

Publication IV

M. Lahelin, M. Annala, A. Nykänen, J. Ruokolainen, and J. Seppälä. 2011. *In situ* polymerized nanocomposites: Polystyrene/CNT and Poly(methyl methacrylate)/CNT composites. *Composites Science and Technology*, volume 71, number 6, pages 900-907.

© 2011 Elsevier

Reprinted with permission from Elsevier.



In situ polymerized nanocomposites: Polystyrene/CNT and Poly(methyl methacrylate)/CNT composites

M. Lahelin^a, M. Annala^a, A. Nykänen^b, J. Ruokolainen^b, J. Seppälä^{a,*}

^aAalto University School of Science and Technology, Department of Biotechnology and Chemical Technology, Polymer Research Group, Kemistintie 1, P.O. Box 16100, FI-00076 Aalto, Finland

^bAalto University School of Science and Technology, Department of Information and Natural Sciences, Molecular Materials Research Group, Puumiehenkuja 2, P.O. Box 15100, FI-00076 Aalto, Finland

ARTICLE INFO

Article history:

Received 7 June 2010

Received in revised form 7 February 2011

Accepted 13 February 2011

Available online 16 February 2011

Keywords:

A. Polymer–matrix composites (PMCs)

A. Carbon nanotubes

B. Mechanical properties

B. Electrical properties

D. Electron microscopy

ABSTRACT

Carbon nanotubes (CNTs) were incorporated into polystyrene (PS) and poly(methyl methacrylate) (PMMA) matrices via *in situ* emulsion and emulsion/suspension polymerization methods. The polymerizations were carried out using various initiators, surfactants, and carbon nanotubes to determine their influence on polymerization and on the properties of the composites. The loading of CNTs in the composites varied from 0 to 15 wt.%, depending on the CNTs used. Morphology and dispersion of the CNTs were analyzed by transmission and scanning electron microscopy techniques. The dispersion of multi-walled carbon nanotubes (MWCNT) in the composites was excellent, even at high CNT loading. The mechanical properties, and electrical and thermal conductivities, of the composites were also analyzed. Both electrical and thermal conductivities were improved.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Since Iijima et al. brought carbon nanotubes (CNTs) to the attention of the scientific community, the development of CNT-based nanocomposites has been an topic of interest for researchers around the world [1]. Carbon nanotubes have several outstanding properties, such as very high mechanical strength combined with low density, which makes them good filler candidates for polymers. The Young's modulus for single-walled carbon nanotubes (SWCNTs) has been calculated to be in the 1 TPa range; for multi-walled carbon nanotubes (MWCNTs) the Young's modulus values are lower, but still very respectable. There are still significant differences between calculated and experimental values of Young's modulus for CNTs, which is mainly due to difficulties in measuring modulus values for single CNTs [2]. The CNTs also have excellent electrical properties; in theory, metallic CNTs can have electrical conductivities more than 1000 times greater than metals such as copper. When using MWCNTs, and taking into account the defects in CNTs, the electrical conductivities are lower by one or two orders of magnitude, which still means they have outstanding electrical conductivities. The electrical percolation threshold of composites depends on what kind of carbon nanotubes (SW or MW) are used, the preparation method of the carbon nanotubes, the ma-

trix polymer, and especially the dispersion of the CNTs. For these reasons, an exact percolation threshold cannot be given for CNTs, although the electrical percolation threshold is usually about 0.1–3 wt.% CNTs [3]. Besides electrical conductivity, CNTs also have extremely high thermal conductivity. SWCNTs have theoretical thermal conductivities up to ~6000 W/mK at room temperature, and thermal conductivities for MWCNTs are at ~3000 W/mK at room temperature. Purely amorphous polymers, like polystyrene (PS) and poly(methyl methacrylate) (PMMA), on the other hand, have thermal conductivities of ~0.1–0.2 W/mK, and (semi)crystalline polymers, like polyethylene (PE) and polypropylene (PP), have thermal conductivities up to a few W/mK. So, theoretically, polymer composites with a low percentage (0.1–5 wt.%) of well-dispersed CNTs should have excellent thermal conductivities. In practice, this is not the case. Numerous research groups have reported that dispersing CNTs into a polymer matrix improves the thermal conductivity of the composite only slightly, if at all. For composites based on amorphous polymers, thermal conductivities up to ~1 W/mK are achievable, and for composites of crystalline polymers, thermal conductivities of a few W/mK are possible. However, in the latter case most of the improved thermal conductivity seems to come from crystalline structures in the composites. The high crystallinity of the polymer reduces the interfacial thermal resistance by providing more “bridges” between CNTs. Mathematical theories also predict that the bulk of the heat flow through the CNTs is carried by the outer layer while the contribu-

* Corresponding author. Tel.: +358 9 47022614; fax: +358 9 462373.

E-mail address: jukka.seppala@tkk.fi (J. Seppälä).

tion of inner layers is insignificant. This is also one factor that gives a smaller than expected value of the effective conductivity. It has also been shown that the effective conductivity is especially sensitive to the MWCNT diameter [4–7].

The key factors in effective CNT/polymer composite design, as with any composite, are the dispersion of the filler material into the matrix and adhesion between the filler particles and matrix polymer. The CNTs, especially SWCNTs, are strongly bundled together; they will re-aggregate, after the initial dispersion mechanism, such as ultrasonication, is removed. There are numerous methods which have been used to produce CNT/polymer composites with reasonable dispersion and stress transfer between the polymer matrix and CNTs. These include extrusion, melt processing, and the use of surfactants to aid dispersion. From an industrial point of view, a direct melt-based processing method for producing CNT/polymer composites would be ideal; unfortunately the results for direct blending have been limited at best [8–16]. One interesting approach would be to use functionalized CNTs to improve the properties, especially mechanical, of CNT-based composites. Again from an industrial point of view, the functionalization processes for CNTs, like acid functionalization, are rather time consuming and expensive [17–20].

In this paper, we prepared CNT/polystyrene and CNT/poly(methyl methacrylate) composites via *in situ* emulsion and emulsion/suspension polymerization methods. Several commercial CNT types were used as fillers; the maximum CNT loading was up to 15 wt.%. The initial break-up of CNT bundles was carried out with mild ultrasonication to avoid excessive CNT shortening. The polymerization product was dried, and processed via hot pressing, which allowed us to further observe the stability of the CNT dispersion. The mechanical properties of the samples were analyzed by DMA (dynamic mechanical analysis). The electrical and thermal (for PMMA) conductivities were also analyzed. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize the dispersion of the CNTs and the morphology of the composite samples.

2. Experimental

2.1. Materials

Two MWCNT types were used: Nanocyl NC7000 and Bayer C 150 HP (Bayer Baytubes). Nanocyl NC7000 (Nanocyl SA, Belgium) is manufactured via a chemical vapor deposition (CVD) process, the carbon purity is ~90%, average diameter ~9.5 nm, and average length ~1.5 μm . Bayer C 150 HP (Bayer, Germany) is also manufactured via a CVD process, the carbon purity is >99%, average diameter 13–16 nm, and average length >1 μm . The double-walled carbon nanotube (DWCNT) type used was Nanocyl NC2100 (Nanocyl SA, Belgium). NC2100 is manufactured via CVD; the carbon purity is >90%, average diameter ~3.5 nm, and average length 1–10 μm . In most polymerizations, the CNTs were used as received. For some polymerizations, the CNTs were acid functionalized. Firstly, to remove metallic residues the CNTs were treated with strong hydrochloric acid at 60 °C for 24 h. The solution was then diluted with distilled water, filtered and washed with distilled water. Then, purified CNTs were mixed with a mixture of strong nitric acid and sulfuric acid (1:3) and treated in an ultrasonic bath at 40 °C for 4 h, filtered and washed with distilled water [21]. Fig. 1 shows transmission electron microscopy (TEM) images of pristine CNTs.

Monomers, styrene (purity >99%) and methyl methacrylate (purity >99%) were supplied by Fluka (Sigma–Aldrich). Both monomers were treated with aluminum oxide (supplied by Fluka) to remove inhibitor. Initiators, potassium peroxydisulfate (KPS, purity

>99%) and azobisisobutyronitrile (AIBN, purity \geq 98%) were supplied by Fluka (Sigma–Aldrich). The surfactants, sodium dodecyl benzene sulfate (DBSA, Fluka) and sodium dodecyl sulfate (SDS, Sigma–Aldrich), and the buffer, sodium hydrogen carbonate (NaHCO_3 , purity \geq 99.5%, Merck), were used as received.

2.2. Polymerization and sample preparation

The seed emulsion was prepared ultrasonically. CNTs, surfactant, NaHCO_3 , and distilled water were introduced into the 250 mL three-neck round bottom flask, cooled in an ice bath and the mixture was deoxygenated by bubbling with argon. Ultrasonic treatment was carried out with the probe of an ultrasonic horn immersed directly into the mixed system. The power output was set at 100 W and the system was sonicated 30 min. After ultrasonic treatment the flask was transferred into an oil bath and fitted with a stirrer, using a stirring rate of 300 rpm. The system was deoxygenated with argon. In the case of KPS as an initiator (emulsion polymerization), the KPS was dissolved in water and the solution was fed into the reactor before monomer. The monomer was added drop by drop with a membrane pump at 0.03 mL/min. In the case of AIBN as an initiator (combined emulsion/suspension polymerization), the AIBN was dissolved in the monomer and the solution was fed into the reactor with the membrane pump at 0.03 mL/min. Styrene polymerizations were conducted under argon atmosphere for 15–18 h at 60 °C with KPS and for 3 h at 80 °C with AIBN. MMA polymerizations were carried out at a temperature of 65 °C (KPS as an initiator), and at a temperature of 75 °C (AIBN as an initiator). The polymerization times were 20–21 h.

After polymerization, the emulsion was dried in an oven for at least 48 h at 50 °C. The dried polymer powder was hot pressed (force: 150 kN) at 165 °C for PMMA, and 170 °C for PS, to produce approximately 1 mm thick rectangular samples.

2.3. Characterizations

Pristine CNTs were studied by TEM (Philips/FEI CM200 FEG). The TEM samples were prepared by dissolving the CNTs in ethanol with an ultrasound bath, and dropping the solution onto a copper grid and drying. The morphology of the composites was also studied with transmission electron microscopy (TEM, Tecnai 12 Bio Twin). The samples were embedded into epoxy, trimmed, and finally cut with an ultramicrotome to ~70–80 nm thick slices. The electron micrographs were taken using an acceleration voltage of 120 kV. Also, scanning electron microscopy (FE-SEM, Jeol JSM-6335F) was used to study the morphology of composite samples. The hot pressed composite samples were fast frozen in liquid nitrogen and fractured. The fractured surface samples were coated with chromium in order to stabilize the samples under the electron beam and to enhance image contrast. The electron micrographs were taken using an acceleration voltage of 5.0 kV.

Molecular weights (M_w) and molecular weight distributions (PD) were determined with respect to polystyrene standards by size exclusion chromatography (SEC, The Waters Associates system). The dried samples were dissolved in tetrahydrofuran (THF), and THF was used as eluent. The samples were filtered through a 450 nm (pore size) filter to remove the MWCNTs and grafted MWCNTs, and the filtrate (soluble polymer) was subjected to SEC testing. The samples were analyzed at room temperature.

The mechanical properties of the composites (~1 mm thick hot pressed samples) were analyzed with DMA (TA Instruments Q800) at 25 °C using a single cantilever 20 mm (effective length 10 mm) probe. The glass transition for PMMA samples was also measured with DMA using a heating rate of 3 °C/min from 0 °C to 180 °C. DMA measurements were done in amplitude mode (100 μm) to

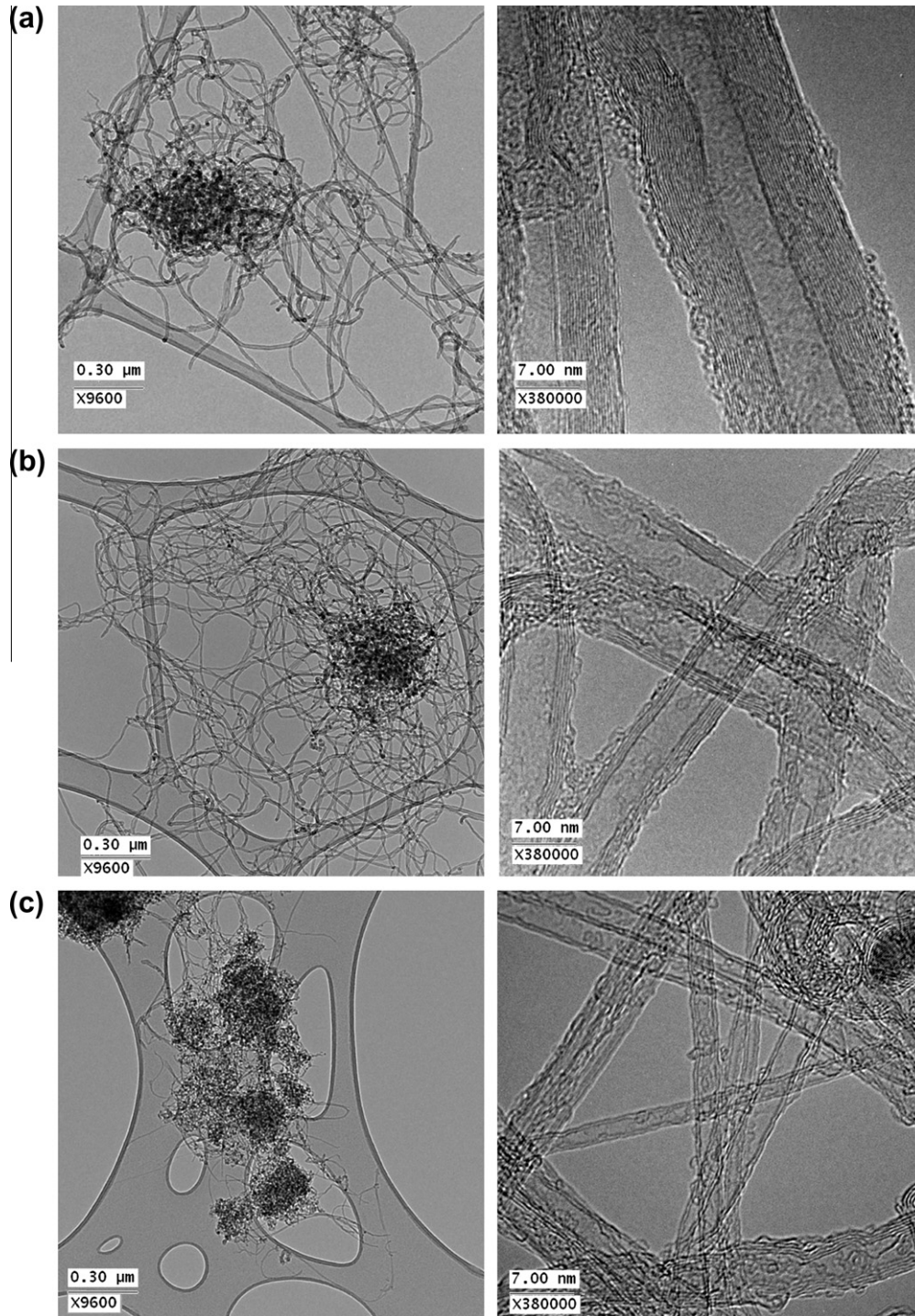


Fig. 1. TEM images of pristine CNTs: (a) Bayer Baytubes (MWCNT); (b) Nanocyl NC7000 (MWCNT); (c) Nanocyl NC2100 (DWCNT). Magnifications: $\times 9600$ (left) and $\times 380,000$ (right).

get reliable data at temperatures over the polymer T_g . A frequency of 1 Hz was used for all tests. At least two samples were tested for each condition and the data was averaged.

Electrical conductivity was measured from the surface of DMA samples by the four-probe method (Keithley 2400 Sourceter). The distance between probes was approximately 1 mm. The sample surfaces were finished with grid 600 paper to remove the polymer skin. Thermal conductivity was measured from hot pressed (diameter 12 mm, thickness 2 mm) samples using a Hot Disk Thermal Constants Analyzer combined with a Keithley 2400 Sourcem-

eter. The samples were stabilized for 30 min; the measurements were done at 0.05 W for 30 s.

3. Results and discussion

3.1. The morphology of CNT/polymer composites

Microscopy (TEM and SEM) were used to characterize the morphology, and especially CNT dispersion, of the composites. Fig. 2

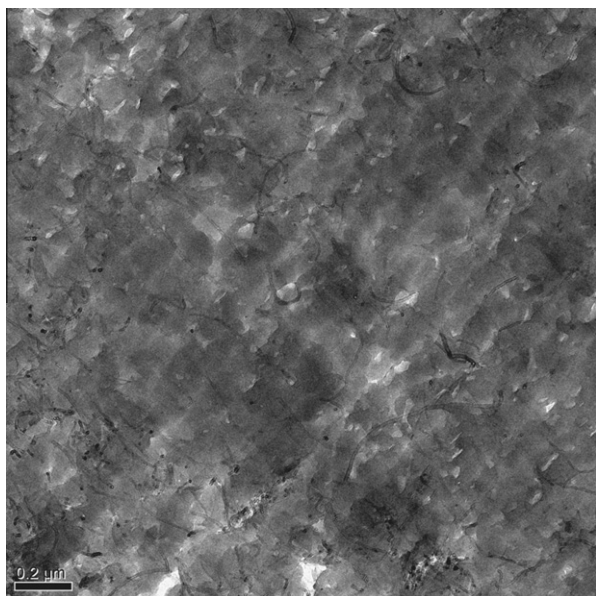


Fig. 2. TEM image of PS (KPS, SDS) sample with 3.0 wt.% MWCNTs (Nanocyl NC7000).

shows a typical TEM image of PS/MWCNT (3.0 wt.% of Nanocyl NC7000) composite sample. Fig. 3 shows TEM images of PMMA/MWCNT composite samples (3.0 wt.% of Nanocyl NC7000 and 3.0 wt.% of Bayer Baytubes). There were no significant aggregates of MWCNTs in the composites. The MWCNT bundles were broken up during the ultrasound treatment and the CNTs were well dispersed into, and isolated within, the polymer matrix. TEM images were also taken from composites based on Nanocyl NC2100 DWCNTs; the DWCNT dispersion was not as good as for MWCNTs. The DWCNT bundles were “loosened” during the ultrasound treatment, but complete unbundling was not achieved. The ultrasound treatment was probably too weak to achieve that. The DWCNTs were also significantly longer than in either of the MWCNT types, which made the complete DWCNT unbundling more difficult to achieve. The length of dispersed CNTs was difficult to estimate from the TEM images, as the ultramicrotome cutting broke, and even pulled out, CNTs. The average length of Nanocyl NC7000 MWCNTs was under 1 μm. Bayer Baytubes appeared shorter, which was reflected in their electrical conductivities. Overall, the mild ultrasonication required to break-up the CNT bundles conserved the CNT length relatively well, as with ultrasonication some shortening was always expected. TEM images were taken from DMA test specimens, which had been melt processed after drying the emulsions. Images confirmed that *in situ* polymerization provided stable dispersion of CNTs even after thermal processing.

As adhesion between the filler and matrix polymer is crucial for any functional composite, SEM images were taken of composite samples to estimate the interface between the polymer and CNTs. Fig. 4 shows typical SEM images for PMMA-based composites. MWCNTs were well dispersed into the polymer, and did not show any large aggregates. For DWCNTs, the dispersion was not as good, as areas with partially opened DWCNT bundles could be seen in the images. Both PS and PMMA covered the CNTs (both MWCNTs and DWCNTs) during the polymerization, so polymer wettability to CNTs was at least moderate. Further evidence of favorable composite morphology was seen from glass transition temperatures. For MWCNT/PMMA composites the glass transition temperature increased about 20 °C (tan δ peak from DMA) when MWCNT loading increased from 0 wt.% to 10/15 wt.%; which indicates that the MWCNTs were enhancing the confinement of matrix polymer mol-

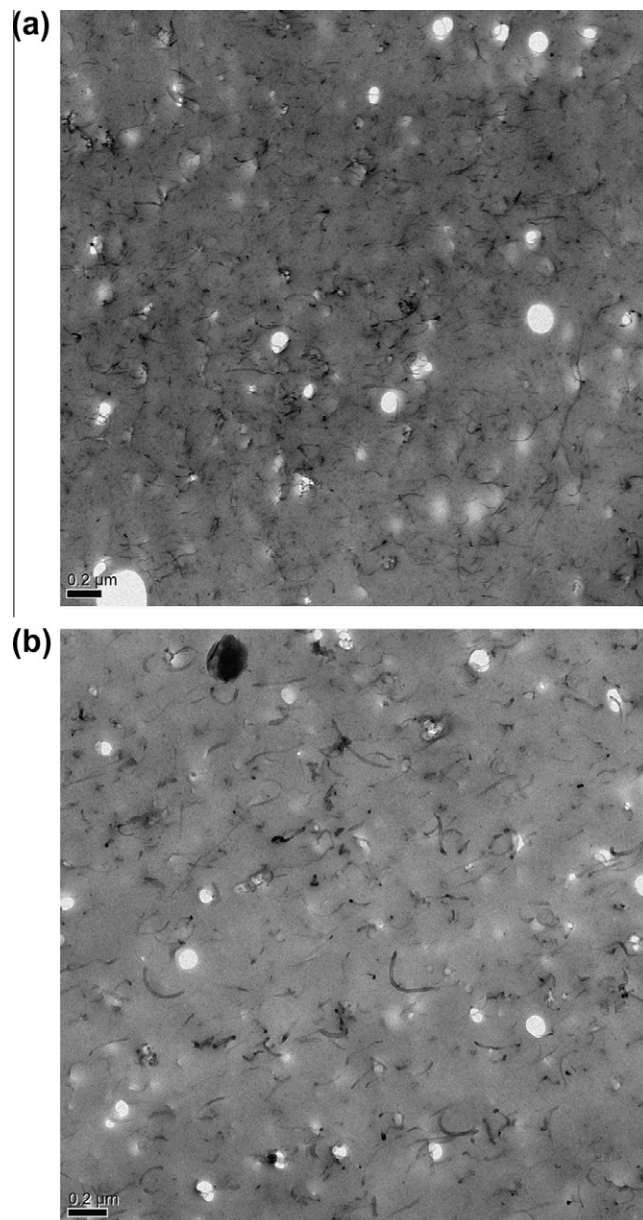


Fig. 3. TEM images of PMMA samples: (a) KPS, DBSA, 3.0 wt.% MWCNTs (Nanocyl NC7000); (b) KPS, DBSA, 3.0 wt.% MWCNTs (Bayer Baytubes).

ecules. There was also a greater increase in modulus in the rubbery region than in the glass region, which is typical for nanoscale fillers [22]. Part of the increased T_g resulted from increased molecular weights, as the CNTs were participating in the polymerization process. Higher molecular weight PMMA (comparable to PMMA/CNT composites) was polymerized, and glass transition temperatures measured. The T_g values increased by 5–7 °C, which indicated that the major part of the increase in T_g for the PMMA composites was caused by the added MWCNTs. For DWCNTs, the effect was smaller, as the dispersion of the DWCNTs was not as complete and the CNTs had less surface area.

3.2. Mechanical properties of CNT/polymer composites

Descriptions of mechanical properties of polymer-based composites are usually based on Young's modulus. Other factors, like strain at break, are often understated, even though they are very important for any applications or further composite processing.

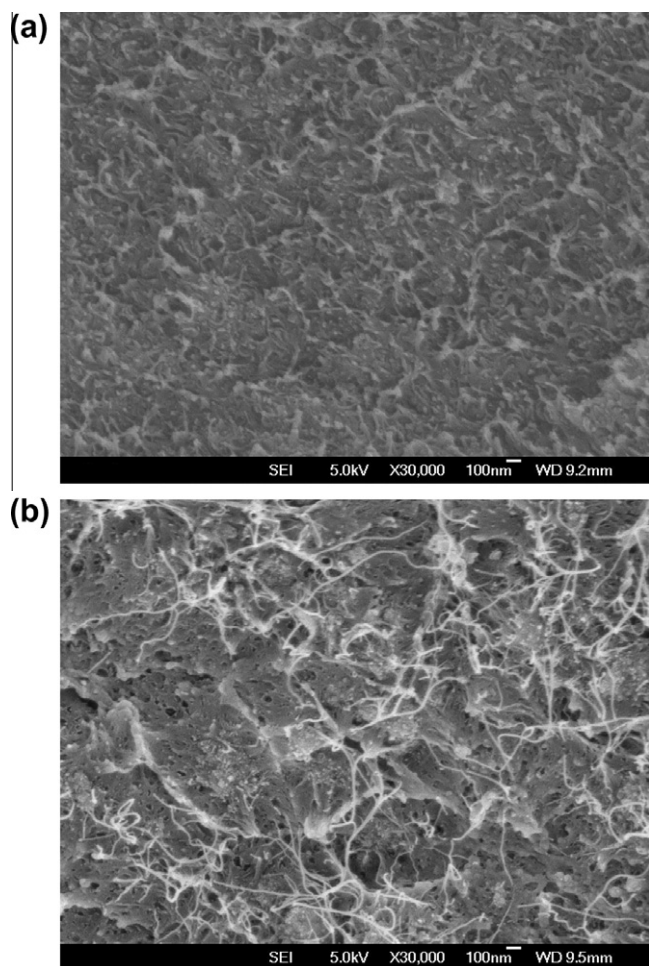


Fig. 4. SEM images of PMMA samples: (a) AIBN, DBSA, 6.0 wt.% MWCNTs (Nanocyl NC7000); (b) KPS, DBSA, 3.0 wt.% DWCNTs (Nanocyl NC2100).

There are numerous CNT/polymer composite articles that make the same statement: low amount (often ~ 0.1 wt.%) of dispersed CNTs act as reinforcement. However, increasing the nanotube content even more causes the Young's modulus values to stabilize or even start to decrease. The material will become brittle. Poor dispersion of fillers is the most likely explanation for this; another possibility is crystallinity. CNTs can affect the crystallinity of the composite, in either a positive or negative way. The crystallinity of the composites can have a significant effect on mechanical properties, as well as on electrical and especially thermal conductivities [16–17]. One additional factor is molecular weight, and to a lesser degree the polydispersity, especially with *in situ*-based CNT/polymer composites. In this paper, we polymerized both thicker (Bayer Baytubes) and thinner (Nanocyl NC7000) MWCNTs, and DWCNTs (Nanocyl NC2100), with different initiators and surfactants. Also, acid functionalized MWCNTs were used to estimate whether the functionalization had a positive effect on composite properties. The molecular weights and polydispersities of the composites varied significantly with different CNTs, CNT loading, and initiators, so it was difficult to estimate to what degree the improvement in mechanical properties was induced by CNTs. Fig. 5 shows typical stress–strain curves of MWCNT/PS composites. By adding a low amount (up to 3.0 wt.%) of pristine MWCNTs (Nanocyl NC7000) to the polystyrene, the mechanical properties were improved; the Young's modulus was improved, and the strain at break values doubled. The molecular weights (measured by SEC) increased moderately when AIBN was used as an initiator. However, when KPS was used as an initiator,

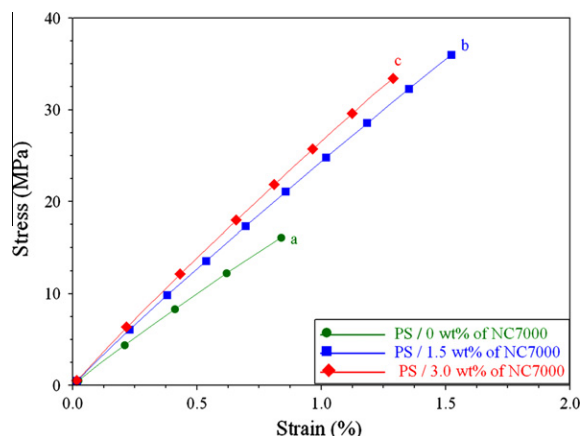


Fig. 5. Stress–strain curves for MWCNT (Nanocyl NC7000)/PS samples: (a) Pristine PS; (b) MWCNT/PS composite with 1.5 wt.% loading; (c) MWCNT/PS composite with 3.0 wt.% loading.

the molecular weights increased significantly more, which was partially responsible for the increased modulus values. Table 1 shows a summary of mechanical properties, molecular weights (M_w), and polydispersities (PD) of PS/CNT composites. AIBN as initiator and DBSA as surfactant were the best combination for mechanical properties for PS/CNT composites when thin pristine Nanocyl NC7000 MWCNTs were used. The thicker pristine Bayer Baytubes (MWCNT) gave poor results for mechanical properties, even though the dispersion of the CNTs was excellent.

For poly(methyl methacrylate)-based composites, the improvements in mechanical properties were on a smaller scale than for PS/CNT composites (Table 2). The Young's modulus improved, especially when AIBN was used as an initiator. With non-functionalized MWCNTs, the strain at break values remained stable or improved slightly up to 6 wt.% of MWCNTs, when KPS was used as an initiator. With AIBN as an initiator, the strain at break values started to decrease at lower MWCNT (between 1.5 and 3 wt.%) loading. The AIBN probably reacted with the surface of the CNTs, introducing some additional bonding, as with PS [12]. For mechanical properties, the optimal concentration of Nanocyl NC7000 MWCNTs was around 3 wt.%; for thicker Bayer Baytubes MWCNTs the optimal concentration was higher, between 6 and 15 wt.%. As with PS, the CNTs participated in the polymerization process, which increased the molecular weight as the CNT loading increased (Table 2). The influence was, however, significantly less for PMMA than for PS, especially with KPS as an initiator. Bayer Baytubes also increased the molecular weights significantly more than Nanocyl NC7000 MWCNTs, which was due to the different surface area of MWCNTs. The use of functionalized MWCNTs gave slightly better mechanical properties, especially strain at break values, than pristine MWCNTs. The reason for the improved mechanical properties was probably an increased amount of bonding between the matrix polymer and functionalized CNTs. The increase of molecular weights due to CNT loading was significantly less for functionalized MWCNTs, than for non-functionalized MWCNTs. Overall, thinner MWCNTs (Nanocyl NC7000) improved mechanical properties more than thicker MWCNTs (Bayer Baytubes) with same CNT loading, as could be expected. The dispersion of DWCNTs (Nanocyl NC2100) was incomplete, which was at least partially responsible for the DWCNT/PMMA composites having slightly lower modulus values than pure PMMA.

3.3. Electrical conductivity properties of CNT/polymer composites

Improved electrical conductivity is perhaps the most promising application area for CNTs at the moment. If CNTs are efficiently

Table 1Summary of mechanical properties, molecular weights (M_w), and polydispersities (PD) of PS/MWCNT composites.

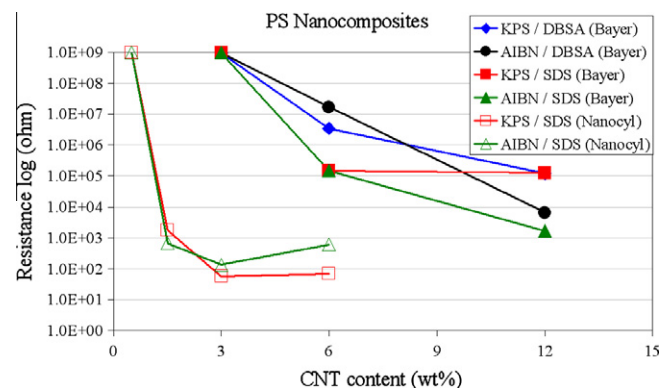
Matrix	Surfactant	Initiator	CNT loading (wt.%)	CNT treatment	Young's modulus (MPa)	Strain at break (MPa)	M_w (g/mol)	PD
PS	DBSA	AIBN	–	–	2100	16	220,000	4.4
PS	DBSA	AIBN	NC7000/1.5	–	2800	36	630,000	4.8
PS	DBSA	AIBN	NC7000/3	–	3000	34	570,000	3.7
PS	SDS	AIBN	–	–	2600	36	560,000	2.8
PS	SDS	AIBN	NC7000/1.5	–	3100	29	690,000	7.2
PS	SDS	AIBN	NC7000/3	–	2300	34	620,000	3.0
PS	DBSA	KPS	–	–	2300	29	380,000	5.3
PS	DBSA	KPS	NC7000/1.5	–	2800	38	1,270,000	3.1
PS	DBSA	KPS	NC7000/3	–	2200	24	1,510,000	4.4
PS	SDS	KPS	–	–	2000	36	720,000	2.6
PS	SDS	KPS	NC7000/1.5	–	2400	19	1,200,000	1.8
PS	SDS	KPS	NC7000/3	–	2300	26	1,240,000	2.0

Table 2Summary of mechanical properties, molecular weights (M_w), and polydispersities (PD) of PMMA/CNT composites.

Matrix	Surfactant	Initiator	CNT loading (wt.%)	CNT treatment	Young's modulus (MPa)	Strain at break (MPa)	M_w (g/mol)	PD
PMMA	DBSA	KPS	–	–	2500	48	144,000	3.7
PMMA	DBSA	KPS	Baytubes/3	–	2500	38	152,000	2.8
PMMA	DBSA	KPS	Baytubes/6	–	2900	43	504,000	2.8
PMMA	DBSA	KPS	Baytubes/15	–	3100	32	661,000	2.9
PMMA	DBSA	KPS	–	–	2500	49	144,000	3.7
PMMA	DBSA	KPS	Baytubes/3	Acid funct.	2900	48	200,000	2.6
PMMA	DBSA	KPS	Baytubes/6	Acid funct.	3200	48	229,000	3.0
PMMA	DBSA	KPS	Baytubes/15	Acid funct.	3800	41	288,000	3.4
PMMA	DBSA	KPS	–	–	2500	48	144,000	3.7
PMMA	DBSA	KPS	NC7000/1.5	–	3600	52	155,000	2.2
PMMA	DBSA	KPS	NC7000/3	–	3400	46	145,000	2.8
PMMA	DBSA	KPS	NC7000/6	–	3300	48	160,000	3.6
PMMA	DBSA	KPS	–	–	2500	48	144,000	3.7
PMMA	DBSA	KPS	NC7000/1.5	Acid funct.	2900	52	175,000	3.2
PMMA	DBSA	KPS	NC7000/3	Acid funct.	2800	53	218,000	3.0
PMMA	DBSA	KPS	NC7000/6	Acid funct.	3200	53	279,000	2.8
PMMA	DBSA	AIBN	–	–	3400	47	235,000	2.3
PMMA	DBSA	AIBN	NC7000/1.5	–	3300	44	412,000	2.4
PMMA	DBSA	AIBN	NC7000/3	–	3400	27	486,000	2.3
PMMA	DBSA	AIBN	NC7000/6	–	4000	30	395,000	2.5
PMMA	DBSA	AIBN	–	–	3400	47	235,000	2.3
PMMA	DBSA	AIBN	NC2100/1.5	–	3300	44	240,000	2.5
PMMA	DBSA	AIBN	NC2100/3	–	3000	51	281,000	2.8

dispersed and yet percolate, a very small amount (even 0.1 wt.%) of CNTs can confer good electrical conductivity on otherwise insulating polymers. The percolation threshold is higher for MWCNTs than for SWCNTs or DWCNTs, usually some weight percents. The percolation threshold depends on the matrix polymer, CNT production method, CNT conductivity, and the processing of the composite [3,8,16]. We used three different CNTs (Bayer Baytubes, MWCNT; Nanocyl NC7000; MWCNT; and Nanocyl NC2100, DWCNT) for both PS and PMMA matrices. For PS composites with Nanocyl NC7000, the percolation threshold was between 0.5 and 1.5 wt.% MWCNTs when SDS was used as surfactant. The percolation threshold shifted to 1.5–3 wt.% MWCNTs when DBSA was used as surfactant. With Bayer Baytubes the percolation threshold was significantly higher. Also, with the Baytubes, SDS used as a surfactant gave better electrical conductivities. Fig. 6 shows surface electrical conductivities for MWCNT/PS composites. With PS, the selection of initiator (AIBN or KPS) did not have a significant impact on electrical conductivity.

With PMMA, the initiator/polymerization method affected the electrical conductivity significantly; use of AIBN as an initiator gave better electrical conductivities for the composites (Fig. 7). For PMMA composites with NC7000 MWCNTs, the percolation threshold was around 1.5 wt.% MWCNTs. With Bayer Baytubes the percolation threshold shifted to 3–6 wt.% MWCNTs. Tests were also conducted with acid functionalized MWCNTs. The electrical

**Fig. 6.** Electrical (surface) conductivities for MWCNT/PS composites.

conductivity was actually slightly better for composites with pristine MWCNTs, which indicated that the acid functionalization process either caused some damage to the CNTs or shortened them. The difference between pristine and acid functionalized MWCNTs was, however, not significant. The conductivity of NC2100 (DWCNTs)-based composites was rather poor (comparable to Nanocyl NC7000 MWCNTs); this was related to the rather poor dispersion of the DWCNTs, which was seen in the TEM images.

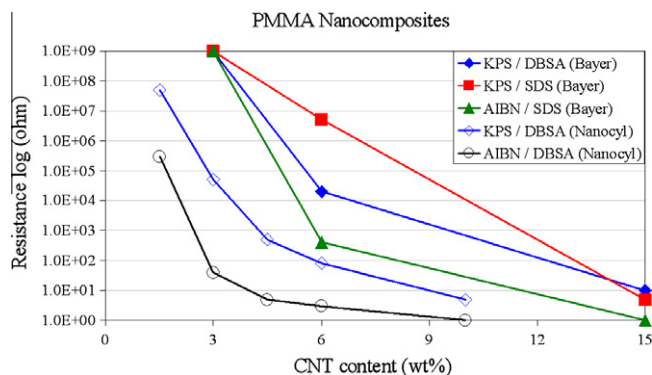


Fig. 7. Electrical (surface) conductivities for MWCNT/PMMA composites.

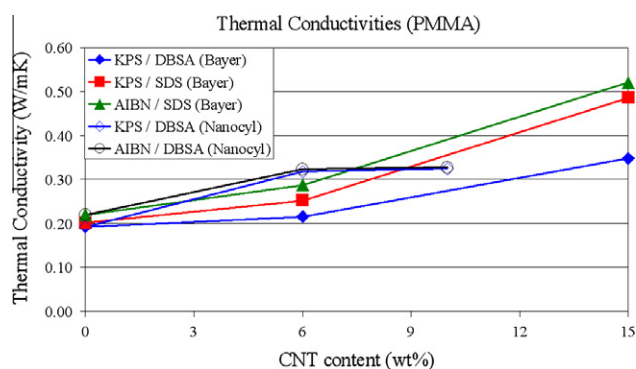


Fig. 8. Thermal conductivities for MWCNT/PMMA composites.

3.4. Thermal conductivity properties of CNT/PMMA composites

Thermal conductivities for PMMA/MWCNT composites were measured using a Hot Disk Thermal Constants Analyzer. Thermal conductivities for pristine PMMA samples were $\sim 0.19\text{--}0.21$ W/mK. The thermal conductivity of neat PMMA is $\sim 1/10,000$ of typical MWCNT thermal conductivity [6,15]. The thermal conductivities for PMMA/CNT composites are shown in Fig. 8. When thin Nanocyl NC7000 MWCNTs were added to the PMMA matrix, thermal conductivity increased about 70% (6 wt.% load), and then stabilized. With Bayer Baytubes, the thermal conductivity steadily increased with MWCNT loading, up to 15 wt.% Baytubes. Thermal conductivities of Nanocyl 2100 DWCNT/PMMA composites were also tested, and were found to improve thermal conductivity like thin Nanocyl NC7000 MWCNTs (up to 3.0 wt.%). Thermal conductivities of PS/CNT composites were not measured, as the thermal conductivity of neat PS is even lower than for PMMA. Thermal conductivity of polymers can be improved by CNTs, but the improvement is negligible for amorphous polymers such as PMMA and PS. The *in situ* polymerization method, where the polymer forms layers around the CNTs during polymerization, is probably not the optimal production method from the point of view of obtaining good thermal conductivity. The heat cannot transfer effectively, as the CNTs are isolated in the polymer matrix and are not physically connected. Thicker MWCNTs had better thermal conductivity at high CNT loading; the initiator (KPS or AIBN) did not have a significant impact on thermal conductivity. The composites that were polymerized with SDS as a surfactant seemed to have slightly higher thermal conductivity.

4. Conclusions

CNT/Polystyrene and CNT/Poly(methyl methacrylate) composites were prepared via *in situ* emulsion and emulsion/suspension

polymerization. The emulsion and suspension polymerization methods are widely used in industry, and composites manufactured via these methods can be mass-produced at a reasonable cost. The selection of initiator, surfactant, and polymerization method had a significant impact on composite properties, as did the type of CNT (MWCNT or DWCNT) used. The dispersion of MWCNTs into the polymer matrix (both PS and PMMA) was excellent; no aggregates were detected in the composites, even at high MWCNT loadings (10 wt.%). The dispersion of DWCNTs was significantly poorer; ultrasonication, CNT length, and water as a medium, limited the dispersion. Electron microscopy confirmed that *in situ* polymerization provided stable dispersion of CNTs even after thermal processing. The mechanical properties of composites were improved at low CNT loadings, but as the molecular weights increased with CNT loading, it was difficult to estimate to what degree the improved mechanical properties were due to CNTs, and to what degree due to the increase in molecular weight. The selection of CNTs had a significant influence on percolation threshold. Thin MWCNTs (Nanocyl NC7000) had percolation threshold around 1.5 wt.%. With thicker Bayer Baytubes, the percolation threshold was higher, between 3 and 6 wt.%. As the dispersion of DWCNTs was not complete, the percolation threshold with Nanocyl NC2100 was the same as with Nanocyl NC7000 MWCNTs. The surfactant and initiator selection also had some influence on percolation threshold. The thermal conductivity of PMMA/CNT composites was also measured. Thick Bayer Baytubes improved the thermal conductivity most, from 0.2 W/mK to 0.5 W/mK (0 wt.% vs. 15 wt.% Bayer Baytubes). Thinner MWCNTs (Nanocyl NC7000) and DWCNTs (Nanocyl NC2100) had better thermal conductivity at low CNT loadings (up to 6 wt.%), but at higher CNT loadings their thermal conductivity values plateaued.

Acknowledgments

The POPROK Graduate School (Ministry of Education of Finland) and Finnish Funding Agency for Technology and Innovation (Tekes) are thanked for their support. We also thank Dr. Hua Jiang (Aalto University School of Science and Technology) for HRTEM images of CNTs.

References

- [1] Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1 nm diameter. *Nature* 1993;363:603–5.
- [2] Coleman JN, Khan U, Blau WJ, Guñko YK. Small but strong: a review of mechanical properties of carbon nanotube-polymer composites. *Carbon* 2006;44:1624–52.
- [3] Bauhofer W, Kovacs JZ. A review and analysis of electrical percolation in carbon nanotube polymer composites. *Compos Sci Technol* 2009;69:1486–98.
- [4] Gojny FH, Wichmann MHG, Fiedler B, Kinloch IA, Bauhofer W, Windle AH, et al. Evaluation and identification of electrical and thermal conduction mechanisms in carbon nanotube/epoxy composites. *Polymer* 2006;47:2036–45.
- [5] Bagchi A, Nomura S. On the effective thermal conductivity of carbon nanotube reinforced polymer composites. *Compos Sci Technol* 2006;66:1703–12.
- [6] Hagenmueller R, Guthy C, Lukes JR, Fischer JE, Winey KI. Single wall carbon nanotube/polyethylene nanocomposites: thermal and electrical conductivity. *Macromol* 2007;40:2417–21.
- [7] Brandrup J, Immergut EH, Grulke EA, editors. *Polymer Handbook*. New York: John Wiley & Sons; 1999.
- [8] Wu W, He T, Chen JF, Zhang X, Chen Y. Study on *in situ* preparation of nanocalcium carbonate/PMMA composite particles. *Mater Lett* 2006;60:2410–5.
- [9] Ding X, Zhao J, Liu Y, Zhang H, Wang Z. Silica nanoparticles encapsulated by polystyrene via surface grafting and *in situ* emulsion polymerization. *Mater Lett* 2004;58:3126–30.
- [10] Priya BR, Byrne HJ. Investigation of sodium dodecyl benzene sulfonate assisted dispersion and debundling single-wall carbon nanotubes. *J Phys Chem C* 2008;112:332–7.
- [11] Park SJ, Cho MS, Lim ST, Choi HJ, Jhon MS. Electrorheology of multiwalled carbon nanotube/poly(methyl methacrylate) nanocomposites. *Macromol Rapid Commun* 2005;26:1563–6.
- [12] Park SJ, Cho MS, Lim ST, Choi HJ, Jhon MS. Synthesis and dispersion characteristics of multi-walled carbon nanotube composites with

- poly(methyl methacrylate) prepared by in-situ bulk polymerization. *Macromol Rapid Commun* 2003;24:1070–3.
- [13] Ham HT, Choi YS, Chee MG, Chung IJ. Singlewall carbon nanotubes covered with polystyrene nanoparticles by in-situ miniemulsion polymerization. *J Polym Sci Part A: Polym Chem* 2006;44:573–84.
- [14] Wu TM, Chen EC. Preparation and characterization of conductive carbon nanotube-polystyrene nanocomposites using latex technology. *Compos Sci Technol* 2008;68:2254–9.
- [15] Cai D, Song M. Latex technology as a simple route to improve the thermal conductivity of a carbon nanotube/polymer composite. *Carbon* 2008;46:2107–12.
- [16] Ji L, Stevens MM, Zhu Y, Gong Q, Wu J, Liang J. Preparation and properties of multi-walled carbon nanotube/carbon/polystyrene composites. *Carbon* 2009;47:2733–41.
- [17] Blond D, Barron V, Ruether M, Ryan KP, Nicolosi V, Blau WJ, et al. Enhancement of modulus, strength, and toughness in poly(methyl methacrylate)-based composites by the incorporation of poly(methyl methacrylate)-functionalized nanotubes. *Adv Funct Mater* 2006;16:1608–14.
- [18] Banerjee S, Tirandai HB. Covalent surface chemistry of single-walled carbon nanotubes. *Adv Mater* 2005;17:17–29.
- [19] Tasis D, Tagmatarchis N, Bianco A, Prato M. Chemistry of carbon nanotubes. *Chem Rev* 2006;106:1105–36.
- [20] Ramanathan T, Liu H, Brinson LC. Functionalized SWNT/polymer nanocomposites for dramatic property improvement. *J Polym Sci Part B: Polym Phys* 2005;43:2269–79.
- [21] Tchoul MN, Ford WT, Ha MLP, Chavez-Sumarriva I, Grady BP, Lolli G, et al. Composites of single-walled carbon nanotubes and polystyrene: preparation and electrical conductivity. *Chem Mater* 2008;20:3120–6.
- [22] Goertzen WK, Kessler MR. Dynamic mechanical analysis of fumed silica/cyanate ester nanocomposites. *Compos Part A* 2008;39:761–8.