PROCESSING OF CARBON NANOTUBE COMPOSITES USING LATEX TECHNOLOGY

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ABSTRACT

In this work, Gum Arabic (GA) has been employed as processing aid to produce a stable dispersion of carbon nanotubes in water. Both multiwall and singlewall nanotubes have been processed using GA. In the case of MWNTs, during the dispersal process graphitic impurities tend to sediment out of the solution, leaving a stable GA-MWNT suspension. In the case of SWNTs, GA is responsible for the exfoliation of bundles. Finally, the suspension of singlewall nanotubes is mixed with PS latex to obtain composite materials. The effect of this novel processing route on the improvement in mechanical and electrical properties of nanocomposites has been evaluated.

1. INTRODUCTION

Since their discovery [1], more than a decade ago, carbon nanotubes have aroused great interest due to their outstanding physical properties [2]. Not only carbon nanotubes have unique electrical properties, but also their mechanical properties make these structures attractive as next generation reinforcing elements for composite materials. However, the production of high-quality nanotube-based composite presents several problems, which need to be solved in order to exploit the extraordinary potentials of nanotubes. Purity, processability and adhesion are the most important issues to be addressed in order to develop a method for the production of good nanocomposites.

In the synthesis of nanotubes, they are found along with other materials, such as amorphous carbon and carbon nanoparticles. A variety of methods aiming to purify nanotubes have been described, but considerable problems still remain for all present purification techniques. The most common method is the oxidation of graphite particles, which often results in significant loss or damage of CNTs. Microfiltration [3] and size exclusion chromatography [4] have been employed to avoid damaging of nanotubes, but these methods tend to be extremely slow.

Secondly, it is widely known that the quality of nanocomposites depends on the dispersion of the reinforcing phase in the polymer matrices. As-produced SWNTs tend to assemble into crystalline ropes due to the strong van der Waals attraction among the tubes [5]. Furthermore, the ropes form tangled networks. Bundled nanotubes exhibit reduced mechanical and electrical properties compared to disentangled tubes. For this reason, exfoliation of bundles is necessary in order to produce high-quality nanocomposites. Researchers have followed different routes to disperse tubes in a polymer matrix: via mechanical mixing or from polymer solutions [6 - 11]. However, this point is still a great challenge for chemist and material scientists, since much work needs to be done to optimise the conditions required for the best dispersal of nanotubes.

In addition to dispersion, like in all composite materials, a necessary condition to take advantage of the very high strength of carbon nanotubes is the formation of good interfacial bonding, required to achieve load transfer across the filler-matrix interphase.

2. EXPERIMENTAL PROCEDURE

The polystyrene latex was produced using a standard emulsion polymerisation. The reaction was carried out in a 1.5 L four-neck reactor at 75 °C equipped with a condenser, a mechanical stirrer, a thermocouple, and inlet for nitrogen. 160 g of styrene was introduced into the reactor containing an SDS aqueous solution (0.75 wt %) at room temperature with a stirring rate of 300 rpm. A small amount of sodium carbonate was added to control the ionic force. The mixture was purged with nitrogen and nitrogen was fluxed during the entire polymerisation procedure. The mixture was then heated to 75 °C, and after additional 20 min equilibration time, a potassium persulfate aqueous solution (10 wt%) was added and the mixture was reacted for 24 h.

The nanotubes dispersions were produced as follows. 5.02 g of Gum Arabic (GA) are dissolved in 246.03 g of water. 1.012 g of MWNT soot is added to 30.14 g of GA solution. The suspension is sonicated for 30 min using a low-power sonic bath to ensure good dispersal and homogeneity. The resulting dispersion is centrifuged at 5000 rpm for 30 min to allow any impurities to sediment out. The homogeneous dispersion is carefully separated from the sediment by decantation. The dispersion appears to be completely homogeneous and stable over months. The sediment is re-dispersed in 20.081 g of GA solution and this procedure is repeated a number of times until all the nanotubes are removed from the sediment.

The components (sediment and solution) were characterized for MWNTs and graphitic particles (GP) content using electron paramagnetic resonance (EPR). EPR measurements were made at room temperature using 100 kHz field modulation and a microwave frequency of approximately 9.7 GHz.

The same procedure was carried out using singlewall nanotubes to obtain a stable dispersion of well-separated nanotubes in water. The SWNTs/PS composites were produced as follows. The SWNTs water-dispersion is mixed to the PS latex. The dispersion is freeze-dried to obtain a powder, which is then compression moulded into thin films and plates. Finally, from the plates, bars and dog-bone specimen are cut for the mechanical and electrical measurements.

DMA was performed in constant frequency and controlled force modes using a Perkin Elmer DMA-7. Three point bending test were performed according to ASTM D 790M – 86 with a support span of 30 mm and a rate of cross-head motion of 1.7 mm/min. Conductivity measurements were made using a Keithley Model 6517A Electrometer.

3. RESULTS AND DISCUSSION

3a. MWNTs purification

The multiwall nanotubes used in this study are formed in the cathode deposit during the Krätschmer-Huffman arc process. The deposit consists of a tube-rich core surrounded by a fused carbon shell. The core material contains tubes that are 2-15 nm in diameter, 1-10 μm long, with 5-20 graphitic layers. The core contains 10-40% tubes. The remainder is multi-layer polygonal carbon nanoparticles and amorphous and graphitic carbon nanoparticles. A SEM micrograph of the as-received material is reported in Fig.1.

An interesting method, which has proved successful in isolating the tubes, is mixing the soot with a polymer host in solution, forming a composite material. Coleman and co-workers [12] studied the ability of different type of polymer to suspend carbon nanotubes in toluene and they found that poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) (PmPV) was the most efficient, because of its highly conjugated structure. In this study, Gum Arabic has been employed as hosting polymer. Gum Arabic is a natural polysaccharide extracted from *Acacia Senegal* trees. Its macromolecular structure is unknown, but some information about its composition is available in literature [13]. It consists of two distinct populations. About 80% of the material consists of highly branched polymer. The rest is mainly composed

of heterogeneous protein complex of high molecular weight. Studies concerning the use of GA to produce a stable suspension of SWNTs in aqueous solution have been reported in literature [14]. Bandyopadhyaya *et al.* developed a procedure to disperse as-produced SWNT powder in aqueous solution of Gum Arabic. In a single step, they are able to produce a stable dispersion of well-separated tubes, apparently due to physical adsorption of the polymer to the surface of the nanotubes.

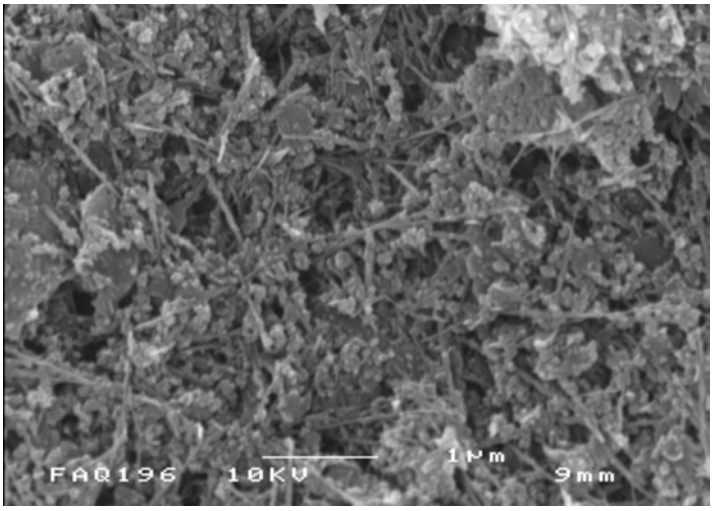

Fig. 1. SEM picture of as-received MWNT

Electron paramagnetic resonance (EPR) measurements have been used by Coleman *et al.* [12] as a quantitative tool to track the presence of nanotubes in different environments. They studied EPR of carbon nanotubes in a range of host materials and crude Krätschmer generator powder at room temperature. They found *g* value of 2.011 for MWNTs and 2.020 for (GP).
In Fig. 2, the spectra of as-received soot and purified MWNTs are reported. While the soot spectrum has clearly two well-defined components, the GA/MWNTs spectrum exhibits only the low *g* line, representative of carbon nanotubes. This demonstrates that nanotubes are stable in GA solution, while GP tend to sediment out. This effect is extremely important because it allows separating nanotube material from other graphitic impurities.

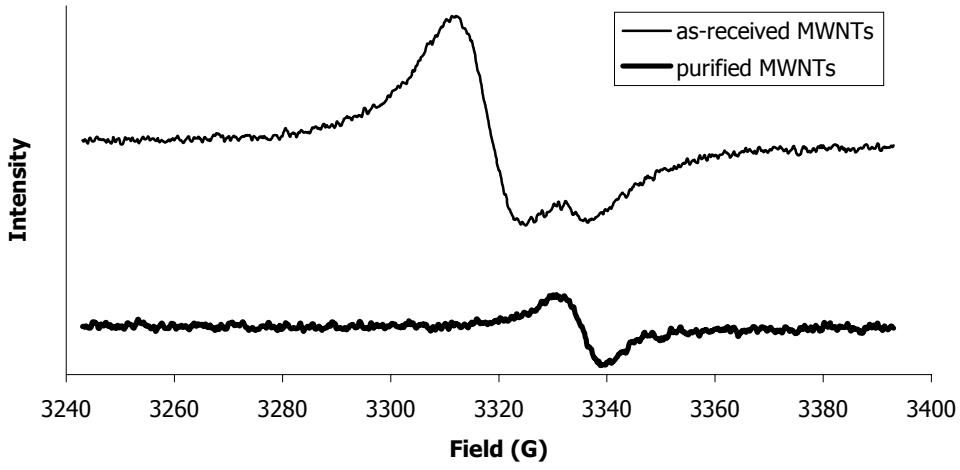

Fig. 2. EPR spectra of as-received MWNTs and purified MWNTs.

The formation of a stable solution of MWNTs in water is due to the creation of noncovalent aggregates between nanotubes and Gum Arabic. MWNTs are in the hydrophobic interiors of the corresponding micelles. The presence of aromatic groups in the hydrophobic part of Gum Arabic allows an especially strong interaction with the graphitic sidewall of nanotubes because effective π-π stacking interactions can then be formed. Furthermore, emulsification is particularly enhanced due to the molecular flexibility of Gum Arabic, which allows greater surface interaction with the tubes.

3b. SWNTs bundles exfoliation

As-produced SWNTs tend to assemble into crystalline ropes due to the strong van der Waals attraction among the tubes. Ropes are typically composed of 100 to 500 tubes and pack in a triangular lattice [5].

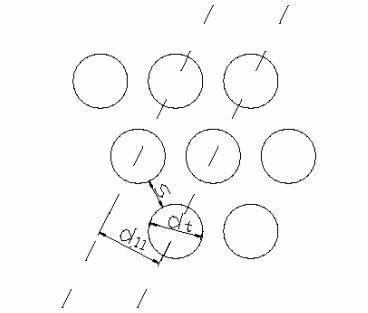

Fig. 3. Schematic diagram of the crystalline lattice of SWNTs [modified from 15].

The average tube diameter $\langle d_t \rangle$ can be calculated from the (11) peak position according to the relation: $\langle d_t \rangle = d_{11}/\cos 30^\circ - s$ where s is the intertubule spacing taken to be 0.32nm and d_{11} is the distance between (11) planes of tubes in the bundle. The value of s used is midway between the interplanar spacing in graphite (0.335nm) and the interfullerene distance in solid C_{60} (0.29nm) [15].

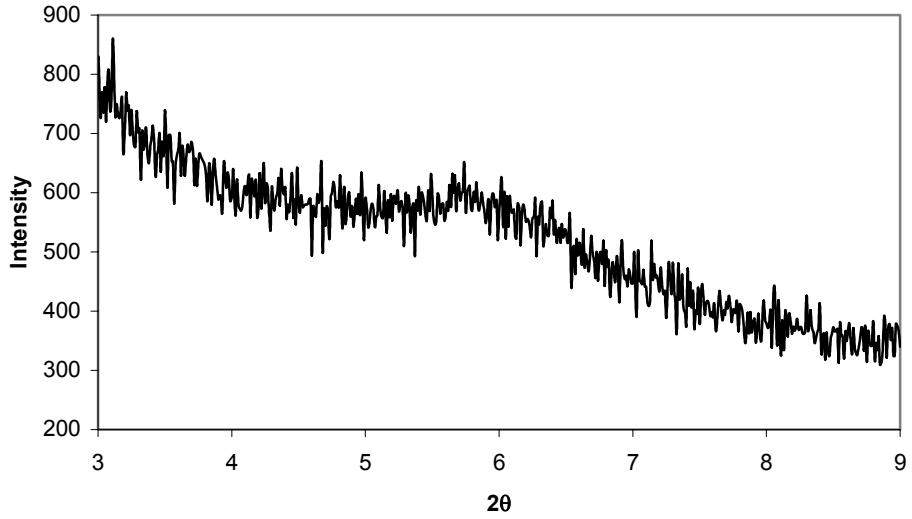

Fig. 4. XRD pattern of as-received SWNTs.

In Fig. 4, we present the XRD spectrum of as-received SWNTs. The peak at a 2θ value equal to 5.832°, which corresponds to a *d*-spacing of 1.514225 nm, is representative of the intertubule spacing within a bundle. The position of the (11) XRD peak was used to estimate the average SWNT diameter produced in the macroscopic sample, and this value is in good agreement with the value provided by the supplier (d_t =1.428 nm)

Bandyopadhyaya and co-workers [14] developed a method to disperse as-produced SWNT powder in aqueous solution of Gum Arabic. Their technique led to the adsorption of a layer of GA onto the surface of the nanotube leading to exfoliation of the bundles. They directly observed the exfoliation process using a high-resolution transmission electron microscope. In Fig. 5, the HR-TEM image of dried solution of SWNT in GA is reported, showing that adsorption of GA leads to disruption of the intertube interactions in the ropes.

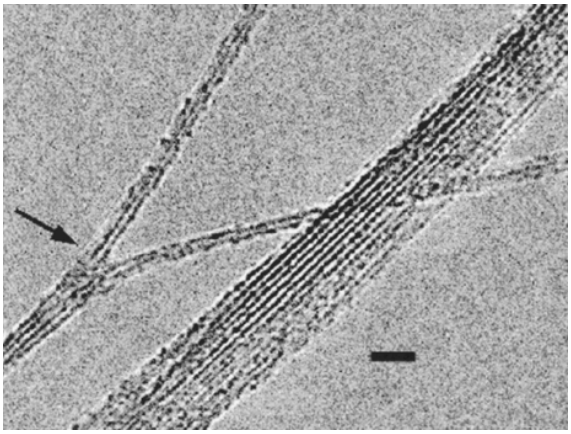

Fig. 5. High-resolution TEM image of dried solution of 0.05 wt% SWNT in 1 wt% GA [14].

In Fig. 6, we report XRD spectrum of a PS/SWNTs nanocomposite produced using GA as processing aid. In the XRD spectrum, we can observe that the (11) peak completely vanishes, which could mean that an exfoliated nanocomposite has been formed. However, considering the weakness of the peak in the raw material, the disappearance of the (11) peak could be interpreted as a dilution effect.

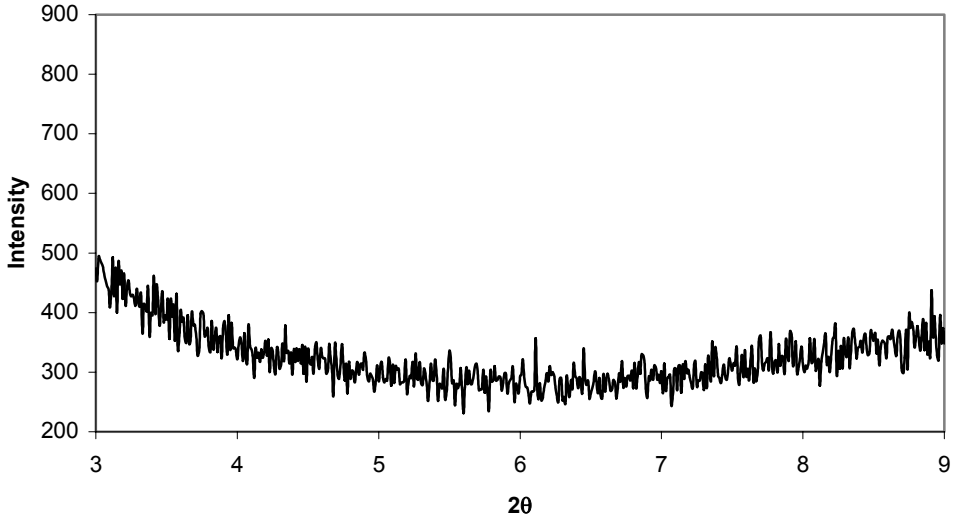

Fig. 6. XRD pattern of PS/GA/SWNTs composite.

3c. Mechanical properties

The thin films were characterized using DMA in constant frequency and controlled force modes. The storage moduli of the different samples are summarized in Table 1. The storage modulus is affected by the addition of both Gum Arabic and carbon nanotubes. The addition of Gum Arabic led to a moderate decrease in storage modulus, whereas the addition of both GA and nanotubes increase the storage modulus by 35% as compared to the pure polystyrene. It may be more informative to compare PS/GA/NTs sample with PS/GA sample, because the latter was the actual reference material for the PS/GA/NTs sample. This comparison gave 48% increase in storage modulus with the addition of only 1 wt% of carbon nanotubes. As the elastic entropy theory suggests, the reinforcing effect of carbon nanotubes is more efficient when the polymeric matrix is in its rubbery state, since the filler acts as supplementary crosslinks inside the composites [16]. Above the T_g, the increase in storage modulus is 94% and 146% as compared to pure PS and PS/GA samples respectively.

Table 1. Storage moduli of the composite samples

Material	Storage Modulus @ 40˚C (GPa)	Storage Modulus @ 90˚C (MPa)
PS	1.09	4.61
PS+GA	0.99	3.64
PS+GA+1wt%SWNT	1.46	8.96

In order to examine the influence of nanotubes on deformation and fracture behaviour of the composites, static three-point bending tests were performed on the composites. In addition to the increase in modulus, the use of SWNTs results in improvement in the ultimate strength as compared to the PS/GA sample. However, compared to pure PS, the strength is slightly reduced for all the composites due to the large amount of GA needed to incorporate the nanotubes in the samples.

Table 2. Flexural moduli and strength of the composite samples

Material	Modulus (GPa) @ RT	Stdev	Strength (MPa) @ RT	Stdev
PS	2.71	0.246	76.3	1.93
PS+GA	2.51	0.478	70.3	0.91
PS+GA+1wt%SWNT	2.85	0.038	75.0	2.49

3d. Electrical properties

Enhancements in the electrical conductivity of polymeric materials by the introduction of inorganic fillers (e.g., carbon black, iron powder, etc.) have been long pursued by researchers [17]. Recently, the use of carbon nanotubes has been demonstrated as more advantageous than carbon black, because of the need of smaller loads to reach the percolation threshold [18].

Using the latex technology we have found that SWNTs can effectively disperse inside the host matrix and form multiple tube-tube contacts modifying the electric response of the composite. Table 3 summarizes the data corresponding to DC electrical resistivity measurements for SWNT-PS composites at three different loadings.

Table 3. DC electrical conductivity data at room temperature

Material	SWNT loading (wt%)	Conductivity (Sm^{-1})
PS	-	4.17E-09
PS+GA	-	2.67E-11
PS+GA	1.6	1.90E-10
PS+GA	2.7	8.00E-10
PS+GA	3.0	1.00E-08

Although an increase of three orders of magnitude is observed for 3wt% loading as compared to PS/GA sample, the conductivity values are still low in comparison to composites made with low nanotubes loading in epoxy resins [18].
The origin of such smaller conductive capacity of the nanotube network can be attributed to the internal resistance of an adsorbed layer of GA that reduces the number of electrical contacts. In fact, TEM analysis of SWNT-PS film showed evidence that a layer of GA was adsorbed on the nanotube surface. In Fig. 7, a TEM micrograph shows a nanotube pulled out from the PS matrix, after the composite film broke due to the exposure to the electron beam in the microscope. The nanotube surface is coated with a thin layer of polymer, which means that there is strong interfacial interaction between nanotube and polymer.

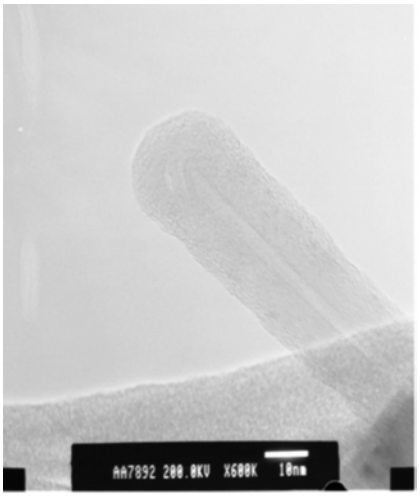

Fig 7. TEM micrograph of a composite film after fracture due to the exposure to the electron beam in the microscope.

4.CONCLUSIONS

- Gum Arabic can be employed for the purification of arc-grown MWNTs, because of its ability to separate nanotubes from the graphitic impurities present in the arc soot by selective solubilization, but a great amount of GA is needed for this process. In order to improve the quality of the nanocomposites, the removal of Gum Arabic is necessary.
- Microscopy studies suggest a good interfacial bonding in the PS/GA/NTs composites.
- The addition of nanotubes led to an increase of both macroscopic mechanical and electrical properties.

ACKNOWLEGMENTS
The support of the Dutch Polymer Institute (DPI) in the Netherlands is gratefully acknowledged. Furthermore, the authors would like to thank Dr Steve Rigby for EPR analysis.

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