Chem. Mater. **2007,** *19,* 3787−3792

On the Crucial Role of Wetting in the Preparation of Conductive Polystyrene−Carbon Nanotube Composites

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Received December 18, 2006. Revised Manuscript Received May 15, 2007

Polystyrene−single-wall carbon nanotube (PS−SWNT) nanocomposites were prepared by directly mixing aqueous suspensions of exfoliated SWNTs and PS latex particles. After freeze-drying and compression molding, homogeneous polymer films were obtained with well-dispersed carbon nanotubes, as evidenced by scanning electron microscopy imaging. The nanocomposite films display a low percolation threshold and high levels of electrical conductivity. Simultaneously, a considerable increase in the glass-transition temperature of PS is achieved, provided that a sufficient amount of low-molar-mass PS is present in the matrix material. It is suggested that a certain extent of molar mass segregation occurs in the samples, with shorter PS chains preferentially adsorbed onto the nanotube surface. The latter wetting mechanism is indispensable for obtaining favorable electrical and thermal properties.

Introduction

There is nowadays a growing interest in nanotube (NT)−polymer nanocomposites, not only for the study of fundamental aspects of these materials but certainly also bearing in mind the development of possible novel applications. As a matter of fact, because NTs are at the nanoscale level and have a high aspect ratio (i.e., length over diameter ratio, *L*/*D*), the potential filler−matrix interface area is huge. Furthermore, NTs possess exceptional properties[1,2] that justify why they are expected to be extremely valuable fillers. Especially in view of their high *L*/*D* values, property enhancement can already be achieved at very low loadings without losing processability. Electrical conductivity is obtained with filler loadings well below 1 wt %, provided that a good dispersion of the carbon nanotubes is achieved.[3,4] Note that filling degrees ranging from 7 to 15 wt %[5,6] are often required with traditional fillers, such as carbon black, to provide a similar enhancement of the electrical properties.

However, nanotubes (NTs) tend to agglomerate in thick bundles because of Van der Waals interactions,[7] and hence exfoliation of the nanotube bundles into individual tubes and their incorporation into a highly viscous polymer matrix remains a challenge. The key issues for making technologically interesting NT−polymer nanocomposites are the degree of exfoliation of the NTs in the polymer matrix, as well as the quality of the filler−matrix interface.

The present paper deals with a relatively novel methodology for preparing “conductive plastics”, filled with well-dispersed single-wall carbon nanotubes (SWNTs), obtained by means of a latex-based process. Here, we report the results on the incorporation of carbon nanotubes into polystyrene (PS). However, the described process can be applied to any polymer prepared by emulsion polymerization, or brought into the form of a polymer latex otherwise.[8,9] The characterization of the final composites obtained shows the importance of the matrix properties, especially with respect to the molar mass distribution of the polymer.

Nanocomposites prepared with two different PS latexes are investigated and compared with respect to their electrical conductivity and their glass-transition region. A mechanism of molar-mass segregation is proposed to explain the specific behavior observed at the polymer−filler interface, which proves to be directly governed by the molar-mass distribution of the employed PS latex. Actually, the latter appears to be

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10.1021/cm062998o CCC: $37.00

of crucial importance for the final electrical and thermal properties of the nanocomposite.

Experimental Section

Materials. Styrene (99%) and sodium hydrogen carbonate ($NaHCO_3$, 99%) were purchased from the Aldrich Chemical Co.; sodium dodecyl sulfate (SDS, 90%) and sodium persulfate (SPS) were provided by the Merck Chemical Co. SWNTs purchased from Carbolex Inc. (AP grade) were produced by arc-discharge technology and contain ca. 30 wt % impurities (both carbon and residual nickel/yttrium catalyst particles). They were used without further purification. The liquid PS standard was provided by Polymer Laboratories. According to the supplier, its polydispersity is 1.11 and its molar mass is 665 g/mol. PS10k is a PS standard synthesized in our laboratories by ionic polymerization. The synthesis was carried out at room temperature in cyclohexane, with *n*-butyllithium as the initiator. The obtained PS10k has a polydispersity of 1.073 and a molar mass of 10 800 g/mol.

Sample Preparation. *Emulsion Polymerization:* The emulsion polymerization runs were carried out in an oxygen-free atmosphere. For PS1, 292 g of styrene was mixed with 728 g of water in the presence of 13 g of SDS surfactant and 1.1 g of NaHCO3 buffer. The temperature was kept in the range 50−60 °C. The reaction was initiated by 1 g of SPS. PS2 was prepared under similar conditions (200 g of styrene, 695 g of water, 13.4 g of SDS, 1 g of SPS), except that the polymerization temperature was higher (around 65−70 °C).

Preparation of PS3: First, the fractional surface coverage of the PS2 latex particles with SDS has been determined by soap titration (Maron's titration[10]). This allowed us to calculate the amount of SDS to add to reach almost complete surface coverage of the latex particles, in order to ensure complete colloidal stability of the whole system when the low-molar-mass polystyrene is incorporated into the particles. The artificial incorporation of low-molar-mass PS into the PS2 latex has been achieved by the following procedure: 130 g of PS2 latex was directly mixed with 624 mg of SDS, followed by the incorporation of 715 mg of PS standard. The resulting dispersion became subject to high shear forces for 3 min by using an Ultraturrax T50 (Ika Labortechnik, Germany**)** at minimum speed (4000 rpm).

Nanocomposites: SWNTs were directly mixed with an aqueous solution containing 1 wt % SDS (SDS:NT ratio of 1:1), sonicated at 20 W for 15 min in order to exfoliate the nanotubes (Sonics Vibracell VC750)[11] and then centrifuged at 4000 rpm for 30 min (Heraeus Sepatech Varifuge RF). The remaining SWNT dispersion was then mixed with the polymer latex and freeze-dried (Chris Alpha 2-4). The resulting powder was degassed and processed into films by compression molding at 180 °C/100 bar for 2 min (Collin Press 300G).

Preparation of PS10k Samples: PS10k powder was directly mixed with 0, 5, or 10 wt % SDS; the resulting powder was then dissolved in acetone and dried on a heating plate in order to evaporate the solvent. For the nanocomposite preparation, PS10k powder was mixed with an aqueous solution containing equal amounts of NTs and SDS (1 wt %). This mixture was then directly dissolved in acetone for homogenization. A nanocomposite containing 2 wt % SWNTs was obtained after evaporation of the solvent.

Characterization. The molar mass of the different PS studied were analyzed at 40 °C by gel permeation chromatography (GPC) using a Waters model 510 pump system with mixed packed columns preceded by a guard column PLgel mixC. Injections were done by a Waters model WISP 712 auto-injector. Tetrahydrofurane (THF) was used as an eluent, and the elution volumetric flow rate was maintained at 1.0 mL/min. The measurements were carried out with a refractive index detector Waters model 410, and a model 486 UV detector operating at 254 nm. Data acquisition and processing were performed using Waters Millennium32 (v3.2 or 4.0) software. Calibration was done using PS standards supplied by Polymer Laboratories, Inc.

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

Morphological characterization of the as-prepared nanocomposites was performed using scanning electron microscopy.[12] The SEM (XL30 ESEM-FEG, Fei Co., Eindhoven, The Netherlands) was equipped with a field-emission electron source. High vacuum conditions were applied, and a secondary electron detector was used for image acquisition. The SEM was operated in either conventional high-voltage or low-voltage mode. No additional sample treatment such as surface etching or coating with a conductive layer had been applied. Standard acquisition conditions were as follows: working distance of ∼5 mm for low-voltage mode and ∼10 mm for high-voltage charge contrast imaging, spot 3, slow scan imaging with approximately 2 min/frame.

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

The low-shear viscosity of the polystyrene matrix materials was determined at 180 °C on a TA Instruments AR-G2 rheometer fitted with 25 mm stainless steel parallel plates.

Results and Discussion

The starting point for the preparation of the PS−SWNT nanocomposites is the preparation of a stable aqueous NT dispersion. First, SWNTs are directly mixed with an aqueous solution of the surfactant, i.e., sodium dodecyl sulfate (SDS). The mixture is sonicated to "break up" the NT bundles and to achieve exfoliation of the NTs. It is then centrifuged to remove some catalyst particles, as well as large bundles that can remain. As a result, the obtained supernatant consists of a stable colloidal dispersion of individual SWNTs or of thin NT bundles of a few units. The stability of this system is guaranteed by steric and electrostatic interactions[13] provided by the adsorption of surfactant molecules onto the NT surface.[14] Subsequently, this supernatant is directly mixed with a polymer latex (PS), which is also stabilized by SDS. As a result, a colloidal system containing SWNTs and

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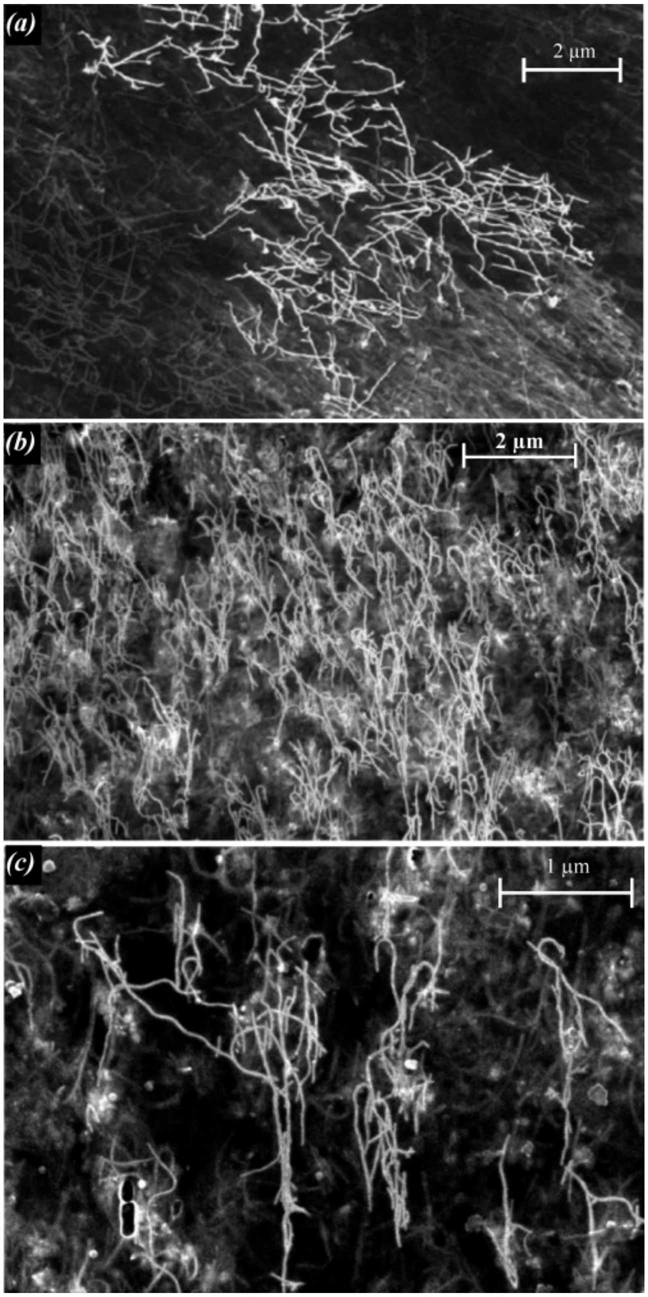

Figure 1. SEM micrographs of the surface of SWNT−PS1 nanocomposites containing (a) 0.3 and (b) 1.6 wt % SWNTs and (c) a SWNT−PS2 nanocomposite containing 1.5 wt % SWNTs. The well-dispersed SWNTs are represented by the white lines, whereas the black background is the polymer matrix.

polymer latex particles is obtained. Note that the average latex particle diameter (from dynamic light scattering) is ca. 100 nm for PS1, and ca. 200 nm for PS2, with overlapping distributions. Hence, particle diameters are on the same order of magnitude and much smaller than the average length of a carbon nanotube (1−2 μm according to the manufacturer). In a last preparation step, the powder obtained after freeze-drying is compression molded into homogeneous films with well-dispersed SWNTs, as confirmed by the SEM images shown in Figure 1. The latter standardized preparation method was used for all investigated systems in order to allow direct comparison of the results. Because of the similar average latex particle diameters with strongly overlapping particle size distribution, and in view of the standardized high-temperature melt processing conditions which induce the deformation by flow of all initial glassy latex particles present right after the freeze-drying step, effects related to latex particle size, polymer flow, and annealing time can be excluded in the present study, as commented upon further.

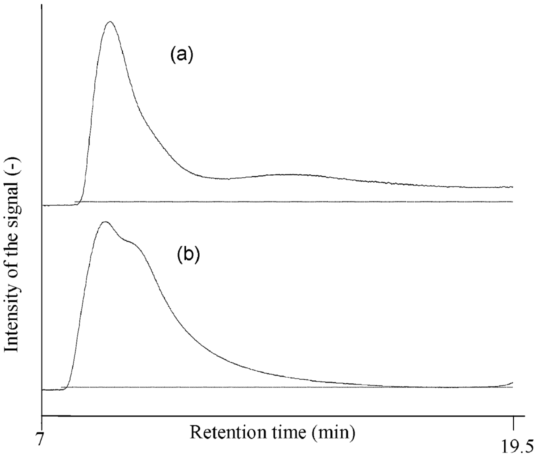

Figure 2. GPC traces showing the molar mass distribution for (a) PS1 and (b) PS2.

Electrical Conductivity. Electrical conductivity measurements were performed for two PS/SWNT systems, prepared with two PS latexes (PS1 and PS2) with different average molar masses and different molar mass distributions, as shown by the GPC traces in panels and b of Figure 2. A series of films with a wide range of SWNT loadings was made for each PS latex. The polymer used for the first series (PS1) has a very broad molar mass distribution, containing high-molar-mass polystyrene as well as a significant amount of low-molar-mass—even oligomeric—species. A rough calculation points to ca. 25 wt % polymer with a molar mass below 20 000 g/mol. Nevertheless, the peak molar mass in the molar mass distribution is located above 1 000 000 g/mol. On the contrary, the second polystyrene (PS2) has a relatively normal polydispersity index of ca. 4 and mainly contains high-molar-mass polystyrene, with a peak molar mass in the distribution around 1 000 000 g/mol. Per comparison with PS1, PS2 contains <5 wt % low molar mass polymer.

In general, the conductivity of composites consisting of a polymer matrix filled with conductive filler particles is described by the so-called percolation theory.[15,18] As expected, the electrical conductivity of both series of composites strongly depends on filler loading (see Figure 3). At low filler concentrations, the conductivity remains close to that of the electrically insulating matrix polymer, because the filler occurs only individually or in small clusters. From a critical filler volume fraction onward, the conductivity drastically increases by many orders of magnitude with very little increase in filler loading. This so-called percolation threshold coincides with the formation of a conductive network of filler particles in the continuous polymer phase.

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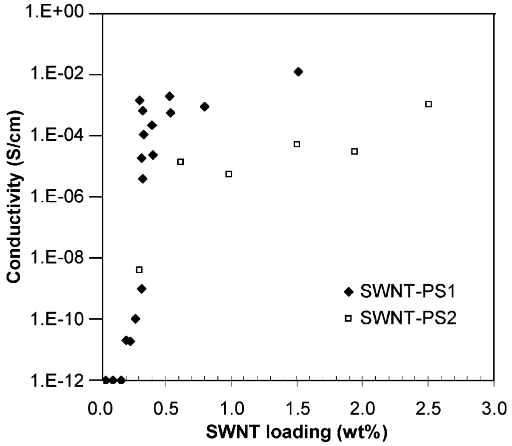

Figure 3. Electrical conductivity (four-point measurements) as a function of nanotube loading for nanocomposites based on PS1 and PS2 latexes.

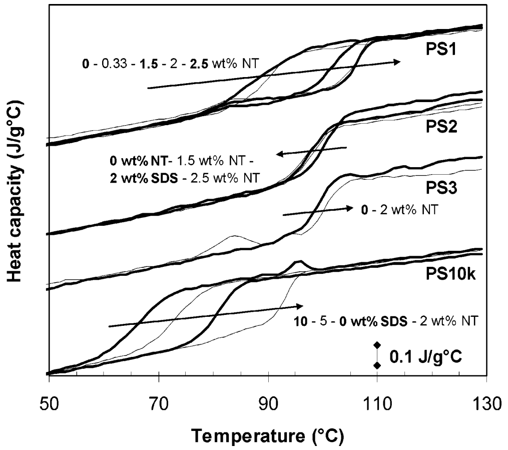

Figure 4. Glass-transition region of various nanocomposites as investigated by means of MTDSC (sample compositions are indicated by the sense of the arrows).

In the present case, the percolation threshold is attained at a loading of about 0.3 wt %, which, in view of the very high molar mass of the matrix polymers,[17−19] is relatively low compared to what has been reported in some recent studies. Upon further increasing the loading, the conductivity levels off at a certain value, i.e., the maximum conductivity of the composite, which obviously depends on the molar mass distribution of the polymer latex used. The presence of a significant amount of oligomeric species in latex PS1 (see Figure 2) clearly increases the maximum achievable conductivity, suggesting that this is essential in view of achieving good electron transport through the nanocomposites, more specifically through the insulating polymer films that surround the highly conductive nanotubes and act as a potential barrier to internanotube hopping.[20,21] Note that the conductivity data are reproducible within a factor 5, hence the experimental error is much smaller than the factor 1×10^3 difference between the plateau levels of SWNT-PS1 and SWNT-PS2.

In this respect, it is worth mentioning that the filler network structure plays an important role in, for example, the electrical properties of particle-based systems, as demonstrated by numerical methods as well as by experimental observations in nonflowing polymer systems.[22,23] In the absence of polymer flow, when the continuous matrix phase is formed after compaction of rigid polymer particles, the polymer particle diameter strongly influences the filler network structure.[22] Similarly, the latex particle diameter can be expected to influence the nanotube network structure because of a structured percolation induced by the latex packing. The extent to which the latter phenomenon may occur in the presently reported flowing systems requires further investigation. It is reasonable to assume, however, that its importance is relatively limited when considering the applied melt processing step and associated flow of the polymer matrix, which occurs in the present systems at 180 °C despite the high viscosity of the matrix materials (2.8×10^5 and 8.5×10^5 Pa s for PS1 and PS2, respectively, as determined from steady-shear rheometry). Note also that if segregation of any kind would remain after compression molding as a result of the unaffected particle integrity, gaps in the final microstructure would on average have sizes of 100−200 nm. Such morphology is not observed in the SEM images. In view of the very comparable latex particle diameters in the considered systems, the question of network structure will not be further addressed in the present paper. Nevertheless, the importance of latex particle size and melt annealing time is currently under investigation for latexes with significantly different diameters (differing by at least a factor 5−10), and this will be the subject of a forthcoming paper.

Glass-Transition Region. To elucidate the role of the low-molar-mass fraction in the PS matrix, a study of the glass-transition region of the nanocomposites has been conducted by means of modulated temperature differential scanning calorimetry (MTDSC). The thermograms of the various nanocomposite series are shown in Figure 4. The unfilled PS1 has an unusually low glass-transition temperature (T_g) of ca. 90 °C (as compared to the normally reported value for high molar mass PS of ca. 100 °C[24]), which moreover is rather broad. Upon addition of SWNTs, the glass-transition region of PS1 narrows ,and T_g strongly increases until an ultimate value of ca. 107 °C is attained at 2 wt % SWNT loading. Further increasing the filler content is no longer beneficial, suggesting that a maximum T_g increase of about 17 °C can be achieved over that of unfilled PS1, which was rather low in itself because of the plasticizing effect of low-molar-mass species such as PS oligomers and SDS surfactant.

When, on the other hand, polystyrene latex PS2 is used, which does not contain an oligomeric fraction, T_g is located at the expected value of ca. 100 °C. Upon addition of 1.5 or 2.5 wt % NTs, T_g slightly decreases by about 2 °C, which can be (at least partially) attributed to the plasticizing effect

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of SDS,[25,26] because a similar decrease is observed when 2 wt % SDS is added to PS2 without NTs. An additional T_g decrease might also be due to an increased free volume in the vicinity of the NTs.[27]

Unlike for the nanocomposites based on PS1, however, no T_g increase with increasing filler loading is observed for PS2, nor is there significant narrowing of T_g.

Considering the fundamentally different behavior of the two series of composites prepared according to the same procedure, it seems unlikely that all SDS molecules used to stabilize both the latex and the SWNT dispersion stay at the polymer−SWNT interface in order to favor wetting of the nanotube surface. Therefore, we suggest that at least part of the surfactant diffuses into the polymer matrix in favor of the polymer itself. Good wetting of the filler by matrix PS is then achieved, assisted by favorable interactions between the phenyl groups of polystyrene and the π-electron system of the nanotube walls. This only seems to occur, however, in the case in which low-molar-mass PS is present in the matrix material, capable of displacing the SDS molecules from the nanotube surface. This is confirmed by the observed narrowing of T_g in the case of PS1−SWNT composites, suggesting that the low-molar-mass fraction experiences a proportionally higher T_g increase due to adsorption onto the filler surface and strong mobility restriction. Already at this stage, it is tempting to state that the oligomeric PS molecules are absolutely indispensable for a proper wetting of the NT surface.

To prove the validity of this assumption, we investigated whether the presence of low-molar-mass PS is indeed a prerequisite for achieving a T_g increase. For this purpose, the high-molar-mass latex PS2 was mixed with ca. 2.5 wt % low-molar-mass PS GPC standard with a degree of polymerization (DP) of 5. The obtained system, referred to as PS3, indeed exhibits a T_g that is increased by 2° upon mixing with SWNTs (see Figure 4), despite the fact that a fairly high amount of plasticizing SDS was required to mix the high- and low-molar-mass polymers in this system. Finally, we have investigated nanocomposites based on a PS standard of molar mass 10 000 g/mol and prepared by solution mixing (referred to as PS10k). As shown in Figure 4, T_g strongly decreases upon addition of SDS because of its plasticizing effect. On the other hand, T_g strongly increases by addition of 2 wt % SWNTs (and thus also of 2 wt % SDS). Again, the narrowing of T_g and the more pronounced upward shift of the low-temperature T_g end suggest that the low-molar-mass fraction in the sample experiences a more pronounced mobility restriction than the higher molar masses, which indicates a stronger adsorption onto the nanotube walls for these species. This is not observed for PS2-based nanocomposites, which is in line with the presumed lack of adsorption (and with the adsorption mechanism presented below).

Molar Mass Segregation and Nanotube Wetting. The results collected in Figure 4 allow us to propose a mechanism for the way the sample morphology is obtained in the investigated nanocomposites. We suggest that, during compression molding, the low-molar-mass PS is transported from the bulk polymer to the SWNT surface, onto which it adsorbs by partially replacing the SDS molecules. It is well-established that shorter chains preferentially adsorb onto the interface because of their relatively quick diffusion (kinetic effect).[28] This was demonstrated by Carlier et al. in a study on the impregnation of carbon fibers by PS in solution.[29] They reported that when a bimodal PS solution is brought into contact with carbon fibers for 10 s, a preferential accumulation of low-molar-mass PS chains is observed at the fiber surface. A similar process of molar-mass segregation occurs in the nanocomposites, as attested by our observations on the glass-transition region. Further evidence for this process is found in our system when analyzing the small thermal effects that are observed in the MTDSC heat capacity signal (Figure 4). We have reported the melting and crystallization of organic surfactants in organoclay-based nanocomposites.[30] Similarly, the transitions observed in the present SWNT-based nanocomposites can be attributed to the melting and crystallization of a small amount of SDS, at a temperature well below the melting point of pure SDS (T_m of 204 °C). This transition, however, is noticed only when PS of low-molar-mass is present in the system (PS1 and PS3; T_m of about 80−85 °C), or, in case of PS10k (T_m of about 95 °C), when SDS is present in sufficient amount (>5 wt %), as shown in Figure 4. This suggests that the low-molar-mass PS fraction is essential in view of allowing the SDS molecules to organize into a crystalline or micellar structure, which implies migration of the latter mobile PS fraction toward the NT surface and displacement of the SDS molecules, locally present in high concentrations. The position of the melting transition of these organized SDS domains depends on their size and degree of organization, both obviously more perfect in the case of a low-viscosity PS matrix.

After this first step in the mechanism, there might be some additional migration of high-molar-mass PS chains toward the NT−matrix interface, thus enhancing the stabilization of the system. The creation of a gradient of decreasing molar mass with increasing distance from the NTs might even be envisaged. Such a partial replacement of low-molar-mass chains by high-molar-mass chains can explain the rise in the glass transition of PS1 to a value exceeding that of a high-molar-mass PS (100 °C, see PS2 in Figure 4).

We believe that the abovementioned mechanism is essential in view of achieving a better overall thermal and electrical performance of the nanocomposite material. With respect to the thermal properties, a stronger T_g increase can be achieved upon addition of nanotubes when low-molar-mass species are present, even though the initial T_g of the

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unfilled PS is low. This is clearly demonstrated in our PS1/SWNT nanocomposites, where a strong T_g increase is already achieved at a SWNT loading of 2 wt %, whereas a similar increase was achieved only at filler loadings of about 10 wt % (single and multiwall nanotubes) according to other reports on different matrix materials.[31,32] Comparable PS nanocomposites prepared by solution mixing only showed a T_g increase of 3°, but in that case, the matrix material was a fairly monodisperse high-molar-mass PS, obviously not capable of wetting the nanotubes properly.[33] It appears, moreover, that a sufficiently high amount of low-molar-mass species is required in order to achieve good property improvement. Our PS2−SWNT composite shows a T_g increase only after incorporation of oligomeric PS with a DP of 5 (see PS3 in Figure 4), but the T_g increase is smaller than for PS1 because of the larger amount of plasticizing SDS in this sample (see earlier) and the lower weight fraction of oligomeric PS wetting agent present.

With respect to the electrical properties, similar observations can be made. The beneficial effect of the presence of a significant amount of low-molar-mass species in the nanocomposite system is clearly reflected in the electrical conductivity behavior (see four-point conductivity measurements in Figure 3). A significantly higher electrical conductivity is achieved with PS1 as compared to PS2. Similarly, two-point conductivity measurements revealed a higher conductivity level at the PS3−SWNT nanocomposite surface than for PS2−SWNT (about 6×10^{-4} S/cm vs 6×10^{-5} S/cm, respectively, at 2 wt % SWNT loading). The former matrix material contains 2.5 wt % oligomeric PS species.

Two main charge-carrier transport types can have a significant influence over the final properties of a nanocomposite made of a conductive filler dispersed in an insulating polymer: (i) the filler conductivity and (ii) the electron transport through the insulating polymer films surrounding the conductive nanofiller, which prevent the NTs from being in direct contact with one another. Hence, electrons tunnel from one conductive tube to another through an insulating medium, a process characterized by a so-called “contact resistivity”. With respect to the filler conductivity, it is well-established that changes in the electronic structure of SWNTs, hence in the charge-transport mechanism, can be induced by the presence of different types of surfactant[34,35] or (poly)aromatic molecules[36] adsorbed onto their surface. Similarly, our findings suggest that the possible competition between surfactant and low-molar-mass PS adsorption strongly influences the overall electrical conductivity of the nanocomposites. Therefore, we suggest that the electrical conductivity can be maximized only when the matrix polymer is in intimate contact with the NTs, i.e., provided that it displaces adsorbed SDS from the filler surface and accomplishes proper wetting of the conductive nanofiller. This process is obviously facilitated by the presence of low-molar-mass species (as evidenced by the T_g effect, in accordance with our proposed mechanism), resulting in higher conductivity levels but comparable percolation thresholds (PS1 vs PS2).

Conclusions

We have reported that it is possible to efficiently and homogeneously disperse SWNTs into a polymer matrix using latex technology. PS nanocomposites prepared by this versatile and environmentally friendly method display remarkable electrical properties, i.e., a high conductivity level. The investigation of the glass-transition region of the nanocomposites by means of MTDSC has pointed out that the presence of low-molar-mass PS in the system is very beneficial for improved nanocomposite properties. We suggest that this fraction considerably assists the wetting of the filler surface by matrix polymer, as it helps to displace the surfactant molecules adsorbed onto its walls. The occurrence of the latter process is attested by the better overall thermal and electrical performance of nanocomposites based on a matrix containing low-molar-mass species.

Acknowledgment. This research is part of the research program of the Dutch Polymer Institute (Project 416). The work of H. E. Miltner is supported by a grant of the Fund for Scientific Research−Flanders (FWO−Vlaanderen).

CM062998O

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