

## Dispersion and rheological aspects of SWNTs in ultra high molecular weight polyethylene

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**Abstract:** A new method is developed to homogeneously disperse single-walled carbon nanotubes bundles (SWNTs) in an intractable polymer, for example, ultrahigh molecular weight polyethylene ( $M_w > 3 \times 10^6$  g/mol) (UHMWPE). The dispersion is obtained by spraying an aqueous solution of SWNTs onto a fine UHMWPE powder directly obtained from synthesis. The SWNTs are adsorbed on the surface of the polymer powder. Crystallization of the UHMWPE melt followed by rheometry shows that the presence of SWNTs enhances the overall crystallization rate. The observed rheological behavior of the UHMWPE/SWNT nanocomposites is rather unusual. Varying the content of SWNTs the dynamic viscosity/storage modulus shows a minimum. The decrease in viscosity is attributed to the selective adsorption of the high molar mass fraction onto the nanotubes surface. The increase in viscosity upon further increasing the nanotube content is attributed to the formation of an elastic nanotube-polymer network. The formed nanotube-polymer network is conductive at percolation threshold of 0.6wt% SWNTs.

**Introduction:** The discovery of carbon nanotubes (CNTs) possessing unique electronic, thermal, optical and mechanical properties and their potential use in the next generation of composite materials has led to considerable attention in academia and industry. CNTs have the ability to affect the material properties at low loading due to their extremely high aspect ratio (length to diameter ratio) of up to 1000. This offers CNTs an important advantage over conventional fillers. However, for intractable polymers this potential has not been realized, mainly because of the difficulties in the solubility. In solution, strong interactions between the CNTs result in their agglomeration.

Different approaches are reported to improve the dispersion of CNTs in solvents or polymers. The dispersion of CNTs in solvents or polymers in presence of surfactants is another important method that does not require chemical reactions. A single-step solubilization scheme has been developed in which nanotubes are mixed with surfactants in low-power, high-frequency sonicators. This process enhances the exfoliation of CNT bundles without much breakage of the tubes. CNTs suspended in aqueous media as individuals or bundles surrounded by surfactants such as, sodium octylbenzene sulfonate, sodium dodecylbenzenesulfate (SDS), or copolymers (or oligomers) such as poly(m-phenylenevinylene) (PmPV), poly(aryleneethynylene)s (PEEs), poly(vinyl pyrrolidone) (PVP), Gum Arabic (a highly branched arabinogalactan polysaccharide) etc. In this paper, we report a spraying method similar to that is used for surface coatings in industrial applications. To disperse SWNTs on an intractable polymer, for an example linear ultra high molecular weight polyethylene (UHMWPE), first an aqueous solution of surfactant/SWNTs is made. The solution is sprayed onto the surface of the as synthesized fine polymer powder of UHMWPE. The SWNTs in the solution are preferably adsorbed on the surface of the nascent polymer. Melt crystallized films are prepared from the CNT coated UHMWPE powder. In contrast to the reported rheological studies, we observe a minimum in the dynamic viscosity with varying content of nanotubes.

**Experimental:** Experiments are carried out on purified HiPco (>95% pure) SWNTs. Two different grades of UHMWPE are used in this study. A commercially available UHMWPE (Montell 1900 LCM) (Grade A) with an average molecular weight of  $M_w \sim 4 \times 10^6$  g/mol and

$M_w/M_n \sim 10$  and a self synthesized UHMWPE (Grade B) with  $M_w \sim 4 \times 10^6$  g/mol and  $M_w/M_n \sim 2.8$ . Sodium dodecylbenzenesulfate (SDS) is used as a surfactant, and xylene as a solvent. Both were purchased from Aldrich. Oscillatory shear measurements in the linear viscoelastic region are performed using an Advanced Rheometrics Expansion System (ARES). Measurements are carried out using parallel plate geometry (8mm diameter) at 160°C under nitrogen atmosphere. Frequency sweeps with an angular velocity between 0.001 and 100 rad/s are performed in the linear viscoelastic regime at low strain of 1%. Samples are left to equilibrate for 15 minutes prior to measurement. The obtained values are corrected for the true dimensions between the plates. Electrical conductivity of the nanocomposites is measured at room temperature with a two-probe method.

### Results and Discussions

To disperse SWNTs in UHMWPE an aqueous solution of SWNTs is prepared using SDS as surfactant, according to a reported method. A 20ml solution containing 0.044g SWNTs and 1 wt% SDS based on H<sub>2</sub>O is ultra sonicated for 15 min and then centrifuged at 3000 rpm for 20 minutes. After sonification, about 90% of SWNTs are suspended in the aqueous solution, whereas the remainder is deposited. The morphology of the suspension of SWNTs is shown in Figure 1. From the figure it may be stated that the SWNTs are dispersed in the form of fine bundles with an average diameter of  $\sim 10$  nm. These bundles are rather flexible to coil back, forming loops.

#### Influence of SWNTs on the UHMWPE melt:

Oscillatory shear measurements are performed on samples in the viscoelastic region at low strain ( $\gamma=1\%$ ) at different frequencies ( $\omega=10^{-3}$ - $10^2$  rad/s) and temperatures ranging between 160°C-220°C. The master curves are obtained by using the time-temperature superposition principle. Since the SDS concentration in the nanocomposites is similar to the tube concentration, first the experiments are performed to study the influence of SDS on UHMWPE. No measurable influence of SDS on the rheological behavior of UHMWPE on SDS loadings ranging from 0.1 to 1wt%. In the 5wt% SDS sample a decrease in storage modulus is observed (7%), where the phase angle remains unchanged. However on dispersing SWNTs with SDS in UHMWPE a complicated rheological

situation arises that may be attributed to interactions between polymer and nanotubes.

Figure 2a shows master curves for storage modulus at 160°C varying from 0 to 0.2wt% of SWNT/UHMWPE composite. The figure is divided into two regions, Region I and Region II. In the Region I, considering the high molecular weight ( $\sim 4 \times 10^6$  g/mol) of the polymer, the probing time in the experiment is too short for chains to relax. Therefore UHMWPE behaves rubber-like and  $G'$  is nearly independent of frequency. The resulting plateau modulus is a combination of the elastic polymer network and elastic nanotube network.

In the Region II that lies at low frequencies, a striking observation is that at these low frequencies, the storage modulus decreases considerably with an addition of low amount of SWNTs in the UHMWPE ranging from 0.05 to 0.2wt%. Whereas at high frequencies (100 rad/s), in the Region I, the storage modulus also decreases but to a much lesser extent.

The phase angle,  $\delta$ , for the different compositions of SWNTs are depicted in Figure 2b. It is seen that upon increasing the amount of SWNTs from 0wt% to 0.1wt% the phase angle increases in the Region II, indicating that the composite behaves less elastic than the pure polymer. To our knowledge there are no studies that report the observed decrease in storage modulus for such a low loadings of nanotubes. But similar effects are reported in some recent studies when nanofillers (particle size 0.5 to 3 nm) are blended with linear polymers.

On increasing the SWNT content beyond 0.2 wt%, the storage modulus at low frequencies becomes independent of frequency, showing a second plateau in the Region II, see Figure 3a. It is known from literature, that interconnected structures of anisometric fillers result in an apparent yield stress which is visible in the dynamic measurements by a second plateau, as seen in the Region II. In the figure 3a, the second plateau is observed at low loading of 0.6wt% of SWNTs. With increasing amount of SWNTs in the polymer matrix the second plateau modulus increases. This increase is attributed to more pronounced connectivity of the nanotubes.

The phase angle depicted in the Figure 3b shows a subsequent decrease with the increasing amount of SWNTs in the Region II. The phase angle goes through a maximum. The frequency at which the phase angle shows a maximum increases with increasing amount of SWNTs in the polymer matrix. Shift of the maximum to

higher frequencies indicate a more dominant nanotube network with increasing SWNTs concentration. Presence of a maximum also suggests a change in the viscoelastic response with frequency -i.e. from viscous to elastic like response on going from Region II to I. The distinct minimum in dynamic viscosity with the varying amount of SWNTs becomes more evident in Figure 4a where the dynamic viscosity at low frequency ( $3.5 \times 10^{-4}$  rad/s) is shown as a function of SWNTs content. The figure depicts a minimum in the dynamic viscosity at 0.1-0.2 wt% of SWNTs. The variation in the storage or plateau modulus as a function of SWNTs content, at high frequency (100 rad/s) is given in Figure 4b. The plateau modulus decreases up to approximately 1 wt% after which the modulus increases.

The minimum in storage modulus (or dynamic viscosity) with increasing amount of SWNTs, at both high and low frequencies, requires an explanation. What follows is a possible explanation for the drop in the viscosity at relatively low content of nanotubes.

First, we recall that UHMWPE used for the present studies has a broad molar mass distribution. Due to the van der Waals interaction PE chains tend to be adsorbed on the nanotubes. Within the experimental time frame the probability of the high molar mass to remain adsorbed on the nanotubes will be higher than the low molar mass chains. The adsorbed polymer, especially of high molar mass, can be considered as an immobilized part of the nanotube. Thus the polymer forming the remaining matrix will effectively have a lower average molecular weight than the pure polymer. This would cause faster relaxation of chains thus a decrease in the storage modulus (or viscosity) and subsequently a higher phase angle, as depicted in the Figure 3. The observed drop in viscosity at such a low concentration of filler is in agreement with recent findings reported elsewhere. To quote, Mackey et al [2] reported decrease in viscosity in polystyrene filled with cross-linked polystyrenes, whereas Jain et al [3] observed a similar drop in viscosity using silica nanoparticles as filler. In nanocomposites filled with silica, an explanation provided for the viscosity drop was the selective physico-adsorption of polymer chains onto nano-particles surfaces.

When the nanotube content is increased beyond 0.2 wt % the nanotube network is formed. The formation of this network gets evident from the appearance of the plateau

region at lower frequencies. The elastic strength of this network increases with increasing amount of the nanotubes. To strengthen the concepts on selective adsorption of high molecular weight fraction, experiments are performed on a grade (Grade B) having molecular weight similar to the Grade A but a lower polydispersity, i.e. 2.8 instead of  $\sim 10$ . Figure 12 in ref 4 shows that similar to the Grade A (Figure 3) the storage modulus in the Region II of the Grade B becomes independent of frequency at a SWNTs concentration of 0.6wt%. This implies the formation of a mechanical nanotube network. However, unlike the Grade A, the Grade B does not show a minimum in the storage modulus in the Region II. This can be explained by the difference in polydispersity; since in the Grade B all polymer chains are relatively long ( $M_n \sim 1.3 \times 10^6$  g/mol) and are of similar length, no clear distinction in the molecular weight between the polymer matrix before and after the adsorption of chains to nanotubes exist. Therefore increasing the nanotube content simply results into a stronger nanotube network.

**Conclusions:** Experiments reported above clearly demonstrate that the viscoelastic response of polymer/CNT composites is strongly influenced by the polydispersity. The simple spraying technique used to obtain the UHMWPE nanocomposites opens an opportunity to overcome the intractable problem of UHMWPE, for details see ref 4.

#### References:

1. Regev, O.; Elkati P. N. B.; Loos, J.; Koning C. E. *Adv. Mater.* **2004**, *16*, 248
2. Mackay, M.E.; Dao, T.T.; Tuteja, A.; Ho, D.L.; Brooke van, H.; Kim, H.C.; Hawker, C.J.; *Nature Materials* **2003**, *2*, 762.
3. Jain, S.H., PhD Thesis, "Nano-scale events with macroscopic effects in polypropylene/silica nanocomposites; effect of polymer adsorption on processability and properties", Technische Universiteit Eindhoven, 2005 (ISBN 90-386-3046-8) [http://alexandria.tue.nl/extra2/2005118\\_23.pdf](http://alexandria.tue.nl/extra2/2005118_23.pdf)
4. Dispersion and rheological aspects of SWNTs in intractable polymers; QH Zhang, D. Lippits, S. Rastogi, *Macromolecules* 2006, *39*(2), 658-666

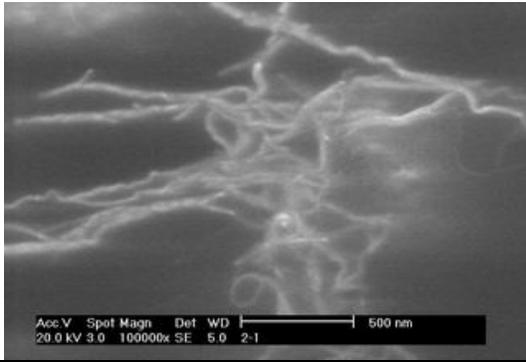


Figure 1. SEM image of SWNTs

Figure 3a

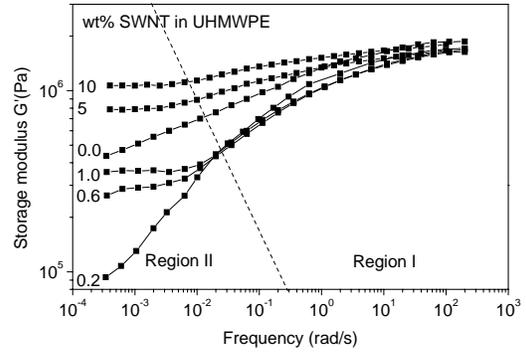


Figure 2a

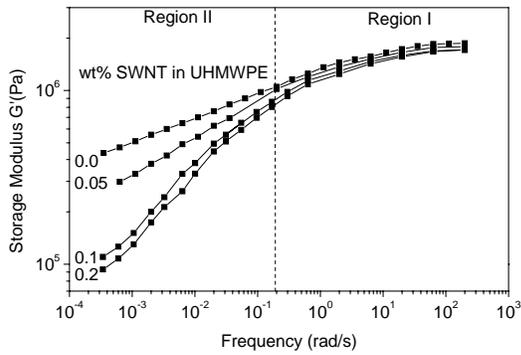


Figure 3b

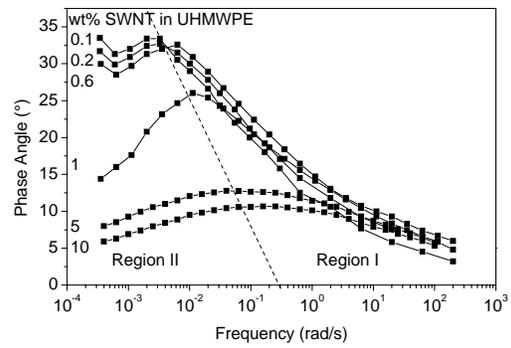


Figure 2b

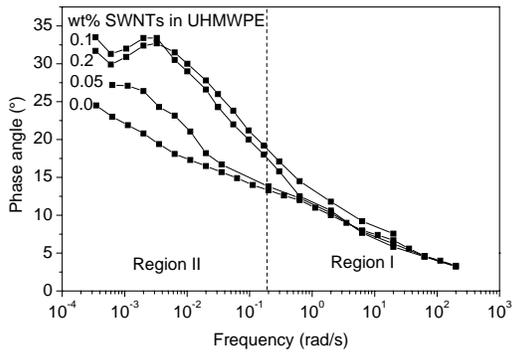


Figure 4

