ADVANCED MATERIALS

Preparation of Conductive Nanotube–Polymer Composites Using Latex Technology**

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Single-wall nanotubes (SWNTs) are tightly bundled as a result of strong van der Waals interactions, which constitute the current bottleneck to their application. Few techniques for dispersing and exfoliating as-produced SWNT powder in organic,[1] aqueous polysaccharide,[2] and surfactant[3] solutions have been developed. The use of these exfoliated nanotubes as a polymer filler offers an important advantage over conventional fillers: the extremely high aspect ratio of the SWNT implies that low loading of the NT is sufficient to change a desired property (e.g., conductivity) without sacrificing other inherent properties of the polymer. They could be applied in, e.g., electromagnetic interference shielding[4] or in the fabrication of nanoelectronic devices such as thin-film transistors.[5]

In most studied NT–polymer composites the polymer is also used as the NT dispersing agent (direct mixing). Therefore, the polymer is optimized to exfoliate or at least to disperse the nanotube bundles, but not to tune the properties of the composite.[6] As a consequence, most reported NT-based composites consist either of polymers that have been specially synthesized to disperse the NTs,[7,8] or, alternatively, the NTs are functionalized[9] to enhance the interaction with the polymer. The former method introduces a serious limitation on the spectrum of target polymer matrices, while the latter is reported to impair some of the properties (e.g., conductivity) of the bare NTs.[10] Moreover, the ability of the polymer to disperse and exfoliate the NTs is not necessarily coupled with the optimized properties of the target matrix. In some cases the dispersant is able to disperse but not to exfoliate the SWNTs.[11]

We have developed a new approach to reinforce a highly viscous polymer of basically any type by a network consisting of *individual* or bundles of few SWNTs. We use a surfactant to disperse and exfoliate bare SWNTs in water. The SWNTs are then mixed with latex nanoparticles (obtained by emulsion polymerization) in aqueous solution to form, after drying and subsequent processing, a composite consisting of homogeneously dispersed SWNTs in a polymer matrix of choice. Pioneering studies using an emulsion-based approach for integrating single-[12] and multi-walled[13] NTs in polymer films have been recently reported, indicating conductivity percolation threshold (p_c) values in the range of a few weight percent NTs. Much lower p_c values were reported for direct mixing of MWNT with poly[(*m*-phenylenevinylene)-*co*-(2,5-dioctyloxy-*p*-phenylenevinylene)] (PmPV) or poly(vinyl alcohol) (PVA).[14] As a model system we chose highly viscous polystyrene (PS, $M_w = 400$ kg mol^{-1}), in which SWNTs were reported not to be dispersible,[6] hence requiring the functionalization of the SWNTs prior to their integration into the matrix.[15,16] However, when we mix an aqueous polystyrene latex solution with an aqueous dispersion of sodium dodecylsulfate (SDS) and bare SWNTs, freeze-dry the dispersion, and subsequently mold it, we find that the p_c value of the resulting PS film is as low as 0.28 wt.-% SWNTs. Moreover, electron microscopy shows that nanotubes are indeed well-dispersed in the highly viscous polymer matrix. We demonstrate a new, simple, and versatile approach, which makes use of one additional component (surfactant) for dispersing both the latex and the SWNTs in an aqueous solution. We demonstrate that the combination of latex technology with an exfoliated NT dispersion makes this method polymer type-independent, i.e., a homogeneously dispersed SWNT network could be used as a filler for any polymer that can be made in a latex form.

Arc-grown (catalyzed by Ni–Y nanoparticles) SWNTs were successfully dispersed in aqueous solutions of either anionic surfactant (sodium dodecyclsulfate (SDS)[3,13,17,18]) or polysaccharide (gum arabic (GA)[2]), shaken for few seconds, and then sonicated. After centrifugation, the solution phase-separated into an insignificant amount of solid precipitate and an ink-like supernatant, which was decanted and used further. Calculation of the amount of SWNT in weight percent is based on the assumption that all NTs are in solution. We then employed cryo-transmission electron microscopy (cryo-TEM)—a direct, model-independent, imaging technique[19]—to characterize the exfoliated SWNTs in the vitrified solution using different dispersing agents.

We found that a concentration of a few weight percent of dispersant is sufficient to disperse a similar weight percent concentration of SWNTs in water. A cryo-TEM image of an aqueous dispersion of 1 wt.-% SWNTs in 1 wt.-% SDS (1:1 w/w SWNT/SDS) is shown in Figure 1A.[20] Similar results have been reported for SWNT–GA solutions,[21] and a detailed study on SDS self-assembly on the surface of the NTs has recently been published.[22]

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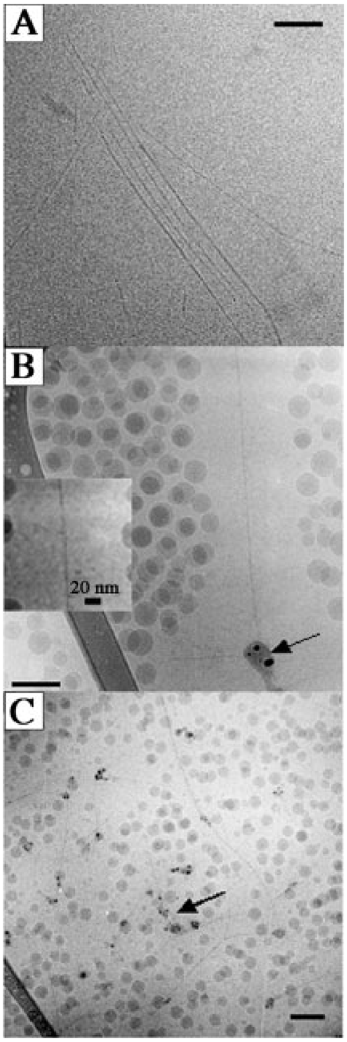

Figure 1. Cryo-TEM micrographs of A) a 1:1 w/w SWNT–SDS aqueous solution; B) 1:1 w/w SWNT–GA in an aqueous, 5 wt.-% dialyzed PS–latex solution. Note the strong SWNT–latex repulsion; C) 1:1 w/w SWNT–GA in an aqueous, 5 wt.-% PS-latex solution, to which 0.5 wt.-% NaCl had been added to overcome the repulsion. Note the growth of *individual* or bundles of very few SWNTs from the Ni–Y catalyst nanoparticles (arrows in parts (B) and (C) and inset in part (B)). Scale bar = 100 nm.

When dialyzed PS latex (average diameter of 75 nm) is added to the GA-dispersed SWNTs and shaken, a strong repulsion between the SWNTs and the latex is clearly seen (Fig. 1B). We attribute this to electrostatic repulsion between the GA-dispersed SWNTs and the SDS-dispersed latex: GA is a weak polyelectrolyte; it carries carboxylic acid groups and is thus negatively charged above pH 2,[23] above which our measurements are performed. SDS is also negatively charged, which results in electrostatic repulsion. The Debye length, λ_D, is given, at room temperature for 1:1 electrolyte, by:[24]

$$\lambda_D = \frac{0.3}{\sqrt{C_S}}\ [\text{nm}] \tag{1}$$

where C_S is the molar salt concentration.

One would, on account of the screened Coulomb interaction, expect the NT and the latex particles to remain, on average, at least a distance λ_D from each other. In other words, the depletion layer of the latex particles should be of the order of λ_D.

From Figure 1B one measures a depletion layer of ≈ 100 nm for the latex particles, which, according to Equation 1, gives a salt concentration of 10^{-5} M, a reasonable value for a dialyzed solution.

Both electrostatic and steric repulsions are expected to diminish with increasing ionic strength of the solution. The reasons are, first, that upon addition of salt, electrostatic screening induces less repulsion between GA and SDS. Secondly, since GA is charged, salt addition causes a collapsed conformation of the GA chains[25,26] (lower radius of gyration, R_G) and reduces steric repulsion between the NT and the latex.

Indeed, addition of salt (0.5 wt.-% NaCl) to the GA-dispersed SWNT dialyzed latex solution suppressed the repulsion and resulted in a well-dispersed NT–latex solution (Fig. 1C). The Debye length for this salt concentration is now 1.9 nm and the solution is most probably sterically stabilized.[27] Similar images to those presented in Figure 1C were obtained when SDS-dispersed SWNTs were used.

In the SDS-dispersed SWNT–latex solution, both the latex particles and the SWNTs are negatively charged and the repulsion is resolved either by salt addition or usage of non-dialyzed latex.

The SWNTs are still connected in a spider-like form to the black Ni–Y catalyst nanoparticles from which they were initially grown (Fig. 1B). Note also the individual nature of the exfoliated nanotubes (diameter of a few nanometers, Fig. 1). The solution was freeze-dried over night and the resulting dry powder was compression molded, resulting in melting and complete deformation of the latex particles.[28] From the well-dispersed SWNT–latex (Fig. 1C), we obtained a flexible, continuous, and optically homogeneous film.[29] However, composites containing dialyzed latex with a nanometer-range phase separation between SWNTs and PS in solution (Fig. 1B) yielded a macroscopic inhomogeneity in the molded film (shown as millimeter-size black dots, demonstrating bad SWNT dispersion), indicating a direct link between nanoscopic and macroscopic morphology. Such an inhomogeneous film is not conductive.

However, electrical conductivity measurements on the well-dispersed SWNT–SDS–PS system indicate a p_c of 0.28 wt.-% SWNTs (Fig. 2, □). According to classical percolation theory[30] the conductivity, σ, follows a power law close to the threshold

$$\sigma \propto (p - p_c)^t \tag{2}$$

The fit in Figure 2B suggests a critical exponent, t, of 1.58, consistent with previous measurements.[14] The conductivity increases by ten orders of magnitude from 10^{-10} S m^{-1} for the pure PS to 10^0 S m^{-1} for the nanocomposites having an NT

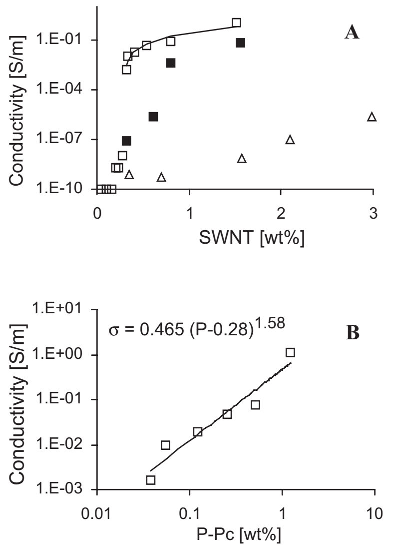

Figure 2. A) Conductivity measurement of composite films containing SDS-dispersed SWNT in PS (□) and in PMMA (■) matrices. GA-dispersed SWNT in PS (△). PS/SDS, PMMA/SDS = 30:1 w/w, PS/GA= 30:5 w/w. B) Conductivity vs. reduced mass fraction for SWNT in PS. The solid lines are fits to a power-law dependence of the conductivity and the reduced mass (Eq. 2).

concentration above p_c. Note the relatively high conductivity value above p_c. Increasing the PS–latex diameter to 210 nm did not affect the conductivity curve. Much higher p_c values are found for the SWNT–GA–PS system (Fig. 2, △). We attribute the difference to the high molecular weight of the GA (250 kD), which could induce local steric hindrance and concomitant contact resistance to the percolating conductive SWNT network. Therefore, a higher SWNT–GA w/w ratio was needed for efficient dispersion of the SWNTs. Note that in most reported nanocomposites having a similar polymer matrix as in our study,[12,13,31] conductivity percolation threshold values of 3–10 wt.-% are found. For epoxy-based systems, for which the NTs are directly dispersed in low viscous epoxy resin monomers, percolation threshold values below 0.1 wt.-% have been reported.[7] Moreover, further processing and shaping (e.g., by molding) of our dry, latex-based powder is much easier because of its thermoplastic nature, relative to the cured epoxy-based thermoset composites, which are usually cured in the form of the end product. Finally, the same film-preparation procedure was repeated for a poly(methyl methacrylate) (PMMA) latex, and the conductivity of the resulting films indicated a similar increase in conductivity (Fig. 2).

Further room-temperature TEM characterization of the composite films was conducted after sectioning of the molded SWNT–SDS–PS film by microtome (Fig. 3, 0.3 wt.-% NTs). The catalyst nanoparticles show up as the dominant objects in the image, signaling the location of the SWNTs (Figs. 1B,C) from which they were initially grown. Even after molding, most SWNTs are still fixed to the catalyst nanoparticles, as clearly demonstrated in Figure 3B, where a section was taken parallel to the long axis of an SWNT. Since the catalyst nanoparticles are homogeneously dispersed in the PS matrix (Fig. 3A), we infer that the bare SWNTs are also homogeneously dispersed in the highly viscous PS matrix.

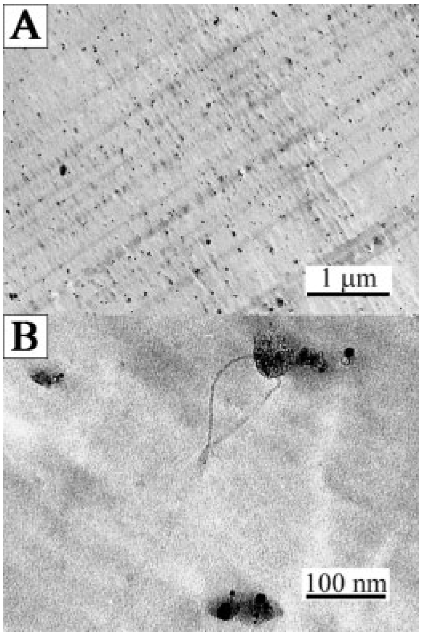

Figure 3. TEM micrograph of a cross-section of a conductive nanocomposite consisting of 0.3 wt.-% of 1:1 w/w SWNT–SDS in PS. A) Overview with homogeneously distributed catalyst nanoparticles (black dots). B) High-resolution image showing a curved SWNT fixed to a catalyst nanoparticle.

Besides conductivity measurements, additional evidence for the formation of a homogeneous NT network is obtained by a scanning electron microscopy (SEM) study of the conductive composites. In Figure 4 the straight and curved lines, which are polydisperse in length,[32] represent the SWNTs. They possess excellent contrast due to the different charge-transport properties of the conducting SWNTs with respect to the insulating PS matrix, hence inducing an enriched secondary-elec-

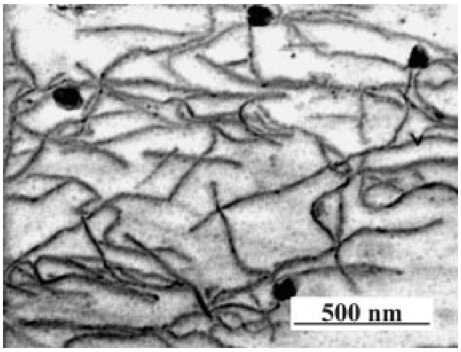

Figure 4. SEM micrograph of a PS nanocomposite containing 0.3 wt.-% SDS-dispersed SWNTs. The SWNTs are represented by the dark lines; the Ni–Y catalyst nanoparticles (black dots) are similar to those imaged by cryo-TEM in solution in Fig. 1B.

tron yield at the position of the SWNTs. However, the local charging[33] of the polymer matrix around the SWNTs may have resulted in an average diameter of the SWNTs of 30 nm, one order of magnitude higher than the measured value for an individual SWNT. The connectivity of the NT network is clearly imaged[31] in the presence of the catalyst particles as discussed earlier (Figs. 1B,C and Fig. 3).

In conclusion, we have demonstrated that SWNTs are easily integrated into a polymer matrix of choice, using a new, versatile, and extremely simple approach based on latex technology. In the introduced technique we circumvent the need for specific polymer–SWNT interaction, hence expanding the spectrum of possible reinforced polymer matrices. We confirmed that bare SWNTs are both exfoliated and dispersed in water by conventional surfactants, similar to what has been shown for GA. After mixing the SWNT–SDS solution with PS or PMMA latex nanoparticles and drying, the resulting powder can be easily processed. The resulting composite contains homogeneously dispersed SWNTs, giving rise to low p_c values for highly viscous composites based on PS or PMMA.

Experimental

Raw SWNTs from Carbolex (SWNT-AP) and sodium dodecyl sulfate (Aldrich) were used as received. Polystyrene and PMMA were prepared by emulsion polymerization (with SDS) and contain 30 wt.-% solids with 75 or 210 nm diameters [34]. Dialysis was performed in DTV12000.11 (Visking) bags for 14 days (replaced daily) and the conductivity was measured repeatedly. The solution was sonicated (20 W for 15 min) and centrifuged (4000 rpm, for 20 min at a 5420 g, Varifuge RF 4655F with a Sepatech rotor (11 cm)). A Christ Alpha 2–4 freeze dryer was operated at 0.25 mbar and –80 °C overnight. Compression molding was conducted at 170 °C between poly(ethylene terephthalate) sheets using a Collin Press 300G. Electrical conductivity was measured using a Keithley 237-6517A setup, and contact lines were drawn on the film with graphite conductive adhesive (EMS). Cryo-TEM was conducted using an FEI Tecnai 20 (Sphera) operated at 200 kV, equipped with a Gatan 794 CCD camera using a low-dose mode of the electron beam. Room-temperature TEM was performed on JEOL FX2000 operated at 80 kV with microtomed samples from Reichert-Jung Ultracut E. SEM Analysis was performed using a Philips XL30 environmental-SEM equipped with a field-emission gun.

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