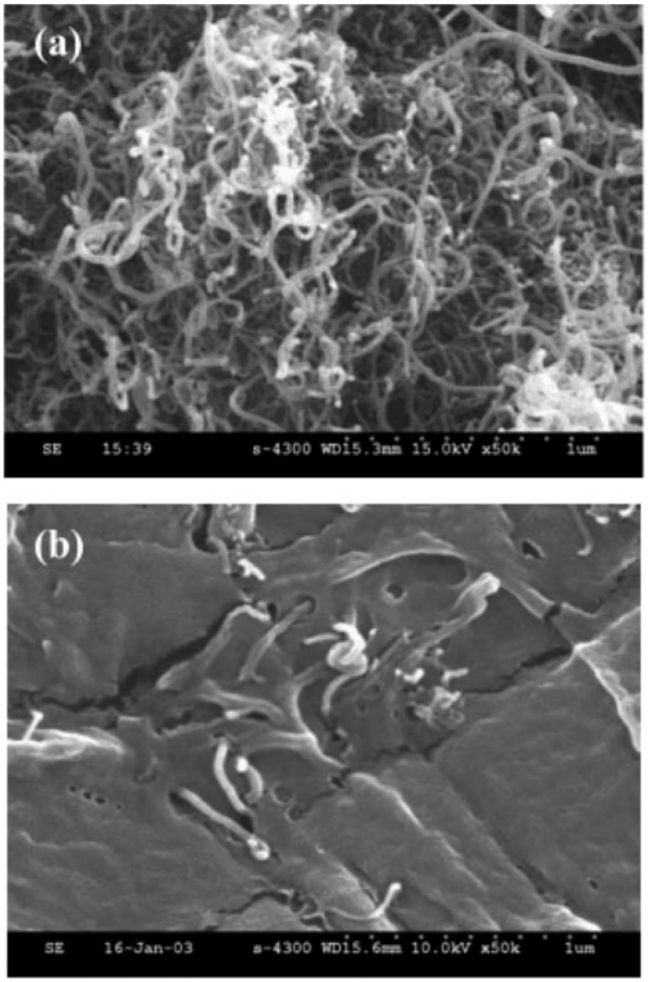

Figure 4. SEM images of (a) acid-treated MWNT and (b) the fractured surface of MWNT (0.1 wt %)−PMMA composite. (From ref 51. Reprinted with permission of Wiley & Sons, Ltd.)

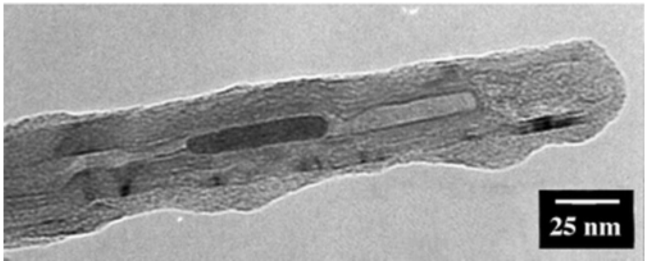

Figure 5. TEM of a single-grafted MWNT coated by a thin layer of polystyrene. (From ref 52. Reprinted with permission of the Royal Society of Chemistry.)

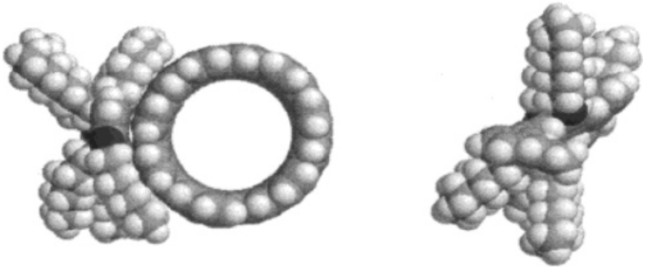

Figure 6. Modeling of PmPV−SWNT interaction. The polymer conformation can be seen to change dramatically due to the interaction with the nanotube lattice. The PmPV backbone has an imposed curvature, and the side groups are bound on the cylindrical substrate provided by the SWNT. (From ref 54. Reprinted with permission of the American Chemical Society.)

which the grafting technique is being used focus on the synthesis of the composites without studying the mechanical or electrical properties of the materials.

A crucial parameter for the production of this type of conductive nanocomposites is the control of the degree of grafting on the NT walls: it should not be too high in order not to significantly disturb the π electron system of the NT walls, and thus affect the electrical properties, but it should be sufficient to provide a good compatibility between filler and polymer matrix, i.e., a good wetting at the interface between the polymer and the NTs. Further investigations are necessary, in particular to determine the exact location of the grafted groups and to obtain an accurate estimation of the degree of functionalization. Most reports on the chemical modification of SWNT walls[53] led to a loss of structure of the NTs due to significant functionalization, and thus subsequent conversion of the sp^2-hybridized carbons forming the conductive NT walls, to sp^3. Oxidation of the NTs appears promising since the modifications are presumed to be localized and mostly restricted to the caps at the NT ends. As a result, the electronic capabilities of the NTs should remain the same and their electrical properties unchanged.

2.2.2. Modification of the Polymer. Another approach consists of synthesizing a polymer having a structure tailored for interaction with the NTs. It is realized by using conjugated polymers, which can associate with the NTs by means of $\pi-\pi$ electronic interactions with the NT lattice. This interactive binding leads to substantial modification of the optical and vibrational spectroscopic properties of the conjugated polymers. The results of a microscopic and spectroscopic study of such composites (study carried out on both SWNT− and MWNT−PmPV (poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene)) has been reported by McCarthy and co-workers.[54] They suggested polymer wrapping onto the NT surface due to considerable polymer−filler interactions, which results in an excellent wetting of the NTs by the polymer. Due to interactions with the NT walls, the PmPV conformation is dramatically modified and curved, leading to a structured wrapping of the polymer around the NT (Figure 6). Contrary to McCarthy, Chen et al.[55] used short, rigid polymers, poly(phenylene ethynylene) (PPE) to disperse NTs. Here, the major interaction between the backbone of the conjugated polymer and the NTs surface is of the nonwrapping type.

Systems consisting of NTs and conjugated polymers may form the basis for nanocomposite materials with device applications, as well as for a possibility of modifying and enhancing the optoelectronic properties of conjugated polymers. For example, composites made with aligned NTs in a polypyrrole polymer matrix have shown exceptional charge storage capacities, which may in the future lead to potential applications in supercapacitors and secondary batteries.[56]

It has also been shown that the conductivity of several nanocomposite systems such as those based on poly(*m*-phenylenevinylene-*co*-2,5-dioctyloxy-*p*-phenylenevinylene)-(PmPV)−NT[57] and polypyrrole (PPy)−NT[58] is dominated by percolation. For nanocomposites made of NT-conjugated polymers, a mixed conduction process exists, since both the filler and the polymer matrix are conductive. Please note that the conductivity of most conjugated polymers is strongly

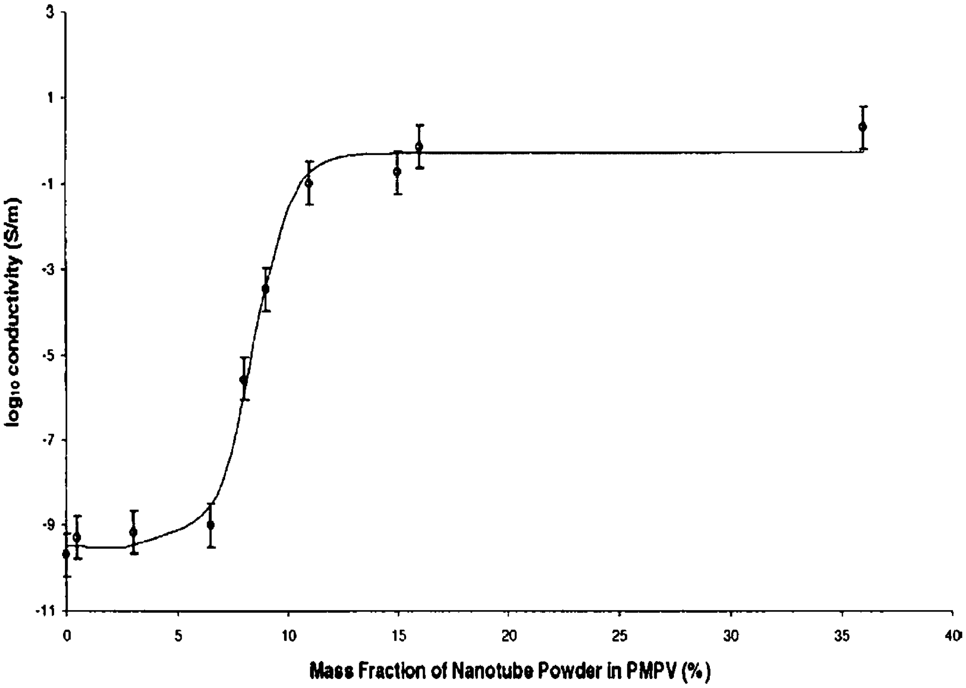

Figure 7. Semilogarithmic plot of the conductivity of the SWNT−PmPV composite for various mass fractions of NT powder. The sharp increase of the conductivity is partly due to the intrinsic conductivity of the polymer matrix and not only to the formation of a connective NT network in the nanocomposite polymer matrix. (From ref 57. Reprinted with permission of the American Physical Society.)

dependent on molecular weight distribution, defect concentration, conformation, and degree of purity. Consequently, it is not possible to describe the conductivity behavior of such systems by a model based on the percolation theory (mentioned earlier in this review). Below the true percolation threshold, which corresponds to the formation of a connected NT network throughout the polymer matrix, an increase of conductivity can be observed, due to the introduction of charge carriers into the polymer, even if there are no completely connected conductive paths through the system. For the calculation of the true percolation threshold, it is thus important to be able to determine if the conductivity increase is due to a combination of increased carrier donation by the NTs and the increase in partial conductive paths (still below the percolation threshold), or if it is due to the increase of the number of complete conductive paths (above the true percolation threshold, i.e., after formation of the first complete NT conductive path).

Coleman et al.[57] prepared SWNT−PmPV composites by mixing SWNT powder, prepared in a Kratschmer reactor[59] with PmPV in toluene. They calculated that the true percolation threshold of the resulting composite was located between 8 and 9 wt % of NTs (Figure 7). The incorporation of NTs increased the conductivity by 10 orders of magnitude, from 2 10^{-10} S/m for the pure PmPV polymer to 3 S/m at 36 wt % of NTs.

Long et al.[58] focused on the study of MWNT−PPy nanocomposites. First, they exfoliated as-produced MWNTs prepared by CVD in water, with the help of surfactant (cetyltrimethylammonium bromide CTAB), under sonication. The resulting mixture was then mixed with pyrrole monomer in the presence of an initiator, ammonium persulfate. The in situ polymerization was finally carried out under sonication and resulted in NT−PPy nanocables (Figure 8). Conductivity measurements carried out on the resulting composites revealed an increased conductivity, ranging from 7.3 × 10^{-1} S/m for the pure PPy up to 23 S/m with a NT loading of 23.1 wt %. The estimated true percolation threshold was between 15 and 20 wt % of NT.

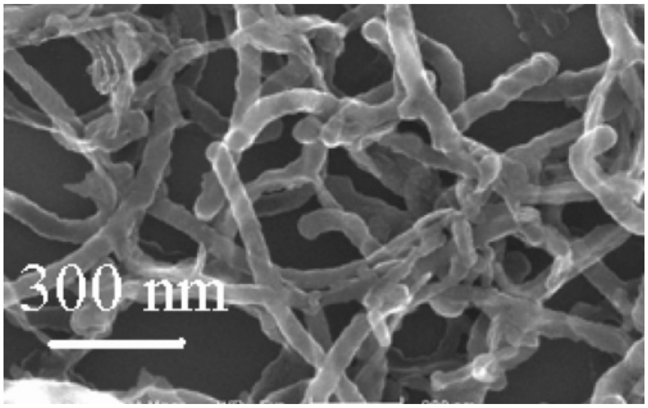

Figure 8. SEM MWNTs coated by PPy; 9.1 wt % NTs. (From ref 58. Reprinted with permission of IOP Publishing Ltd.)

NT−polyaniline (PANI),[60−62] as well as NT−polyimide composites,[63] prepared by similar in situ polymerization techniques, have also been reported and show similar properties.

2.3. Use of a Third Component. The third route for polymer−NT composites preparation with well-dispersed NTs is based on the use of a third component, assisting the incorporation of exfoliated NTs into the polymer matrix, preferably without altering the intrinsic properties of the NTs. In most cases, the third component is a surfactant, but it can also be a conductive polymer, as shown below.

2.3.1. Use of a Conductive Polymer. Ramasubramaniam et al.[64] incorporated NTs into a polymer matrix by using a conjugated polymer under sonication. As-produced SWNTs

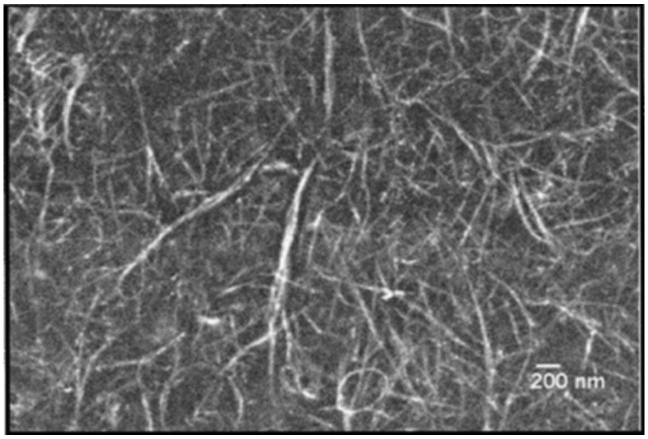

Figure 9. SEM image of the surface of a PS/SWNT composite containing 5 wt % of SWNTs. (From ref 64. Reprinted with permission of the American Institute of Physics.)

(HiPCO) were first solubilized in chloroform together with the conjugated polymer poly(phenylene−ethynylene) (PPE). The resulting PPE-coated SWNTs were then mixed with a host polymer (polycarbonate (PC) or polystyrene (PS)) solution in chloroform. The excess solvent was finally removed by simple heating. Except the first "coating" step, the preparation of the composite is based on the same principles as the solution evaporation method reported by Sandler et al.[45] The PPE-coated SWNTs were well-dispersed and randomly distributed in the form of a three-dimensional network in the polymer host (Figure 9). The percolation threshold measured was reached at 0.045 wt % SWNT loading for the SWNT−PS composite, with a maximum conductivity of 6.89 S/m at 7 wt % of NT loading, i.e., 14 orders of magnitude higher than the conductivity of pure PS. Regarding the SWNT−PC composite, the conductivity increased from 10^{-13} S/m, which is typically the conductivity of pure PC, to 4.81×10^2 S/m at 7 wt % of NTs, with a very low percolation threshold reached at 0.11 wt % of NTs. Already with low NT loadings, these composites show conductivity levels which could be high enough for application as electrostatic dissipation devices, electrostatic painting, and EMI shielding. It should be possible to extend this concept to various polymer matrixes.

2.3.2. Use of Surfactant. In most studies a third component, namely, surfactant, is used to enhance the incorporation of NTs into a polymer matrix. Bundles of surfactant-dispersed NTs are sonicated in an aqueous medium (see section 1.2). During sonication, the provided mechanical energy overcomes the van der Waals interactions in the NT bundles and leads to NT exfoliation, whereas at the same time surfactant molecules adsorb onto the surface of the NTs' walls.[65] The colloidal stability of the dispersion of NTs with adsorbed surfactant molecules on their surface is guaranteed by electrostatic[65] and/ or steric[66−69] repulsion (Figure 10).

The organization of surfactant molecules on the NT surface has already been extensively investigated. Three main arrangements have been considered: structureless random adsorption on the NT walls without any preferential arrangement of the head and tail,[70] hemi-micellar adsorption on the NT surface,[66,71] and encapsulation of the NTs in a cylindrical surfactant micelle.[72] The majority of experimental (AFM[73,74] and adsorption measurements[75]) and theoretical[76] studies dealing with the organization of surfactant molecules on NT walls[66,71] supports the hemi-micelle configuration.

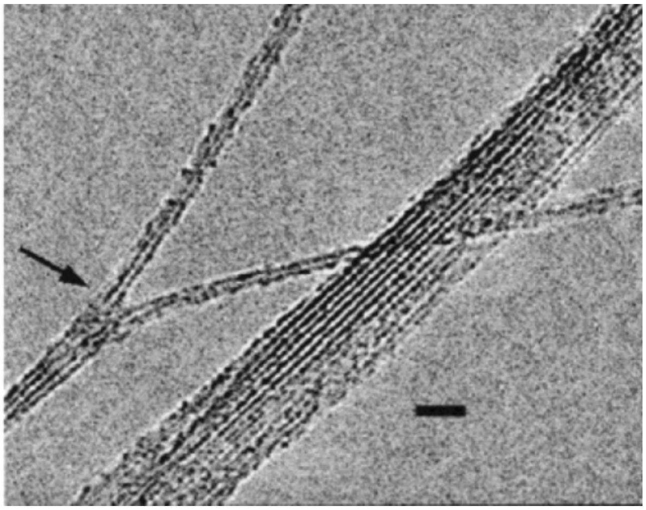

Figure 10. High-resolution TEM image of a dried solution of 0.05 wt % SWNT and 1 wt % Gum Arabic, which has been previously sonicated. The arrow shows the location of bifurcation, where the NTs have started to exfoliate. (From ref 67. Reprinted with permission of the American Chemical Society.) Scale bar: 10 nm.

The incorporation of the filler into the polymer matrix is achieved by obtaining a colloidal system, i.e., a mixture of NTs and polymer particles, both stabilized by surfactant molecules. When this colloidal solution is then dried and processed to get a composite in the solid state, the dispersion and exfoliation of the NTs are preserved in most cases in the polymer matrix.

The colloidal system could be stabilized by in situ polymerization (see section 2.3.3.). Alternatively, the colloidal system can be prepared by direct mixing of the NTs and the polymer host particles,[77−79] after the polymerization has already been carried out.

2.3.3. Use of Surfactant: In Situ Polymerization. Barraza and co-workers[80] prepared SWNT−PS and SWNT−styrene−isoprene copolymer nanocomposites by using an original method based on mini-emulsion technology. SWNTs, synthesized by the AD process, and purified with HNO_3 (86% of carbon content remaining by acidic treatment), were first exfoliated under sonication with the help of the cationic surfactant cetyltrimethylammonium bromide (CTAB). The initiator (AIBN), previously dissolved in ethanol, was then added to the resulting SWNT suspension. The above-mentioned mixture was added under stirring to a mixture of solvent (hexadecane)/catalyst (PS−$AlCl_3$ acid complex/hexadecane)/monomer (styrene or mixture styrene−isopropene). After an additional sonication step to obtain an emulsion, the polymerization was finally carried out. Barraza et al. have shown that a layer of polymer adsorbed on the surface of the NT bundles contributes to a better dispersion of the SWNTs in the polymer matrix. On the other hand, this layer minimizes the maximum conductivity value reached. Nevertheless, the conductivity increase induced by the incorporation of SWNTs into the polymer matrix remains significant (from 10^{-14} S/m for the unmodified PS to 10^{-4} S/m for the SWNT−PS composite with 8.5 wt % of NTs.

Figure 11. Aqueous SDS solution of HiPCO SWNTs after 130 min of sonication at 20 W, corresponding to a total energy input of ca. 150000 J. Mostly individual NTs are observed. (From ref 83. Reprinted with permission of the American Chemical Society.)

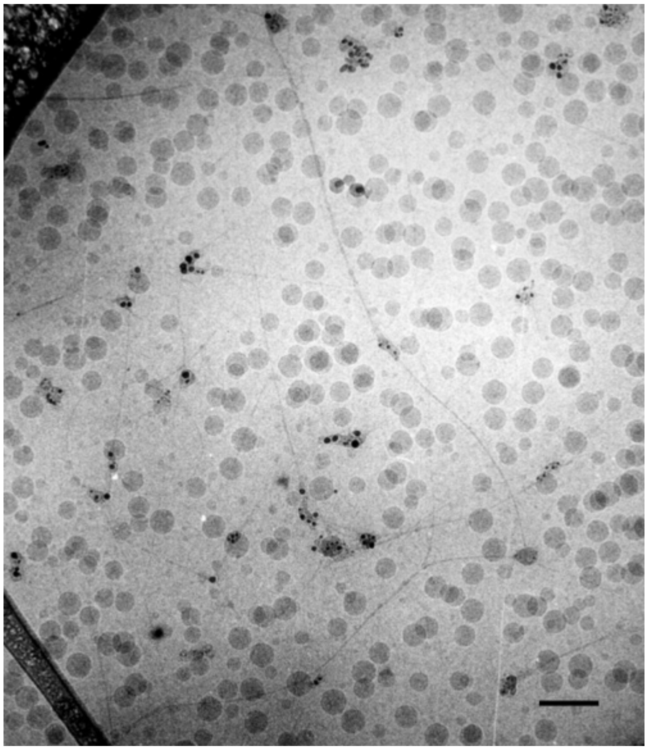

Figure 12. Cryo-TEM of 1 wt % SWNT in an aqueous solution containing 1 wt % of Gum Arabic and 5 wt % of polystyrene latex. Note the growth of individual or bundles of very few SWNTs from the Ni−Y catalyst nanoparticles shown by the arrow. Scale bar: 100 nm. (From ref 77. Reprinted with permission of Wiley & Sons, Ltd.)

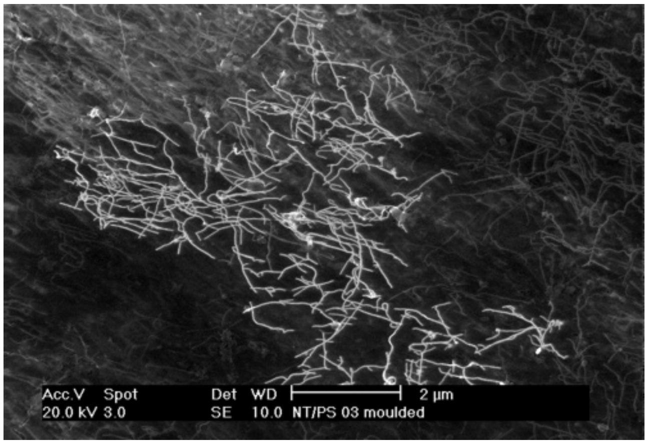

Figure 13. SEM of the surface of a nanocomposite SWNT−PS prepared with the latex-based process. The SWNT concentration is 0.3 wt %. It is possible to observe a network of individualized NTs (in white) in the polymer matrix (black background). Scale bar: 2 μm. (From ref 84. Reprinted with permission of Elsevier.)

The percolation threshold is located between 4 and 8 wt % of NTs.

The in situ polymerization carried out by Deng et al.[81] to produce NT−PANI composites is more traditional in nature. Under continuous stirring, in nitrogen atmosphere, chemicals are incorporated in the following order: first, the surfactant (sodium dodecyl benzene sulfate; SDBS) in solvent (dimethylbenzene) and water, followed by the addition of the NTs (supplied by CNT laboratory of Chenghu Institute of Organic Chemistry). Then the monomer (aniline) is added, and finally the initiator (ammonium peroxydisulfate; (NH_4)-S_2H_8) dissolved in a small amount of water, to start the reaction. The NT network observed is partly due to the formation of some kind of crystalline PANI-chain bridges between the NTs, which act as additional conductive passageways in the amorphous PANI matrix. The incorporation of 10 wt % of NTs in the PANI matrix was shown to increase the conductivity 25 times, from 2.6×10^{-1} S/m to 6.6 S/m for the composite.

2.3.4. Use of Surfactant: Mixing NTs with Polymer Latex. A relatively new approach to incorporate NTs into a polymer matrix is based on the use of latex technology.[77,82] Contrary to the incorporation of the NTs in an in situ polymerization system, the addition of the NTs in this technique takes place after the polymer has been synthesized.

Surfactants (either anionic surfactants such as sodium dodecyl sulfate (SDS) or sodium dodecyl benzene sulfate (SDBS), or polysaccharide (Gum Arabic; GA)) were used to disperse, exfoliate, and stabilize as-produced SWNTs, synthesized by either the AD method (about 30% of impurities) or the HiPCO process (having a catalyst particle content of about 5 wt %) in water by ultrasonication (Figure 11).[83]

The resulting NT suspension was then centrifuged to remove catalyst particles and large, nonexfoliated NT bundles. The aqueous supernatant contains exfoliated NTs or very small NT bundles consisting mostly of two or three tubes. Depending on the quality of the NTs, 15−50% of the material is lost during the centrifugation step. The supernatant is mixed with latex particles (Figure 12). After freeze-drying and subsequent melt-processing, a composite consisting of homogeneously dispersed SWNTs in a polymer matrix of choice is finally obtained (Figure 13).[84] Subsequently, the conductivity is measured as a function of the SWNT content, and a maximum value of about 1 S/m, is obtained for a SWNT−PS nanocomposite.

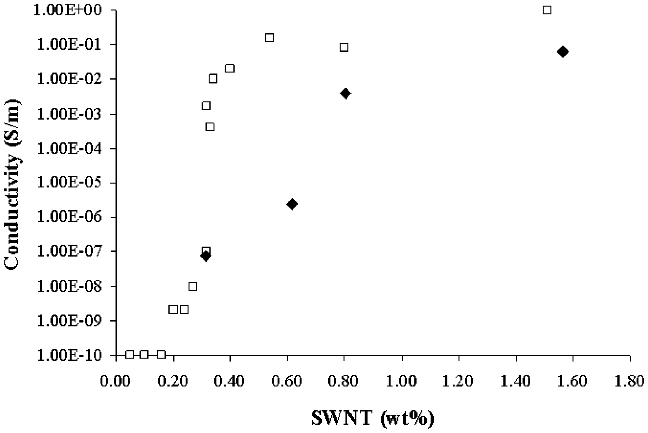

Figure 14. Four-point conductivity measurements of SDS−SWNT composite films in PS (squares) and in PMMA (rhombi). The molar mass distribution of PS is relatively broad and consists of a mixture of high (about 1000000 g/mol for Mw) and low molecular weight oligomeric fraction. For the PMMA, the molecular weight distribution is relatively narrow with a main peak located at 1000000 g/mol. (From ref 82. Reprinted with the permission of the Royal Society of Chemistry.)

The advantages of this technique are obvious: it is easy, versatile, reproducible, and reliable and allows a good incorporation of predominantly individual NTs into a highly viscous polymer matrix. It does not require the use of toxic and inflammable solvents, which is safe and environmentally friendly. Besides, no difficult synthesis of special polymers has to be carried out. Basically, it also exhibits a great degree of flexibility with respect to the choice of the matrix: a homogeneously dispersed NT network can be obtained for any kind of polymer, which can be produced by emulsion polymerization or which can be brought into a latex form. For example, amorphous polymer latex such as polystyrene PS, PMMA, or even semicrystalline polymer (e.g., polyethylene) can be used.[85] Furthermore, since the NT walls are not chemically modified, their properties are preserved. Low percolation thresholds of typically 0.3 wt % SWNTs have been determined for highly viscous composites based on PS or PMMA prepared with the latex-based process (Figure 14).

Polymer latex is nowadays industrially produced at large scale and this type of industry is mature. Since the process previously described is relatively easy (it basically consists of a simple mixing of two aqueous components) and counts a limited number of steps, it offers the prospect of facile scale-up for the future.

A very similar latex-based process to disperse MWNTs produced by CVD into a polymer matrix has been earlier described by Dufresne et al.[78] MWNT dispersions were first obtained by sonicating purified MWNTs in an aqueous SDS solution. After a centrifugation step, the resulting supernatant was mixed with latex obtained by the copolymerization of styrene (35%) and butylacrylate (65%). Films were made by casting in a mold and storing the mixture at a temperature allowing both the water to evaporate and the polymer particles to aggregate and to form a thin polymer film. The conductivity behavior was found to be characteristic for a very anisotropic shape or aggregate formation of the conducting filler, with a percolation threshold around 3 wt % and a maximum conductivity of about 1 S/m.

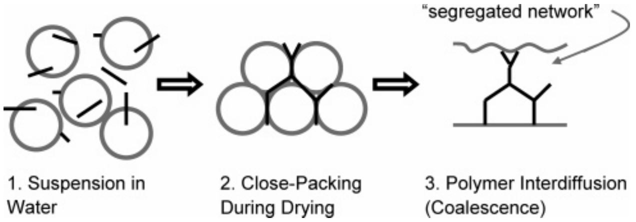

Figure 15. Schematic illustration of the drying process of SWNT-filled polymer emulsion. Initially, the NTs and polymer particles are uniformly suspended in water (left). Once most of the water has evaporated, the polymer particles assume a close-packed configuration with the NT occupying interstitial space (center). Finally, the polymer particles will interdiffuse (i.e., coalescence) to form a coherent film, locking the SWNTs within a segregated network (right). (From ref 79. Reprinted with permission of Wiley & Sons, Ltd.).

Rather recent investigations by Grunlan and co-workers[79] led to an alternative method, which consists of using a polymer brought into a latex form in an artificial way, like poly(vinyl acetate), instead of a polymer latex directly synthesized by emulsion polymerization. Untreated SWNTs produced via the HiPCO process (29 wt % of metal catalyst impurities in the batch used) were exfoliated by sonication. GA was used as a stabilizing agent. Once stabilized, the SWNT dispersion was mixed with a poly(vinyl acetate) (PVAc) emulsion to create a stable colloidal system leading to conductive composites after drying. The percolation threshold is about 0.04 wt % with maximum conductivity of $10^{1.25}$ S/m at 4 wt % of SWNT loading. Grunlan claims that water-based NT−polymer composites should have a lower percolation threshold than similar composites of which the preparation method is based on polymer solutions or melts. Due to the ability of the polymer solution or melt to surround added filler, NTs can freely organize during drying or cooling, whereas in suspension or in polymer latex, solid particles create excluded volume. Consequently, the free volume available for the NTs to form a conductive network is reduced and NTs are pushed into the interstitial space between the polymer particles during the film formation process. This effect should help to significantly reduce the value of the percolation threshold. It has to be mentioned that this assumption is true as long as the drying process of the NT-dispersion/polymer−emulsion system respects the polymer latex particle shape and does not result in flow of the latex particles (Figure 15).

The mechanism of electrical conductivity of surfactant-containing systems, as well as the exact location of the surfactant molecules in the composite, has not yet been addressed in detail. Using a third component to enhance the incorporation of the NTs into the polymer matrix might influence the conductivity. It is likely that part of the surfactant molecules used for exfoliation remain adsorbed on the surface of the NTs after being incorporated into the polymer. It has already been established that the electronic properties of a NT is affected by coupling-interaction with surfactant molecules adsorbed on its surface,[86,87] which leads to band shifts of the spectra recorded for surfactant-coated NTs, compared to the "naked" NTs and to tunneling. Moreover, it has been shown by Regev et al.[77] that the choice of the surfactant can significantly influence the final conductivity of the nanocomposite, probably due to the combined effects of the ability of the surfactant to exfoliate the NTs, its interaction with the NT walls, and its capability to desorb from the NT surface and migrate into the polymer matrix during and/or after processing of the nanocomposite.[88] It has indeed already been observed that, under specific conditions, a competition of adsorption between the surfactant molecules and the polymer matrix occurs on the NT surface, which leads to at least partial desorption of the surfactant.[89]

3. Conclusion and Outlook

There is currently a growing interest in processing NT–polymer nanocomposites, both from the point of view of fundamental properties determination and the development of new applications. As a matter of fact, since the fillers are of the nanoscale, the potential filler–matrix interface area is huge. Furthermore, notably because of their high aspect ratio and their good conductivity, a significant increase of the conductivity of the polymer host can be achieved at very low NT loadings. However, NT–polymer composite applications can be restricted owing, on one hand, to their availability and price and, on the other hand, to the strong tendency of (SW)NTs to bundle. Consequently, the effective utilization of NTs as a filler, to obtain conductive NT–polymer nanocomposites, depends on the ability to disperse the NTs throughout the polymer matrix, without significantly damaging the NTs.

This review covers the main strategies developed over the past decade for incorporation of NTs into a polymer matrix. The authors did not have the pretension to give an exhaustive overview, but the aim was rather to illustrate the main strategies with some appealing examples. Three main strategies were presented: direct mixing of the filler and the matrix, modification of either the NTs or the polymer, and mixing them with the help of a third component.

Direct mixing of the NTs and the polymer, with or without solvent, appears to be the easiest and least laborious way to achieve the incorporation of NTs into a polymer matrix and has proven its efficiency. On the other hand, the dispersion of the nanotubes into the polymer matrix is often rather inhomogeneous, even sometimes with formation of millimeter-scale inhomogeneities. On the other hand, the existence of these agglomerated can be a key factor in lowering considerably the value of the percolation threshold.

Modifying either the NT walls by functionalization, or the polymer matrix, is found to improve the quality of the interface between the components of the nanocomposite by enhancing the interfacial interactions. In one approach, the wetting of the filler by the polymer is realized by covalent binding and, in another, by $\pi-\pi$ stacking. Unluckily, both approaches lead to the disturbance of the delocalization of the π-electrons of the NT walls, which results in a significant deterioration of its electrical properties. Finally, the third strategy is based on the use of a third component, which most frequently is a surfactant. The methods inspired by this strategy are mainly based on latex technology. This route to incorporate NTs into a polymer matrix appears to be very promising since it is simple and environmentally friendly. Furthermore, the production at a large industrial scale can be expected to be relatively easy to achieve in the future. The technique has been reported to be very successful to produce conductive nanocomposites with low percolation thresholds, as well as good conductivity levels. Furthermore, it is very flexible with respect to the choice of the polymer matrix: it can actually be applied to any polymer synthesized by emulsion polymerization, or brought into a polymer latex form in an artificial way.

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