

Electrical and Mechanical Properties of Carbon Nanotube/Ultrahigh-Molecular-Weight Polyethylene Composites Prepared by a Filler Prelocalization Method

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ABSTRACT: The method of preparation and the properties of conductive composites of ultrahigh-molecular-weight polyethylene with different carbon nanotubes (CNTs) as conductive fillers are presented. The composites were prepared through the covering of the surface of polyethylene granules with CNTs and sintering under optimized conditions. The electrical and mechanical properties of the composites were investigated as functions of the CNT concentration and CNT dispersion process for several kinds of single-walled carbon nanotubes (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). The CNTs were not uniformly dispersed in the composites but were prelocalized on the granule boundaries, very efficiently forming conductive networks. It was, however, critically important to ensure the good dispersion of the nanotubes in the microscale, and this was performed by sonication in sol-

vents before dry mixing. Ultralow percolation thresholds were obtained: 0.095 wt % for SWCNTs and 0.05 wt % for MWCNTs (ca. 0.045 vol % for SWCNTs and 0.021 vol % for MWCNTs). The critical exponents were higher than those for uniformly dispersed conductive particles: 2.2 and 2.6 for SWCNTs and for MWCNTs, respectively. The mechanical properties of the composites were also strongly modified by the presence of CNTs. The modulus and ultimate strength increased by about 100% with 2% CNTs. The elongation at break decreased but was still about 500–1000%. Near the electrical percolation threshold, the mechanical properties were not significantly modified. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 158–168, 2007

Key words: mechanical properties; nanocomposites; sintering

INTRODUCTION

Polymer composites, combining the properties of two or more materials, are widely used in technology because their characteristics can be tailored for particular applications. Practically all polymers produced on a large scale are insulators. Thus, the modification of the electrical properties, particularly to make a polymer material conductive, is possible mostly through the preparation of composites with conductive fillers. Such composites exhibit percolation-type behavior: charge transport takes place through contact of filler particles.^{1,2} Conductive poly-

mer composites with a low percolation threshold have attracted great attention because of their potential applications in industry. Several methods of obtaining such composites have been developed. One of the best is the so-called filler prelocalization method (also called the segregated network concept). According to this method, the filler is not homogeneously dispersed in the polymer matrix, but a three-dimensional (3D) continuous network of filler-rich layers is formed within the polymer. This can be obtained by the hot compaction of mixtures of polymer powders and conductive fillers such as carbon black,³ TiN and TiC,⁴ and graphite.⁵ In such materials, the overall concentration of the filler can be significantly reduced.

Since the discovery of carbon nanotubes (CNTs)⁶ and the determination of their high electrical conductivities and excellent mechanical properties,^{7–9} which are particularly important in nanocomposites, they have been considered very promising conductive fillers. The progress in CNT preparation methods in recent years and the constantly decreasing price have made composites involving nanotubes (NTs) more and more attractive.

This article is dedicated to the memory of Professor Marian Kryszewski.

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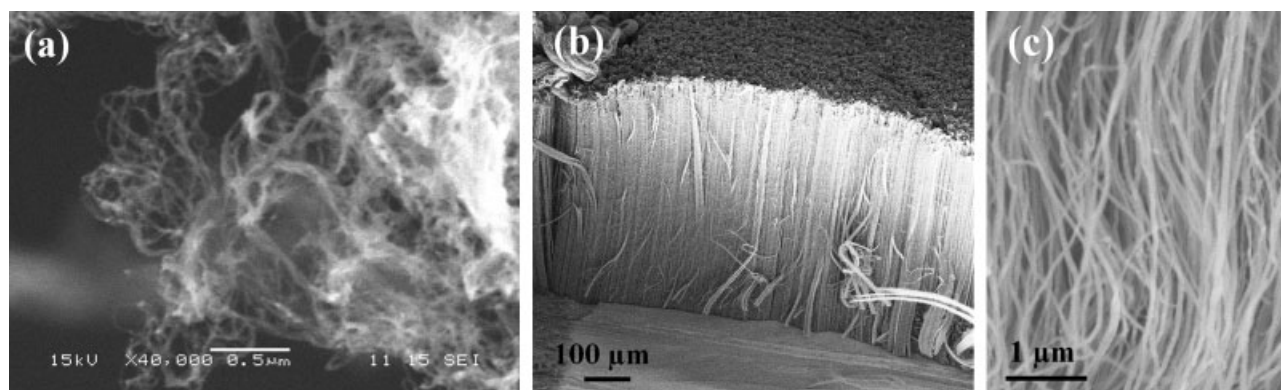


Figure 1 SEM micrographs of (a) SWCNTs and (b,c) MWCNTs produced by the CCVD method.

Many polymer composites with CNTs have been obtained to date.^{8,10–15} Conductive polymer/CNT composites can be obtained at extremely low filler contents because of a large CNT aspect ratio (even >1000). A wide range of values of percolation thresholds and conductivities of CNT composites has been reported, depending on the processing method, polymer matrix, and the CNT type. However, a comparison of the literature data is difficult, and contradictory results can be found because various kinds of CNTs and different preparation methods have been used by different authors.

In this article, we report both on the preparation and on the electrical and mechanical properties of CNT/ultrahigh-molecular-weight polyethylene (UHMWPE) composites. The composites were prepared with the filler prelocalization approach with various kinds of CNTs and different CNT dispersion methods. The composites obtained with the optimal preparation procedure showed ultralow percolation thresholds and good mechanical properties.

EXPERIMENTAL

Materials

UHMWPE (GUR 4120; $M_w = 2000$ kg/mol), purchased from Hoechst Celanese (Somerville, NY), was used as received. It was supplied as a powder with a number-average particle size of $150\ \mu\text{m}$ and showed a typical complex, cauliflower-like morphology.¹² *N,N*-Dimethylformamide (DMF), sodium dodecyl sulfate (SDS), and ethanol (EtOH) were purchased from Aldrich (ACS reagent) and used as received.

Single-walled carbon nanotubes (SWCNTs) were purchased from Aldrich (Milwaukee, WI) [SWCNT diameter = $1.2\text{--}1.5$ nm, purity = $50\text{--}70$ vol %, as determined by Raman spectroscopy and scanning electron microscopy (SEM) according to the producer's declaration] or kindly provided by J. Friedrich (Federal Institute for Material Testing, Berlin, Germany; produced by the arc-discharge method in

a helium atmosphere with a nickel/yttrium catalyst). The high-grade material [Fig. 1(a)] consisted mostly of SWCNTs, and the low-grade material contained significant amounts of amorphous carbon, but the precise purity was not known. SEM images show entangled bundles of CNTs $10\text{--}50$ nm thick [Fig. 1(a) and Fig. 1 in ref. 12].

Aligned multiwalled carbon nanotubes (MWCNTs) were synthesized by aerosol-assisted catalytic chemical vapor deposition (CCVD) from toluene/ferrocene solutions.^{16,17} Figure 1(b) shows a section of a CNT layer that grew on a substrate, looking like a carpet. The CNTs were aligned nearly perpendicularly to the carpet base. The purity of the CNTs was very high because they contained almost no byproducts [Fig. 1(c)]. Their length was about $540\ \mu\text{m}$, and their outer diameter varied over a wide range ($10\text{--}120$ nm), with a majority of the tubes in a $35\text{--}60$ -nm range. The total amount of iron in the sample was about 3 wt %.

Dispersion of CNTs

To dissociate and separate the CNTs forming carpets (MWCNTs) or bundles (SWCNTs), external mechanical energy was supplied from ultrasound with an ultrasonic probe. In addition, in some cases, a surfactant was used to improve the wettability of NTs by the liquid and to stabilize the suspension.¹⁸ The dispersion was performed in different liquid media: distilled water with 1 wt % anionic surfactant (SDS), DMF, and EtOH. Different dispersion procedures involving the variation of the duration and ultrasound power were tested. Their efficiency was determined with respect to the CNT dispersion state by optical microscopy, and the CNT concentration in the suspension was determined by ultraviolet–visible absorption measurements.¹⁹ The best dispersion conditions were found to be 200 min of a pulsed ultrasonic treatment (sonication for 1 s followed by a stop for 1 s to avoid heating) at 260 W for single-walled nanotubes (SWNTs) and multiwalled nanotubes (MWNTs). The same optimized sonication param-

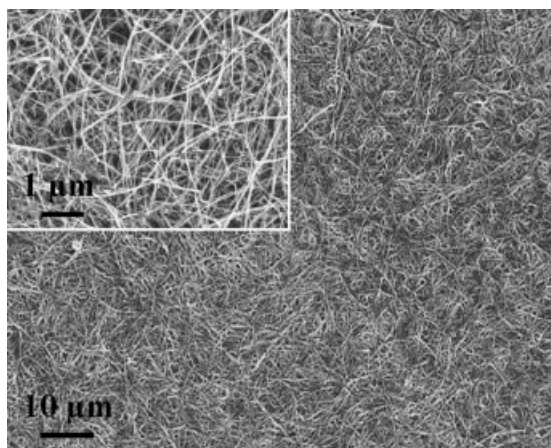


Figure 2 SEM micrograph of MWCNTs after their dispersion in DMF and drying.

ters were obtained for dispersions of MWNTs and SWNTs in EtOH, water/SDS mixtures, and DMF. A typical SEM image of MWCNTs dispersed in DMF and dried is shown in Figure 2. It shows randomly oriented and loosely entangled MWCNTs. CNTs were also broken by ultrasound, and the length of the MWNTs after the optimized dispersion was in the 5–20- μm range. As for SWNTs, it was more difficult to estimate their arrangement and length after dispersion because of their small thickness, which made them difficult to observe in larger areas.

Water/SDS was the best dispersing medium for the MWCNTs because the stability of the suspension was really longer than that of the other liquid media. However, it had the disadvantage that SDS remained in the composites after drying.

Nanocomposite preparation

The method of preparation of the polyethylene (PE)/CNT composites was based on the segregated network concept with prelocalization of the CNTs on the PE granule surface.^{3,4,12} The composites were prepared through the mixing of polymer microgranules with CNTs followed by sintering.

Two different methods were employed to disperse CNTs and mix them with the polymer. The first method (procedure dry mixing-sintering) consisted of dry mixing as-received CNTs and UHMWPE in a mortar. The second method (procedure liquid dispersing-dry mixing-sintering) involved a preliminary dispersion of CNTs in a liquid medium (a nonsolvent for PE), followed by the addition of polymer granules and drying (*in vacuo* at 80°C overnight). The dried material was then mixed in a mortar to homogenize the dried mixture. Figure 3(a) shows SEM pictures of a single polymer granule (much smaller than average) covered with MWCNTs after dry mixing.

After the dispersion and mixing steps, the mixture was sintered. Sintering was performed by unidirectional hot pressing. Figure 3(b) shows dispersed MWCNTs inside the polymer matrix after sintering. In Figure 4, the morphology on the fracture surface of the conductive nanocomposite with SWCNTs (Aldrich) is shown. In this case, CNTs could also be seen, but because of their small thickness compared with that of MWNTs, they were much more difficult to observe.

Nanocomposite characterization

The electrical resistivity of the UHMWPE/CNT composites was measured with a Keithley 195A digital multimeter (Cleveland, OH). The resistivity of the conductive samples above the percolation threshold was measured with the four-probe method, which eliminated errors resulting from contact resistance. The sample size for the measurement of the electrical properties was 9 mm \times 3 mm \times 1 mm. Before the attachment of the electrodes, the surface of the sample was polished with sandpaper. Thin metal-wire electrodes were attached with silver paint. In the case of low-conducting samples, the conductivity was

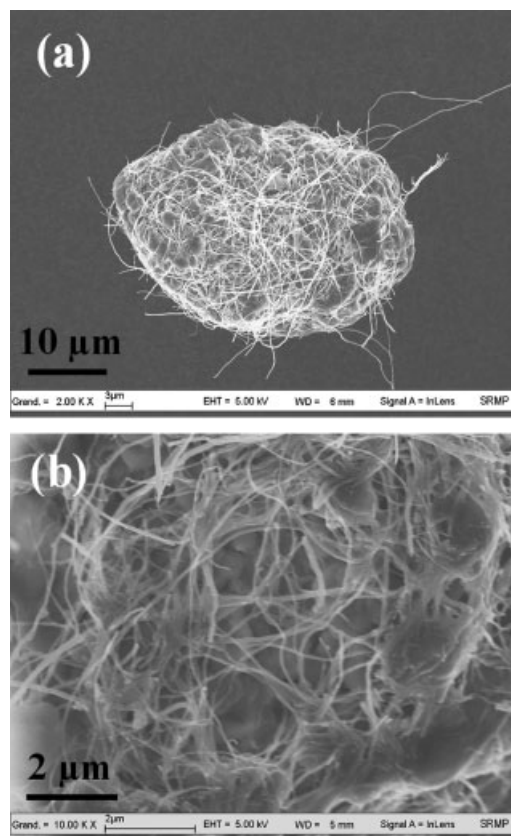


Figure 3 SEM images of (a) a UHMWPE granule covered by MWCNTs after dry mixing before sintering and (b) a cross section of the sintered sample.

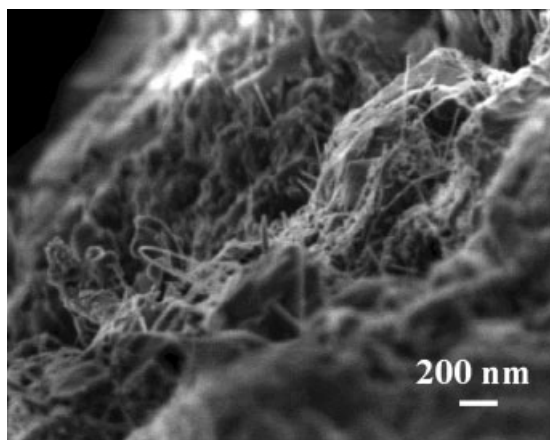


Figure 4 SEM image of the fracture surface of an SWCNT/UHMWPE composite.

measured in the planar configuration with evaporated metal electrodes (0.5 cm^2). The values of the conductivity corresponded to the ohmic range of the current–voltage characteristics (up to ca. 10^2 V/cm).

The mechanical properties were investigated with an Instron electromechanical testing machine. For each CNT concentration, several samples were measured under the same conditions. Tensile testing of dog-bone-shaped specimens (central part = $4.5 \times 25 \text{ mm}^2$) was performed at room temperature and at a constant crosshead rate of 10 mm/min . A JEOL JSM-500 scanning electron microscope was used to study the morphology of the CNTs and composites.

RESULTS

Effects of the processing conditions on the electrical conductivity

The electrical properties of nanocomposites obtained under different elaboration conditions are significantly different. Therefore, the effects of the sintering temperature and pressure, dry-mixing duration, and CNT contents were investigated to determine the optimal preparation conditions.

Sintering temperature

It is well known that the sintering temperature is one of the most important processing parameters and can significantly influence the electrical conductivity of composites.^{3,4,12,20}

Figure 5 shows the dependence of the direct-current electrical conductivity of UHMWPE/SWCNT composites containing 2 or 3 wt % SWCNTs (Aldrich) obtained with DM-S and LD-DM-S procedures as a function of the processing temperature. The composites were sintered for 15 min at 5 MPa. The conductivity of the materials decreases with

increasing sintering temperature. This is probably caused by a higher degree of intermixing of the CNTs and polymer chains in the interfacial regions as a result of the lower viscosity of the polymer at higher temperatures. Polymer chains penetrate between CNTs, increasing the contact resistance. A similar effect of the sintering temperature was obtained by other authors.²⁰

Figure 5 also shows that the preliminary dispersion of CNTs in EtOH before dry mixing does not have a significant influence on the dependence of the electrical conductivity of the composites on the sintering temperature. However, the conductivity increases from 10^{-5} to 10^{-3} S/cm after the dispersion of CNTs.

According to these results, the optimal temperature to prepare UHMWPE/CNT composites should be about 140°C . It is slightly below the melting temperature of pristine PE, as determined by differential scanning calorimetry (DSC) at 10 K/min . The DSC curves of the composites show, however, a lower melting temperature (137°C and no peak around 145°C), indicating that all the PE was molten during the sintering process.²¹

Sintering pressure

Figure 6 shows the electrical conductivity of the UHMWPE/CNT composites containing 2 or 3 wt % CNTs as a function of the processing pressure at 140°C for the two dispersion procedures described. These results show that the effect of the sintering pressure is similar for the investigated CNT concentrations and dispersion procedures. The electrical

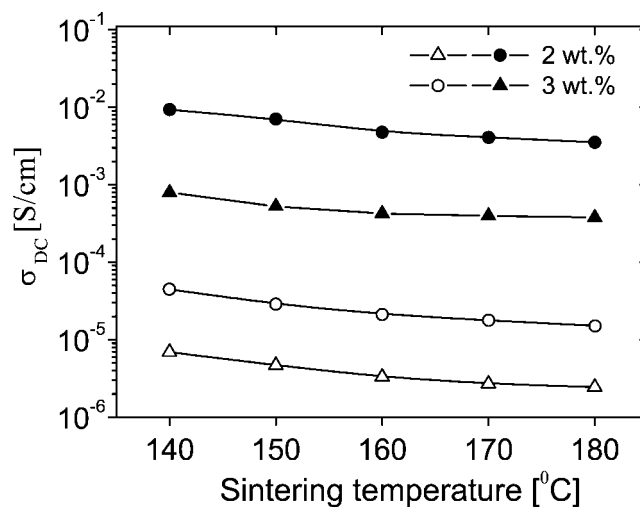


Figure 5 Logarithm of the direct-current electrical conductivity (σ_{DC}) of UHMWPE/SWCNT composites containing 2 or 3 wt % SWCNTs as a function of the processing temperature. The composites were obtained with the DM-S procedure (empty symbols) or the LD-DM-S procedure (filled symbols; the solvent was EtOH).

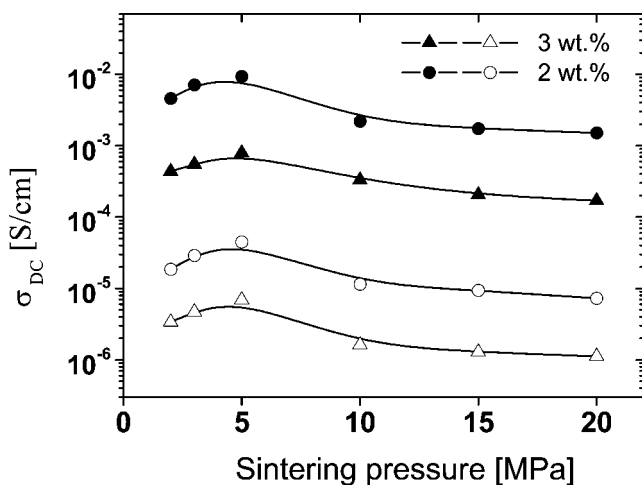


Figure 6 Logarithm of the direct-current electrical conductivity (σ_{DC}) of UHMWPE/SWCNT composites containing 2 or 3 wt % SWCNTs as a function of the processing pressure. The composites were obtained with the DM-S procedure (empty symbols) or the LD-DM-S procedure (filled symbols; the CNTs were dispersed in EtOH).

conductivity slightly increases with the processing pressure when it is lower than 5 MPa and then decreases as the processing pressure is further increased. These results are similar to those found for UHMWPE/ceramic composites⁴ but quite different from those obtained for UHMWPE/carbon black, for which the processing pressure has been found to be an unimportant parameter in the pressure range considered (13.4–44.2 MPa).²²

In our case, the decrease in the conductivity of the UHMWPE/CNT composites due to the increase in the processing pressure can be ascribed to the breaking of some CNTs if the sintering pressure is too high. A reduction of the number of conductive paths in the interfacial regions results in a decrease in the conductivity. The optimal pressure to prepare the UHMWPE/CNT composites was found to be about 5 MPa, and it was used in the systematic studies discussed later.

Dry-mixing time

The effect of the dry-mixing time on the conductivity of the UHMWPE/CNT composites containing 2 or 3 wt % SWCNTs (processing temperature = 140°C, pressure = 5 MPa) is shown in Figure 7.

The dry-mixing time has a significant influence on the electrical conductivity of the composites. As the mixing time is increased, the electrical conductivity initially increases and then reaches a maximum value, which is followed by a slight decrease. Similar behavior was observed for UHMWPE/ceramic composites.⁴ This phenomenon can be understood in the following way. During dry mixing, several pro-

cesses take place at the same time: the mixing of the CNTs with UHMWPE powder, the dispersion of the CNT material on the surface of the PE granules, the breakup of the CNT aggregates and bundles by shear forces, and the possible breakup of individual CNTs. As the dry mixing time is increased, the first two processes result in more and more homogeneous dispersions of the CNTs in the interfacial regions between the UHMWPE particles, building up more conductive paths in these regions and leading to an increase in the electrical conductivity of the obtained composite. At the same time, breaking up the individual CNTs reduces their aspect ratio and thus the network connectivity. When the dry-mixing time is longer than 15 min, the last process probably dominates, and the conductivity of the composite decreases. It is also possible that during prolonged mixing, more and more of the CNT material is transferred from the granule surface to the voids in the cauliflower-like structure, and this makes it practically useless for the formation of the conductive network.

Thus, the optimal dry mixing time for the UHMWPE/CNT composites, based on the results shown in Figure 7, is about 15 min.

CNT contents

Figure 8 presents a plot of the electrical conductivity versus the mass fraction of the composites with SWCNTs and MWCNTs dispersed by dry mixing only (the DM-S procedure). In all cases, the conductivity increases dramatically above a certain CNT concentration (p) as a result of percolation of the conductive

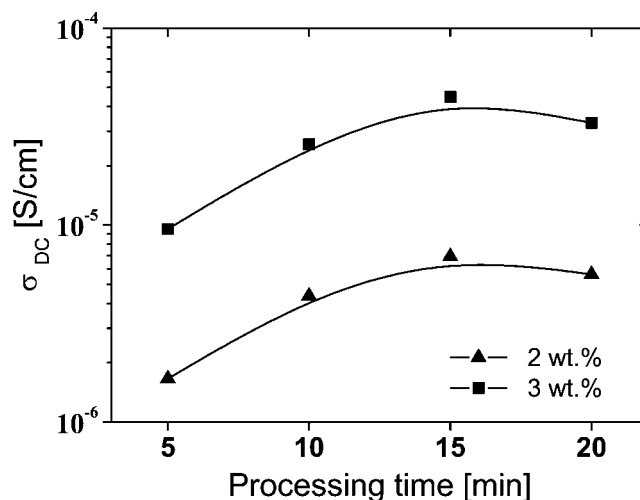


Figure 7 Logarithm of the direct-current electrical conductivity (σ_{DC}) of UHMWPE/SWCNT composites containing 2 or 3 wt % SWCNTs plotted as a function of the dry-mixing time.

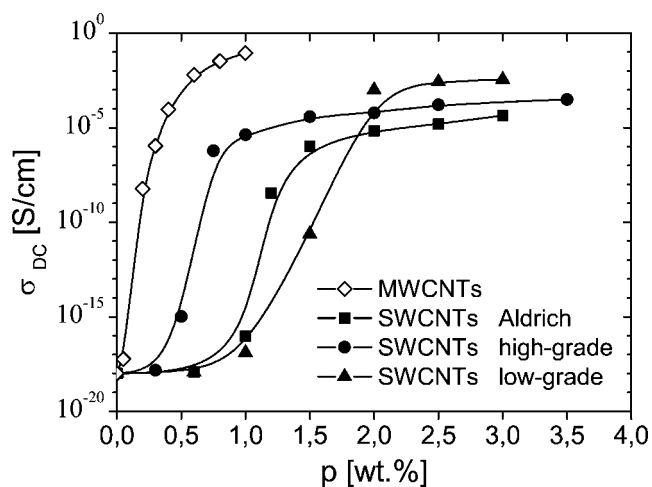


Figure 8 Direct-current electrical conductivity (σ_{DC}) versus the CNT concentration (p) in UHMWPE for MWCNTs and SWCNTs of different origins. The composites were obtained with the DM-S procedure.

phase. According to the percolation theory,^{1,2,23} the increase in the conductivity above the critical concentration (p_C ; i.e., the percolation threshold) can be described by the following equation:

$$\sigma_{(p)} = \sigma_0(p - p_C)^t \quad (1)$$

where $\sigma_{(p)}$ is the percolation conductivity; σ_0 is a pre-factor of the order of filler conductivity; and t denotes a critical exponent, which in principle depends on the dimensionality of the system and not on the detailed model (e.g., bond or site percolation or network connectivity). It should be equal to about 1.1 for two-dimensional (2D) systems and 1.65 for 3D systems (discussed later). In Figure 8, we can see that p_C depends considerably on the kinds of NTs used. The lowest p_C value was obtained for MWCNTs. In the case of SWCNTs, p_C depends considerably on the kinds of CNTs. High-grade SWCNTs are significantly better than the Aldrich product and the low-grade material. The difference is certainly related also to the CNT material purity and CNT length, but the most important factor seems to be the degree of CNT agglomeration and entanglement in the CNT material, which makes homogeneous dispersion difficult during the dry-mixing process.

The dispersion of CNTs in the composites should be improved by the preliminary dispersion of CNTs in a liquid medium before dry mixing (the LD-DM-S procedure). The effect of such an additional treatment is shown in Figure 9(a,b) for SWCNTs (Aldrich) and MWCNTs (CCVD).

Figure 9 presents a plot of the direct-current conductivity versus the mass fraction of CNTs in the composites prepared after the preliminary dispersion

of the NTs in EtOH, DMF, or a water/SDS mixture. The dispersion procedure has a significant influence on the electrical conductivity of the composites with both kinds of CNTs. The effect, is however, much stronger in the case of the SWCNTs. After the preliminary dispersion of the CNTs in DMF, the composite achieves a p_C value below 0.1, whereas for the composite with SWCNTs without the dispersion, this value is equal to 1.24. As for the composites with MWCNTs, p_C changes from 0.3 to 0.045.

According to eq. (1), the values of p_C and t can be determined from the slope of the plot of the conductivity versus $p - p_C$ on a double-logarithmic scale. An example of such a plot is shown in Figure 10, and the values of p_C and t for the composites obtained with various CNTs and dispersion methods are collected in Table I.

The points at the 100% CNT concentration in Figure 10 correspond to pressed pellets of CNTs

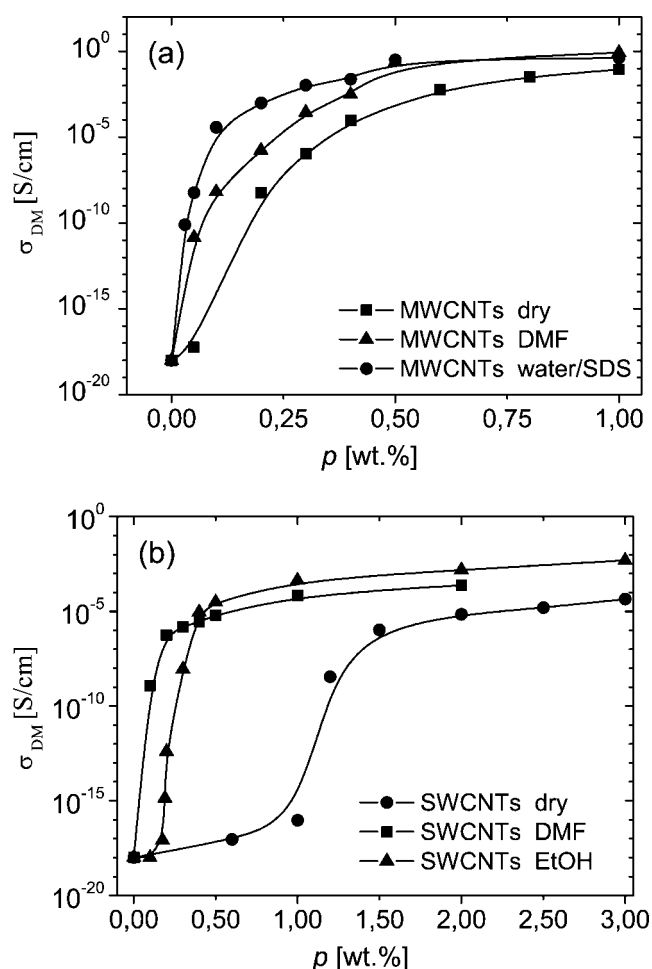


Figure 9 Conductivity versus the CNT content (p) in composites obtained with the DM-S and LD-DM-S procedures: (a) SWCNTs and (b) MWCNTs.

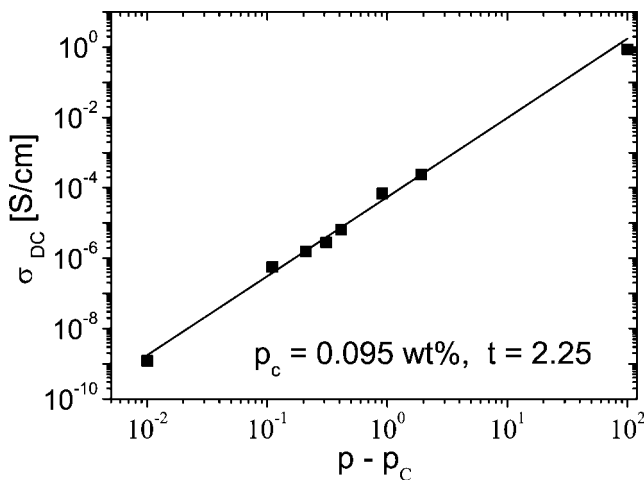


Figure 10 Direct-current electrical conductivity (σ_{DC}) above the percolation threshold versus $p - p_c$ for UHMWPE with SWCNTs from Aldrich in DMF.

without the polymer made under the same conditions. They are of the same order as that given by other authors for CNT mats.²⁴

The p_c values of 0.09 wt % for composites with SWCNTs and 0.045 wt % for the composites with MWCNTs obtained in the experiments are very small compared with the values for the percolation on random networks.^{1,2,23} These small values can be ascribed primarily to the large aspect ratio of the CNTs, which is around 1000–5000, and to the nonhomogeneous dispersion of the filler in the bulk due to its prelocalization on the granule interfaces.

The values of exponent t for our CNT composites are higher than those predicted by the percolation theory for the 3D case (equal to 1.65^{1,2,23}) and higher than those obtained for other CNT composites. This point is discussed later.

The differences in the conductivities above the percolation threshold, observed for the investigated composites (Fig. 8), are most likely related to better or worse dispersion of the starting material. In particular, SWCNTs are only partially disentangled during dry mixing. The low-grade SWCNT material

TABLE I
 p_c and t Values of UHMWPE/SWCNT and UHMWPE/MWCNT Composites Obtained with Different Elaboration Processes

Filler	p_c (wt %)	t
High-grade SWCNTs	0.60	2.18 ± 0.04
Low-grade SWCNTs	1.10	2.33 ± 0.15
SWCNTs from Aldrich	1.20	2.19 ± 0.11
SWCNTs from Aldrich in ETOH	0.25	2.20 ± 0.14
SWCNTs from Aldrich in DMF	0.09	2.25 ± 0.05
MWCNTs	0.28	2.65 ± 0.13
MWCNTs in DMF	0.19	2.67 ± 0.25
MWCNTs in water/SDS	0.045	2.63 ± 0.12

gives composites with the highest percolation threshold but also the highest conductivities at high loadings (>2 wt %). This can be explained by the presence of particles of conductive amorphous carbon, which have a low aspect ratio but being conductive contribute to network formation at sufficiently high loadings. The highest conductivities and the lowest percolation thresholds obtained for the MWCNT composites are due to their better dispersion as well as their greater length and higher purity.

Mechanical properties

Young's modulus

Figure 11 shows the elongation modulus as a function of the CNT content for UHMWPE/MWCNT composites prepared with two CNT dispersion procedures (DM-S and LD-DM-S) with different solvents. A general tendency is that with an increase in the filler content, the Young's modulus increases, but

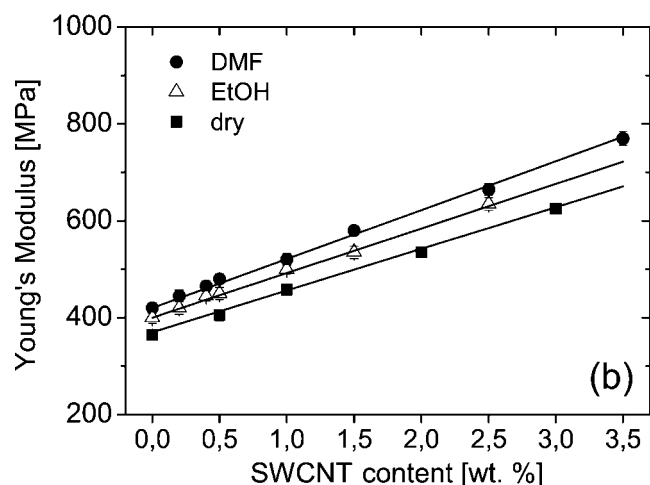
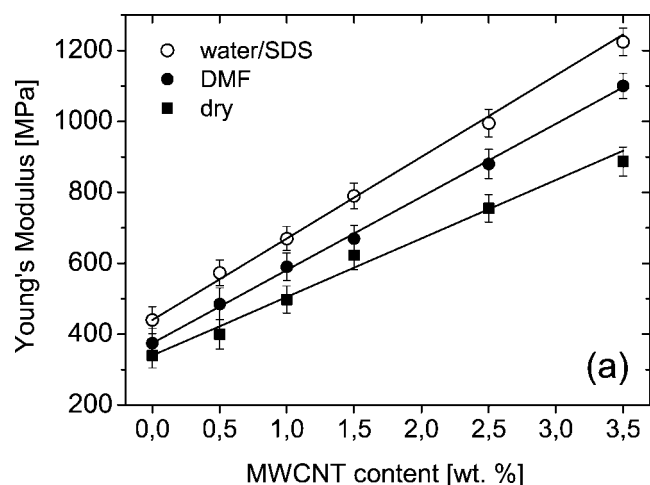


Figure 11 Young's modulus of UHMWPE/CNT composites versus the filler content: (a) composites with MWCNTs and (b) composites with SWCNTs.

the increase is much higher in the case of MWCNT composites, especially those prepared with water/SDS. At the maximum MWCNT content (3.5 wt %, dispersed in water/SDS), the UHMWPE/MWCNT composite has a Young's modulus 30% higher than that of the composite prepared by dry mixing and 10% higher than that of the composite prepared after the preliminary dispersion of CNTs in DMF.

The UHMWPE/MWCNT composite with 3.5 wt % MWCNTs has a Young's modulus of 1200 MPa, showing a 220% increase over that of the pure polymer matrix and a 150% increase over that of the composite containing 3.5% SWCNTs. Pure UHMWPE, treated with the same solvents, also shows a slightly higher Young's modulus. This suggests that the solvent treatment has some influence on the properties of the polymer matrix itself, resulting in a more effective interpenetration of polymer chains on the PE granule interfaces.

The same trend was observed when SWCNTs were used as conductive fillers. Figure 11(b) displays the Young's modulus of UHMWPE/SWCNT composites versus the SWCNT content. The composite material was prepared with the same procedures as the composites with MWCNTs. The highest Young's modulus was obtained when SWCNTs were dispersed in DMF.

The stiffening effect is more evident in the composites with MWCNTs in comparison with the SWCNT composites. This could be due to the fact that MWCNTs are longer and more resistant against cutting or tearing during the dispersion and sintering and thus serve as better reinforcements for the UHMWPE matrix.

The linear dependence on the CNT content might suggest the applicability of the so-called rule of mixtures,²⁵ that is, the additivity of the moduli of the filler and of the matrix. The moduli of the CNTs obtained by extrapolation to $p = 100\%$ are about 10 and 20 GPa for SWCNTs and MWCNTs, respectively. They are by 2 orders of magnitude lower than the theoretical and experimental values (>1 TPa) and even the value of CNT rope (mean value ≈ 250 GPa). They are also lower than that of the polymer/CNT interface (estimated to be >500 GPa; see refs. 7–9 and references therein). This is not surprising if we take into account that most of the NTs are not properly aligned and that the adhesion between the CNTs and PE matrix is too weak to ensure sufficient load transfer. Thus, the assumptions of the rule of mixtures are not fulfilled.

Tensile yield strength of the composites with CNTs

The yield strength of the UHMWPE/MWCNT composites as a function of the filler content is shown in Figure 12(a,b). The yield strength increases with increasing NT content. The yield strength of the

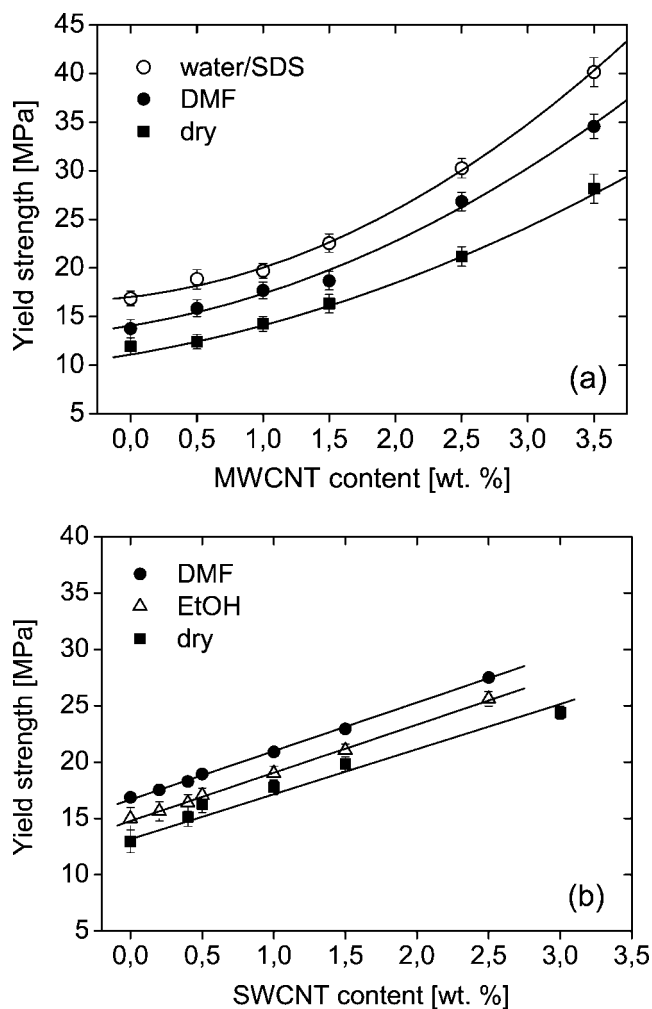


Figure 12 Yield strength of UHMWPE/CNT composites versus the filler content: (a) composites with MWCNTs and (b) composites with SWCNTs.

composites increases with the CNT concentration and depends on the dispersion process. The UHMWPE/MWCNT composite with 3.5 wt % MWCNTs has a yield strength of 40 MPa, showing a 170% increase over that of the pure polymer matrix and a 150% increase in the yield strength over that of the 3.5% SWCNT composite. The enhanced performance of the composite with MWCNTs may be attributed to the better dispersion in the PE matrix and possibly also to better interfacial bonding between the MWCNTs and the polymer, which allows more effective load transfer from the matrix to the MWCNTs.

Ultimate tensile strength

Figure 13 displays the ultimate tensile strength of UHMWPE/MWCNT composites and UHMWPE/SWCNT composites versus the CNT content. It decreases with an increasing CNT loading for both

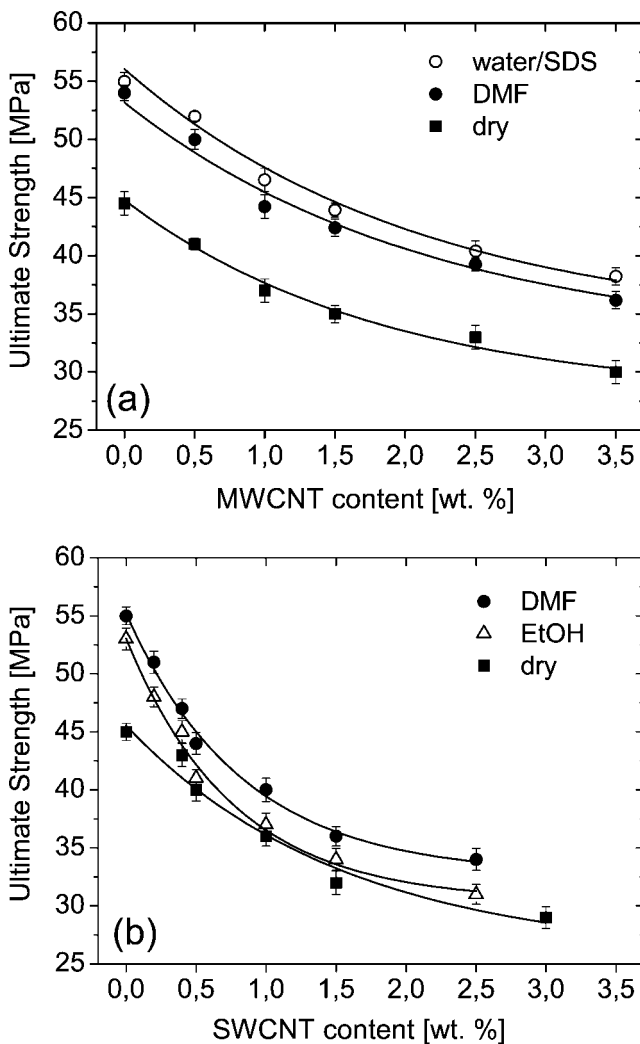


Figure 13 Ultimate strength of UHMWPE/MWCNT composites versus the filler content: (a) composites with MWCNTs and (b) composites with SWCNTs.

kinds of CNTs, regardless of the CNT dispersion procedure. This observation is in contrast to the typical behavior of fiber-reinforced composites and also some composites with CNTs.²⁶ However, the yield strength increases, as expected, and the elongation at break is very high (discussed later). The CNT agglomerates present in the composites probably can cause cracks to initiate and propagate more easily than in pure PE. It is also possible that adhesion between the CNTs and PE decreases at high elongations. The well-dispersed MWCNTs are more efficient than the aggregated SWCNTs in load transfer.

Elongation at break

Figure 14(a,b) shows plots of the elongation at break of UHMWPE/MWCNT and UHMWPE/SWCNT composites as a function of the CNT content. The elongation at break decreases when the content of

CNTs increases. This decrease is relatively fast for low concentrations of SWCNTs and levels off above 1 wt.%. In the case of MWCNTs, the decrease in the elongation at break is slower. The UHMWPE/MWCNT composite with 1.5 wt % MWCNTs has an elongation at break of 1100%, showing a 30% decrease with respect to the pure polymer matrix, whereas a 50% decrease can be observed for the SWCNT composite with the same loading.

DISCUSSION

In the composites prepared according to the segregated network concept, we obtain a particular morphology of the conductive network: a foamlike, 3D network of interfaces between polymer granule surfaces (shells) and an almost 2D network of NTs within the shell. The length scale of the foamlike network is 50–100 μm , and that of the 2D network is of the order of the entangled CNT length, that is, below

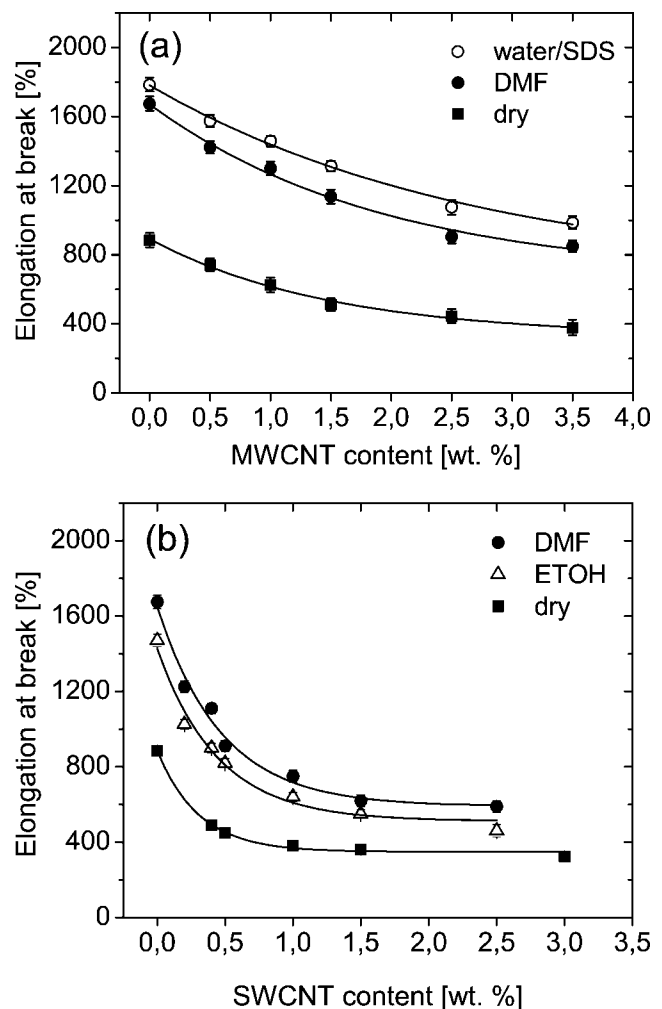


Figure 14 Elongation at break of composites with (a) MWCNTs and (b) SWCNTs obtained at different weight percentages for different elaboration processes.

0.5 μm and about 5 μm for SWCNTs and MWCNTs, respectively.

The thickness of the CNT-rich shell is difficult to estimate. CNTs stick to PE mostly parallel to its surface. The viscosity of UHMWPE is very high, and it is additionally increased in the interface region because of the presence of CNTs.^{11,14,15} In a high-molecular-weight polymer melt, the CNTs can be regarded as rigid chains, and by analogy to the reptation model, their displacements in directions perpendicular to their long axes are strongly hindered. The moves analogous to reptation (along the long CNTs axes) are also not as effective as those in the case of flexible chains because of the lack of random short-range displacements described in the case of flexible chains by the Rouse model.²⁷ The decrease in the conductivity with the sintering time and temperature indicates, however, that the polymer chains penetrate between the CNTs to some extent. Thus, we can expect the CNT-rich shell to be very thin, that is, of the order of a few CNT widths (if a big agglomerate is not present in some particular place). It is, however, not flat because it is formed by highly structured UHMWPE granules together with complex, fractal-like surfaces being pressed together.

Because CNT diffusion is extremely slow, we can assume that the continuous network of CNT-rich intergrain layers exists even at small CNT contents and that the layer thickness is dependent on the sintering conditions but not much on the CNT content (in the investigated range). It is also reasonable to assume that the average nonhomogeneity of the shell is the same for different CNT loadings, as it depends mostly on the initial UHMWPE morphology and processing conditions.

The concentration of the CNTs and network connectivity must be different in different regions of the shell network because during the dry-mixing process, certainly some of the CNT material enters the voids on the PE granule surface. One should also keep in mind that during the sintering process, the granules are deformed to fill empty spaces between them, so the surface concentration of the filler does not become uniform on a bigger scale: the surface layer is nonuniformly extended as the polymer penetrates initially empty spaces, so the filler concentration per unit of area decreases in some places. Most of the PE, inside the granules, is far from the CNT-rich surface, and its properties are not influenced by the presence of the CNTs, as shown by DSC and X-ray diffraction measurements.²¹ This complex morphology should be taken into account for a consideration of the electrical and mechanical properties.

Considering the electrical conductivity, we deal in such a case with two kinds of percolation. One can be called *intershell percolation* and refers to 3D percolation of conductive filler-rich layers on the surface

of the polymer granules. The second is *intrashell percolation* and should be regarded as 2D percolation. The conductivity is controlled by the number and resistance of the contacts between individual CNTs.

Thus, in an analysis of the percolation process, we should take into account that the CNT concentration influences both percolation phenomena, that is, the fraction of conductive regions that can percolate in the 3D network and the 2D conductivity of these regions. Therefore, we can write the following:

$$\sigma = \sigma_0(p_3 - p_{c3})^{t_3}(p_2 - p_{c2})^{t_2} \quad (2)$$

where σ is the conductivity; p_3 and p_2 denote the concentrations of the conductive elements in the 3D and 2D networks, respectively; p_{c3} and p_{c2} are the percolation thresholds for the 3D and 2D networks, respectively; and t_3 and t_2 are the corresponding exponents. In the 2D network, the conductive elements are simply CNTs (or their agglomerates), and in the 3D network, they are bigger regions in which the NT concentration is above the percolation threshold. The fraction of conductive elements in the 3D network must be also related to the CNT content. Assuming that the CNT concentration has a similar influence on both percolation processes, we can write the following:

$$\sigma \propto (p - p_c)^{t_3+t_2} \approx (p - p_c)^t \quad (3)$$

where p is the average NT concentration.

A result of such a model is that the value of t is expected to be of the order of $t_3 + t_2$, certainly higher than that for a 3D case with a random distribution of conductive elements.

Taking the literature data for random 2D and 3D networks (1.65 and 1, respectively^{1,23}), we should expect t to be of the order of 2.6. Indeed, our analysis gives $t \approx 2.2$ for SWCNTs and $t \approx 2.6$ for MWCNTs, and the results reported by other authors for similar systems are similar: 2.78²⁰ or even higher than 3.⁵ On the contrary, in the polymer/CNT composites, in which the NTs are believed to be randomly dispersed, t is close to 1.65, as expected for a 3D case.^{10,11}

The mechanical properties should also be discussed with the composite morphology taken into account. In particular, NTs reinforce only this foam-like network of granule interfaces, a small fraction of the composite volume. It can be estimated to be not more than 10% of the volume, so these layers must have a modulus and ultimate strength higher by at least an order of magnitude. In principle, we could expect some percolation effect also in the mechanical properties as it was found in polycarbonate/CNT composites.¹³ This has not been observed, most likely because the contribution of the CNT-reinforced

fraction is too small even above the percolation threshold because of the dominant contribution of pure PE inside the granules. In the case of the electrical properties, the difference in the conductivities of the filler and the matrix is immense: about 20 orders of magnitude. Therefore, above the percolation threshold, the conductivity of the matrix has a negligible contribution to the conductivity of the composite. The difference in the mechanical properties is much smaller, and the matrix always plays an important role, being necessary to provide load transfer between the CNTs. The changes in the mechanical properties are therefore much smaller, and percolation behavior at low loadings cannot be observed.

In comparison with PE/MWCNT composites (uniformly dispersed CNTs),¹¹ the increase in the yield strength with the NT concentration is much stronger (2.4 times at 3.5 wt % vs 1.2 times), and so is the elongation at break (decreases 1.8 times vs 1.4).

It should also be noted that the elongation at break of composites with good conductivity is very high (of the order of 1000 and 500% for composites with MWCNTs and SWCNTs, respectively), and composites deformed by 300% or even more are still conductive, although the relationship between the elongation and conductivity and its possible anisotropy has not been investigated in detail yet. The mechanical properties could be significantly improved if the preparation conditions were optimized from this point of view. It would be, however, at the expense of the electrical conductivity, and detailed studies are beyond the scope of this work.

CONCLUSIONS

Conductive CNT/UHMWPE composites with ultra-low percolation thresholds can be obtained through the sintering of UHMWPE granules covered with CNTs under optimized conditions. The conductivity and percolation parameters depend on the sintering conditions, on the types of CNTs, and their dispersions. The most important factor is the preliminary dispersion of the CNT material. After the sonication of CNTs in a liquid medium, the percolation threshold decreases by about an order of magnitude. The mechanical properties of the obtained composites are also significantly improved by the NTs, despite their low concentration, but a substantial effect is observed above 1 wt %, that is, well above the electrical percolation threshold.

MWCNTs give composites showing better electrical and mechanical properties than SWCNTs, and this seems to be due to their higher length, mechanical

resistance, and stiffness and also to the low agglomeration in the as-obtained material.

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