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## Macromolecular Nanotechnology

# *In situ* polymerization of methyl methacrylate/multi-walled carbon nanotube composites using cationic stearyl methacrylate copolymers as dispersants

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## ABSTRACT

Novel water-soluble amphiphilic copolymers (poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)]) for dispersing multi-walled carbon nanotubes (MWCNTs) were used to carry out *in situ* methyl methacrylate (MMA) polymerization. The morphology of the poly(methyl methacrylate)/MWCNT composites and the dispersion of the MWCNTs were analyzed by transmission electron microscopy. The dispersion of multi-walled carbon nanotubes in the composites was excellent for cationic SMA (stearyl methacrylate) copolymers, even at high MWCNT loading (6.0 wt.%). The mechanical properties and electrical and thermal conductivities of the composites were also analyzed. Mechanical properties were improved by MWCNTs; the strain at break values remained stable up to 6.0 wt.% MWCNT loading. Both electrical and thermal conductivities were improved by the addition of MWCNTs.

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## 1. Introduction

Carbon nanotubes (CNTs) have remarkable mechanical, electrical conductivity and thermal conductivity properties, which makes them outstanding filler candidates for polymer-based composites. The polymers themselves have greatly varied mechanical properties, but these are only a fraction of the theoretical mechanical properties of the CNTs. Polymers are generally almost completely thermally and electrically non-conductive, except for some electrically conducting polymers like PANI (polyaniline). Hence, combining a matrix polymer with CNTs should result in a composite with sufficiently good mechanical properties that also has controllable electrical and thermal conductivities. However, with real composites, the situation has not worked out as well as expected. Electrical conductivity has

been improved greatly with CNTs, however the thermal conductivity of CNT/polymer-based composites has proven to be an area where the high expectations for CNTs have not been realized. The reported improvements in mechanical properties with CNTs have varied greatly, with a low concentration of CNTs usually giving significant improvement in mechanical properties of composites [1]. However, there are two requirements for this: (1) good dispersion of CNTs into the polymer matrix, and (2) interaction between the polymer matrix and the CNTs. The pristine CNTs are always strongly bundled; these bundles need to be broken up, CNTs dispersed properly, and then re-aggregation prevented. At the same time, the CNTs and polymer matrix should have covalent or equivalent bonding between them, so that the composite structure can transfer mechanical energy. There are various methods to achieve this. Surface modification, or covalent modification, is based on attaching functional groups, like carboxyl, to the CNT surface [1–3]. Although this approach usually gives better mechanical

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properties, it disrupts the  $\pi$ – $\pi$  conjugation of CNTs, and usually leads to poorer electrical properties. The so-called non-covalent approach, on the other hand, depends on weak interaction forces via dispersants or surfactants. The non-covalent approach is usually not as effective as covalent modification, but it preserves the  $\pi$ – $\pi$  interactions on the CNT surfaces. Traditional surfactants, like sodium dodecyl sulphate (SDS), are often combined with *in situ* polymerization to achieve the dispersion of CNTs and polymerization in one step [1,4–5]. One interesting and promising component that might be well-suited to use with the non-covalent approach is block copolymers.

Several research groups have tried different block copolymers to either disperse the CNTs into solvent or to graft the block copolymers directly onto CNTs. The CNTs grafted with block copolymers could be assembled into defined structures if the solvent, copolymer block length, and so on, are selected exactly right. Only a few research reports on this topic exist, but the initial results show at least some promise. A more common use for block copolymers with CNTs is as a surfactant to disperse the CNTs into a suitable solvent. The solvent has an important function with block copolymers: the insoluble block will minimize the contact with solvent, and on the other hand, the soluble block swells in the solvent [6–18]. If water is used as the solvent, an amphiphilic copolymer with a long hydrocarbon segment combined with some strongly hydrophilic segment would be a good candidate as a dispersing agent.

In this study, we produced MWCNT/poly (methyl methacrylate) composites using an *in situ* emulsion/suspension polymerization method with an amphiphilic copolymer (poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)]) as the surfactant and water as the solvent. The maximum MWCNT (pristine Nanocyl NC7000) loading was up to 6 wt.%. The initial break-up of CNT bundles was carried out with mild ultrasonification to avoid excessive CNT shortening. DMA (dynamic mechanical analysis) was used to determine the mechanical properties and glass transition temperatures of the composites. The electrical and thermal conductivities were also analyzed. Transmission electron microscopy (TEM) was used to characterize the dispersion of the CNTs and to understand the morphology of the composite samples.

## 2. Experimental

### 2.1. Materials

MWCNTs (Nanocyl NC7000) were obtained from Nanocyl S.A., Belgium. NC7000 MWCNTs are manufactured via a chemical vapor deposition (CVD) process; the carbon purity is ~90%, average diameter ~9.5 nm, and average length 1.5  $\mu$ m (based on data from the manufacturer). The dimensions of pristine Nanocyl NC7000 MWCNTs were also measured by Simon et al. [19] by TEM; the reported average length was 0.7  $\mu$ m and average diameter 10.4 nm. The MWCNTs were used as received. Fig. 1 shows transmission electron microscopy (TEM) images of pristine Nanocyl NC7000 MWCNTs.

The monomer, methyl methacrylate (purity > 99%), was supplied by Fluka (Sigma–Aldrich). It was passed through aluminum oxide (supplied by Fluka) to remove inhibitor. The initiator, azobisisobutyronitrile (AIBN, purity  $\geq$  98%), was supplied by Fluka (Sigma–Aldrich), and sodium hydrogen carbonate ( $\text{NaHCO}_3$ , purity  $\geq$  99.5%), which was used as buffer, was supplied by Merck. Initiator and buffer were used as received.

Prepolymers for cationic polymers were synthesized with radical polymerization using AIBN as an initiator. The amino groups were then quaternized into the cationic form in order to increase water solubility. The poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)] was water-soluble when the amount of stearyl methacrylate (SMA) was less than 17 mol%. The chemical structure of poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)] (PSMAQ) is shown in Fig. 2. The used chemicals, polymerization process and characterizations for cationic SMA copolymers are described in more detail in [20].

### 2.2. Polymerization and sample preparation

The seed emulsion was prepared ultrasonically. MWCNTs, amphiphilic polymer, buffer ( $\text{NaHCO}_3$ ), 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 (15 min). Ultrasonic irradiation was carried out with the probe of the ultrasonic horn immersed directly into the system (Sonopuls HD 2200, 100 W, 30 min). After ultrasonic treatment the flask was transferred to an oil bath and fitted with a stirrer, using a stirring rate of 300 rpm. The system was again (30 min) deoxygenated with argon. The initiator (AIBN) was dissolved in the monomer and the solution was fed into the reactor with the membrane pump at 0.03 mL/min. Polymerizations were conducted under argon atmosphere for 20–21 h at 75 °C. After polymerization, the emulsion was dried in an oven at least 48 h at 50 °C. The dried polymer powder was hot pressed (force: 150 kN) at 165 °C to produce approximately 1 mm thick samples.

### 2.3. Characterizations

Pristine Nanocyl NC7000 MWCNTs were studied by TEM (Philips/FEI CM200 FEG). The TEM samples were prepared by dissolving the MWCNTs into ethanol with mild ultrasound treatment, and dropping the solution onto a copper grid and drying. The morphology of the composites and dispersion of MWCNTs were also studied with transmission electron microscopy. Samples were embedded into Specifix 20 (supplied by Stuers) epoxy and cured at room temperature. After curing, the samples were sectioned with a Leica Ultracut UTC ultramicrotome and Diatome diamond knife at room temperature. Approximately 70 nm thick sections were collected on copper grids. The sections were observed using a Jeol JEM-3200FSC cryotransmission electron microscope at –188 °C. Micrographs were taken with a Gatan Ultrascan 4000 camera, with the

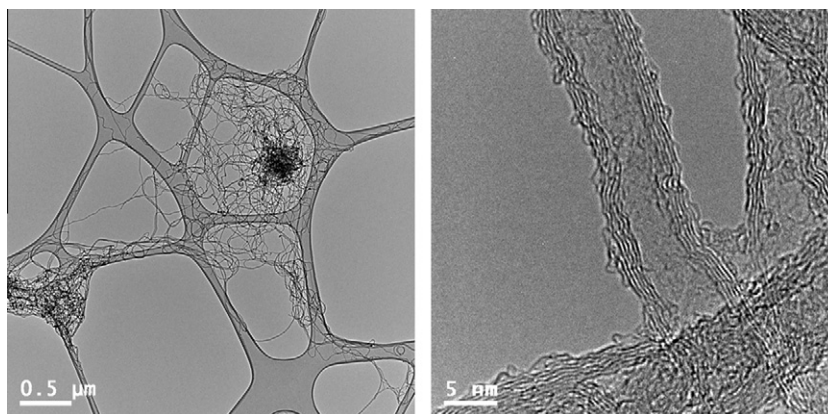


Fig. 1. TEM images of pristine Nanocyl NC7000 MWCNTs: Magnification:  $\times 4200$  (left);  $\times 470,000$  (right).

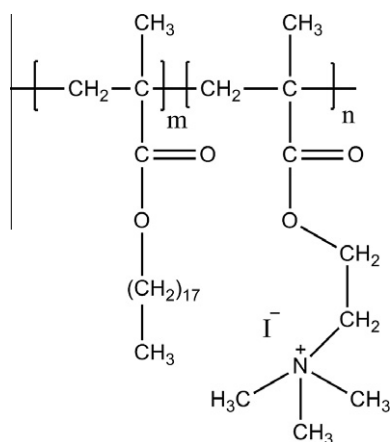


Fig. 2. The chemical structure of poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)] (PSMAQ).

microscope operating in bright field mode, using an acceleration voltage of 300 kV and an Omega type in-column energy filter set to 0–20 eV energy-loss range (zero-loss imaging).

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 chloroform, which was also used as eluent in SEC. Samples were filtered twice through a 450 nm (pore size) filter to remove the insoluble components (MWCNTs and possible polymer chains grafted with MWCNTs), and the filtrate (soluble fraction) was subjected to SEC testing. Room temperature was used for all SEC testing.

The mechanical properties of the composites ( $\sim 1$  mm thick hot pressed samples) were analyzed by DMA (TA Instruments Q800) at 25 °C using a single cantilever 20 mm (effective length 10 mm) probe. The glass transition of composite samples was also measured with DMA using a heating rate of 3 °C/min from 0 to 180 °C. Temperature runs were done in amplitude mode (50  $\mu$ m) to get 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 directly from the surface of DMA samples by the four-probe method (Keithley 2400 Sourcemeter). The distance between probes was about 1 mm. The sample surfaces were finished with grit 600 paper to remove any possible polymer skin. Thermal conductivity was measured from hot pressed (diameter 12 mm, thickness 2 mm) samples by a Hot Disk Thermal Constants Analyzer combined with the Keithley 2400 Sourcemeter. The thermal conductivity samples were stabilized for 30 min; the measurement was done at 0.05 W for 30 s.

### 3. Results and discussion

#### 3.1. Selection of amphiphilic copolymers

Three different polymers were used as surfactants to disperse the MWCNTs, and to form a composite. Two of them were cationic stearyl methacrylate (SMA) copolymers, with 13 and 17 mol% of SMA. The third one was PDM homopolymer, which was used as a reference. The molecular weights of the non-ionic prepolymers were: PSMA13, stearyl methacrylate (SMA) content 13 mol%, molecular weight ( $M_n$ ) 50,600 g/mol; PSMA17, SMA content 17 mol%, molecular weight ( $M_n$ ) 24,700 g/mol; and PDM, SMA content 0 mol%, molecular weight ( $M_n$ ) 62,500 g/mol. The amount of amphiphilic polymer was varied (125, 250, and 500 mg) to estimate the influence of its concentration on polymerization and composite properties.

#### 3.2. The morphology of composites

The dispersion capability of amphiphilic copolymers for MWCNTs in water was tested with 125 mg of amphiphilic copolymer, 125 mg of Nanocyl NC7000 MWCNTs in 100 ml of water (corresponding to actual polymerization with 3.0 wt.% of MWCNTs in the composite). With amphiphilic copolymers, the initial ultrasound treatment dispersed the MWCNTs visually very uniformly into the water; the result was a completely black mixture with no significant

re-agglomeration after one week (7 days). After 30 days some re-agglomeration had occurred, but overall, the stability of the dispersion with SMA copolymers was good. The dispersion of MWCNTs with homopolymer (PDMQ) was significantly worse, with severe re-agglomeration already seen after 1 week (7 days).

Transmission electron microscopy (TEM) was used to characterize the morphology, and especially MWCNT dispersion, of the composites. Fig. 3 shows typical TEM images of PMMA/MWCNT (3.0 wt.% Nanocyl NC7000) composite samples with cationic SMA copolymer. There was no noticeable difference in dispersion quality between PSMA13Q and PSMA17Q amphiphilic copolymers, nor between concentrations of 125 and 250 mg; all showed good dispersion. By comparison, 500 mg of traditional surfactants, like SDS (sodium dodecyl sulphate) or DBSA (sodium dodecyl benzene sulfate), was required to achieve effective dispersion in a comparable reactor system. Quaternized PDM (PDMQ) homopolymer without SMA part was used as a reference; a TEM image of PMMA/MWCNT (3.0 wt.% of Nanocyl NC7000) with PDMQ as a surfactant is shown in Fig. 4. The dispersion of MWCNTs with PDMQ was almost non-existent; the MWCNTs were clustered during the polymerization and a large percentage of the composite showed practically no MWCNTs. The effect of the poor dispersion capability of PDMQ on composite properties will be discussed in more detail later. The thickness of the MWCNTs in the composite was in the range of 10 nm, which indicated that the MWCNTs were either individually dispersed or consisted of bundles with very low numbers of MWCNTs, which further indicated that the cationic amphiphilic copolymer was able to prevent the MWCNTs from re-agglomerating during the polymerization. At 3.0 wt.% MWCNT, the MWCNTs were mainly separated from each other by polymer, which did limit the electrical conductivity. At 6.0 wt.% MWCNT, the number of MWCNTs was high enough that the MWCNTs were overlapping each other. As the TEM sample preparation by ultramicrotome tended to pull out or cut the MWCNTs, the length of dispersed MWCNTs was difficult to estimate from TEM images. The average length of

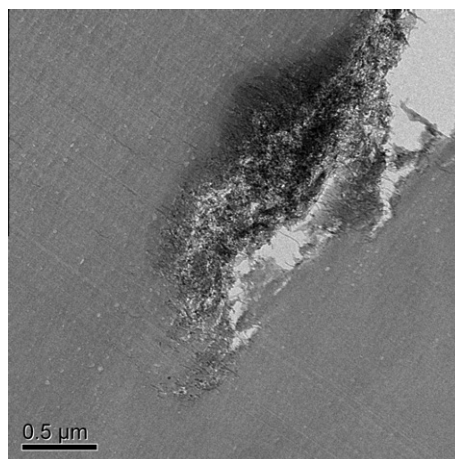


Fig. 4. TEM image of PMMA/MWCNT sample with PDMQ as a surfactant (250 mg of PDMQ, 3.0 wt.% MWCNTs (Nanocyl NC7000)).

Nanocyl NC7000 MWCNTs was  $\sim 0.5 \mu\text{m}$ , which indicated that the initial ultrasound treatment to disperse the MWCNTs into water aided by amphiphilic copolymer might have shortened the MWCNTs to some degree; the length estimate by TEM was, however, quite close to length of pristine Nanocyl NC7000 MWCNTs ( $0.7 \mu\text{m}$ ) estimated by Simon et al. [19]. TEM images were taken from melt processed DMA test specimens, which showed that *in situ* polymerization with cationic SMA copolymers provided dispersions of MWCNTs that were sufficiently stable to sustain thermal processing, a necessary requirement for any larger-scale production and use.

### 3.3. Mechanical properties of composites

The improvement of mechanical properties of polymer-based composites using CNTs has been a very active area of research for almost two decades. There have been numerous articles on the topic, but the actual improvements in mechanical properties have usually been only a fraction of the theoretical expectations. The usual explanation for

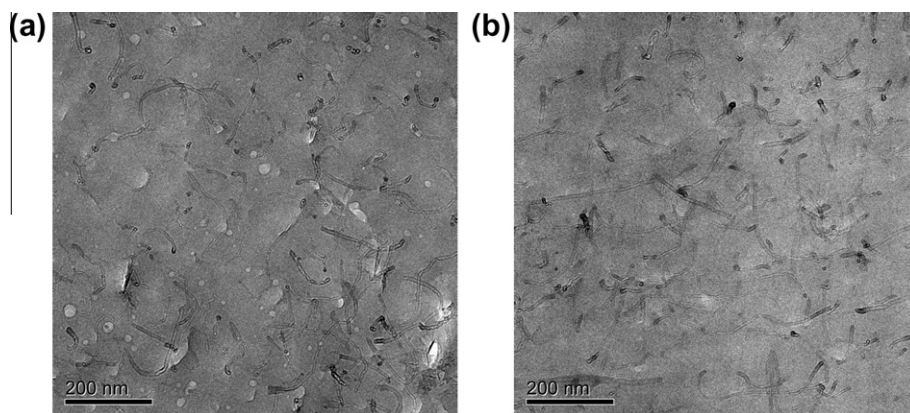


Fig. 3. TEM images of PMMA/MWCNT samples with PSMA17Q as a surfactant: (a) 125 mg of PSMA17Q, 3.0 wt.% MWCNTs (NC7000); (b) 250 mg of PSMA17Q, 3.0 wt.% MWCNTs (NC7000).



this is the poor dispersion of fillers. With *in situ*-based CNT/polymer composites one often-downplayed factor is molecular weight, and to a lesser degree polydispersity. The CNTs can have a significant influence on molecular weight when *in situ* polymerization methods are used; at high CNT loadings the molecular weights can be several times higher than for neat polymer. In this paper, the used amphiphilic copolymers had only a minor influence on the molecular weights of the composites. In some cases, the molecular weights actually decreased with increasing MWCNT loading. When these amphiphilic copolymers were used as a surfactant, the changes in mechanical properties of the composites were induced by the added MWCNTs. A summary of mechanical properties, molecular weights ( $M_w$ ), and polydispersities (PD) of MWCNT/PMMA composites is shown in Table 1. The two amphiphilic copolymers (PSMA13Q (13 mol% SMA) and PSMA17Q (17 mol% SMA)) had nearly identical influences on the mechanical properties of the composites. When 250 mg of amphiphilic copolymer was used as a surfactant, the Young's modulus increased slightly (in the range of 10–25%). The molecular weights of neat composite and composite with 6 wt.% Nanocyl NC7000 MWCNTs were approximately the same, so the increase in modulus was caused by the MWCNTs. For PSMA13Q the strain at break values increased with CNT loading, but for PSMA17Q a decrease was seen at higher CNT loading. When 125 mg of PSMA13Q or PSMA17Q was used as surfactant, the Young's modulus values were comparable to those obtained using 250 mg of surfactant, but the strain at break values

remained high, even at high CNT loading (6 wt.%). Five hundred milligrammes of amphiphilic copolymers was also tested, but the results were negative for mechanical properties. The strain at break values started to decrease significantly at higher CNT loading, so that the composites started to become more brittle. Based on these results, 125 mg of amphiphilic copolymer was the optimal amount of surfactant, in light of the mechanical properties of the composites. If more copolymer was present, the mechanical properties started to degrade. This was possibly due to the formation of a copolymer phase, thus preventing the effective contact between MWCNTs and PMMA matrix, as AIBN is known to react with CNTs and catalyze covalent bonding [21]. Pure PDMQ without the SMA moiety was also tested, to observe the difference between cationic copolymers and cationic homopolymer. The pure PDMQ worked adequately at low MWCNT loadings (up to ~3.0 wt.%), but at 6.0 wt.% the modulus values of the composite decreased by over 50% and strain at break values even more. The obvious reason for this is that the cationic homopolymer was not able to disperse the increasing loading of MWCNTs and severe agglomeration occurred, thus degrading the mechanical properties. Overall, the Young's modulus values for all these composites (with or without MWCNTs) were quite high for PMMA, in the range of 3.3–4.4 GPa (at 25 °C), which indicated that these amphiphilic copolymers were very suitable for PMMA polymerization with AIBN.

The glass transition temperature ( $T_g$ ) is the temperature of the phase change from the glassy to rubbery state.  $T_g$  is a

**Table 1**  
Summary of mechanical properties, molecular weights ( $M_w$ ), and polydispersities (PD) of the composites.

Matrix	Surfactant	Amount of surfactant (mg)	CNT loading (wt.%)	Young's Modulus (MPa)	Strain at break (MPa)	$M_w$ (g/mol)	PD
PMMA	PSMA13Q	250	–	3900	42	452,000	2.2
PMMA	PSMA13Q	250	NC7000/1.5	4000	46	439,000	3.3
PMMA	PSMA13Q	250	NC7000/3	4200	55	403,000	2.6
PMMA	PSMA13Q	250	NC7000/6	4400	47	478,000	2.2
PMMA	PSMA13Q	125	–	3500	38	719,000	2.8
PMMA	PSMA13Q	125	NC7000/1.5	3700	44	482,000	3.5
PMMA	PSMA13Q	125	NC7000/3	3900	42	500,000	2.8
PMMA	PSMA13Q	125	NC7000/6	4200	47	533,000	1.7
PMMA	PSMA13Q	125	NC7000/6	4200	47	533,000	1.7
PMMA	PSMA13Q	250	NC7000/6	4400	47	478,000	2.2
PMMA	PSMA13Q	500	NC7000/6	4300	25	512,000	2.2
PMMA	PSMA17Q	250	–	3800	52	577,000	1.7
PMMA	PSMA17Q	250	NC7000/1.5	4000	51	446,000	3.1
PMMA	PSMA17Q	250	NC7000/3	4100	31	488,000	2.4
PMMA	PSMA17Q	250	NC7000/6	4400	35	585,000	2.3
PMMA	PSMA17Q	125	–	3200	52	493,000	3.9
PMMA	PSMA17Q	125	NC7000/1.5	3700	46	551,000	4.2
PMMA	PSMA17Q	125	NC7000/3	3800	53	582,000	2.8
PMMA	PSMA17Q	125	NC7000/6	4400	49	700,000	2.4
PMMA	PSMA17Q	125	NC7000/6	4400	49	700,000	2.4
PMMA	PSMA17Q	250	NC7000/6	4400	35	585,000	2.3
PMMA	PSMA17Q	500	NC7000/6	3300	32	564,000	2.6
PMMA	PDMQ	250	–	3500	47	409,000	2.8
PMMA	PDMQ	250	NC7000/1.5	3600	44	386,000	3.8
PMMA	PDMQ	250	NC7000/3	3700	46	412,000	2.8
PMMA	PDMQ	250	NC7000/6	1900	18	545,000	2.9

very important property for any composite, as it dictates the operational temperature limits; the mechanical properties drop dramatically at temperatures greater than  $T_g$ . The  $T_g$  is dependent on molecular weight, so that a higher molecular weight means a higher  $T_g$ . For these MWCNT/PMMA composites with amphiphilic copolymer the molecular weight increase with increasing CNT loading was small, or even negative. Therefore, an increase in  $T_g$  can be attributed to the MWCNTs. The glass transition temperature increased by 3–4 °C ( $\tan \delta$  peak from DMA) when MWCNT loading increased from 0 to 6 wt.%, indicating that the MWCNTs had some interaction with the matrix polymer molecules, thus limiting the movement of polymer chains. The increasing  $T_g$  suggested that the dispersion of

MWCNTs was relatively good, as poor CNT dispersion may actually decrease the  $T_g$  by generating more free volume in the matrix. Fig. 5 shows DMA temperature sweeps for PMMA/MWCNT (Nanocyl NC7000) composites with 125 mg of PSMA17Q as a surfactant.  $\tan \delta$  curves (Fig. 5a) showed only one peak, without any noticeable shoulders or broadenings, which suggested that the polymer chains in the composites were relatively uniform in length; meaning the molecular weights of neat polymer and polymer possible grafted with MWCNTs were about the same. The intensity of  $\tan \delta$  peaks also decreased with increased MWCNT loading, which indicated that fewer polymer chains were participating in the  $T_g$  transition. There were two reasons for this: (1) with a higher loading

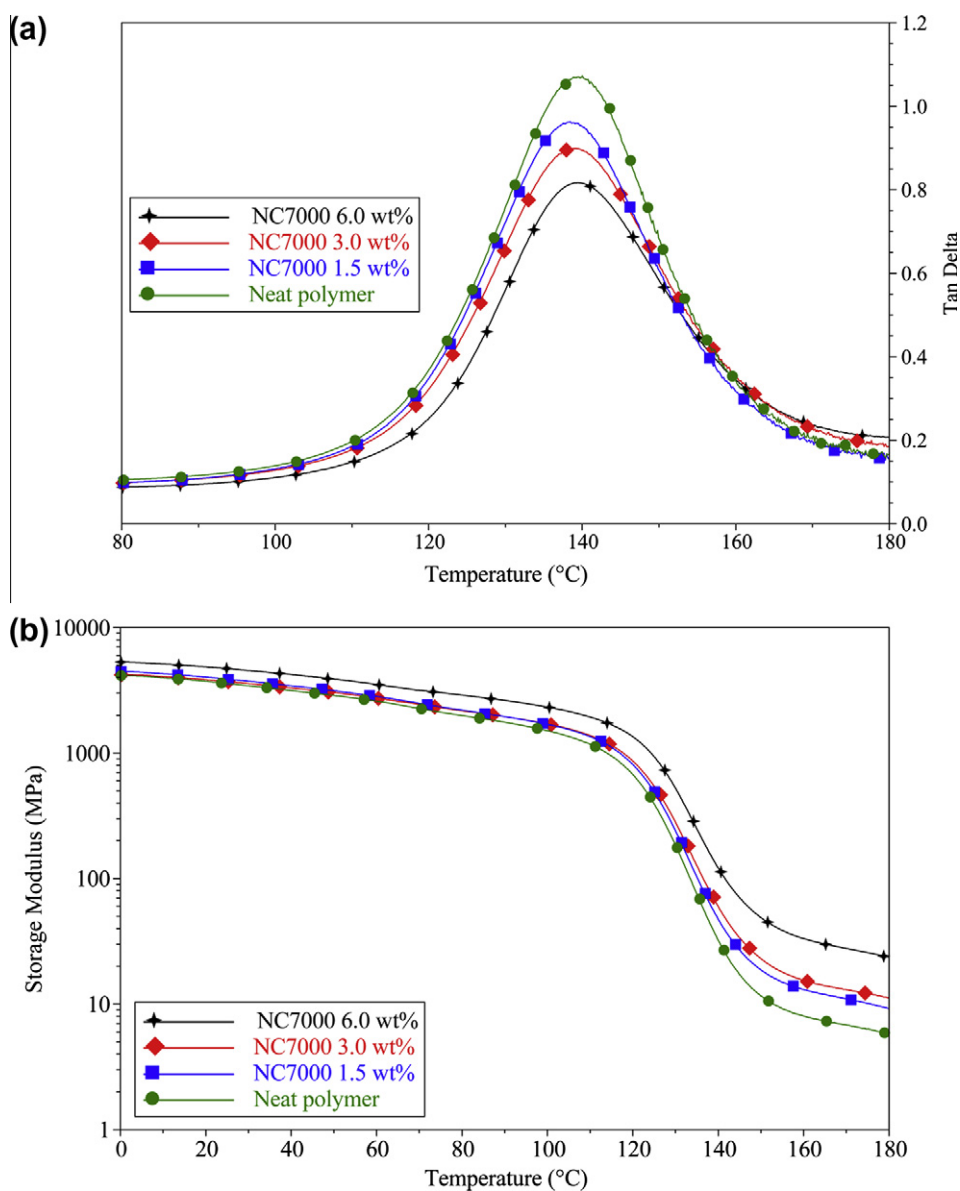


Fig. 5. DMA temperature sweeps for PMMA/MWCNT (Nanocyl NC7000) composites with 125 mg of PSMA17Q as a surfactant: (a)  $\tan \delta$  and (b) storage modulus.

of MWCNTs in the composite, there was additional bonding between MWCNTs and the polymer matrix, and (2) the increasing number of MWCNTs in the composite was restricting the movement of polymer chains. Typical storage modulus curves are shown in Fig. 5b. The storage modulus increased with higher loadings of MWCNTs, and the effect was pronounced in the rubbery region, where the MWCNTs were restricting the movement of the polymer chains.

#### 3.4. Electrical conductivity properties of composites

Improved electrical conductivity via dispersion of CNTs into a polymer matrix may be the most promising area for the use of CNTs in composites. The requirement for electrical conductivity is good dispersion of CNTs. The percolation threshold is the lowest CNT loading ratio necessary to obtain significant conductivity in the composite. The percolation threshold depends on numerous factors, such as CNT dimensions (diameter, length), CNT type, matrix properties, CNT dispersion, interaction between the CNTs and matrix, polymerization method, composite processing, etc. With MWCNTs, the percolation threshold is usually at a low weight percent. Fig. 6 shows surface electrical conductivities for PMMA/MWCNT composites with amphiphilic copolymer as the surfactant. Two cationic copolymers with different percentages of SMA (PSMA13Q (13 mol% of SMA) and PSMA17Q (17 mol% of SMA)) were tested; for both, two different concentrations of copolymer were used (125 and 250 mg). The electrical conductivity was better with a lower amount of surfactant (125 mg). One possible explanation for this was higher coverage of CNTs with the cationic copolymer (or homopolymer, PDMQ) in the composite structure, meaning there was a widening barrier for the electricity to cross as surfactant concentration increased. This would inhibit electrical conduction through the composite slightly. The electrical conductivity with both of the cationic copolymers (PSMA13Q and PSMA17Q) was practically the same. The homopolymer (PDMQ) was also tested for electrical conductivity,

but as shown in Fig. 6, the homopolymer did not work well; without the highly hydrophobic SMA part, the dispersion capability of MWCNTs was poor. Only at a very high MWCNT loading (>5 wt.%) did the composite with quaternized PDMQ become conductive. At that high MWCNT loading, there were so many MWCNTs present that a channel for electricity formed even with the poor dispersion achieved by the homopolymer. The percolation threshold with cationic copolymers was 3.0–4.0 wt.% MWCNTs; with a more optimized concentration of amphiphilic copolymer the percolation threshold could probably be lowered. As was seen from TEM images, the MWCNTs in the composites were short (mostly under 0.5  $\mu\text{m}$ ). Longer CNTs, if they are dispersed properly, have significantly lower electrical percolation thresholds than short CNTs at the same CNT loading [22–24]. With *in situ* polymerized CNT/polymer composites, where the CNTs are separated by a polymer layer, the polymer layer acts as a tunneling barrier which hinders the electron charge transfer between CNTs. Although amphiphilic polymers have been used to disperse the CNTs into polymer matrices, only a few electrical conductivity results have been reported. Hence, for comparison with other types of amphiphilic copolymers little data is available.

#### 3.5. Thermal conductivity properties of composites

Thermal conductivities for PMMA/MWCNT composites were measured using a Hot Disk Thermal Constants Analyzer, which is based on a transient plane source (TPS), one of the leading technologies to measure thermal conductivities of polymers. Thermal conductivity for neat PMMA with amphiphilic copolymer as a surfactant was about 0.19–0.21 W/mK; the thermal conductivity for MWCNTs is  $\sim 3000$  W/mK. The thermal conductivities for PMMA/MWCNT composites are shown in Fig. 7. At low MWCNT loadings (up to 4.5 wt.%) the thermal conductivity was about the same for both concentrations of cationic copolymer (125 and 250 mg). At high loading (6.0 wt.%), the thermal conductivity was better with the

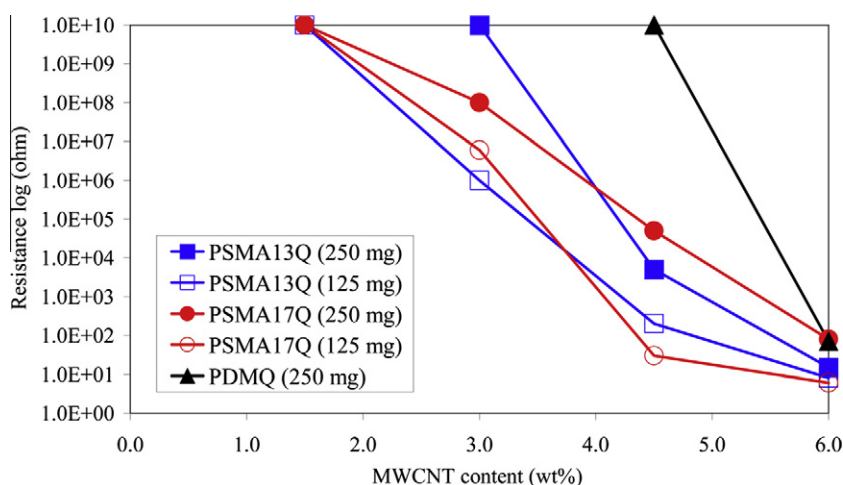


Fig. 6. Electrical (surface) conductivities for MWCNT/PMMA composites.



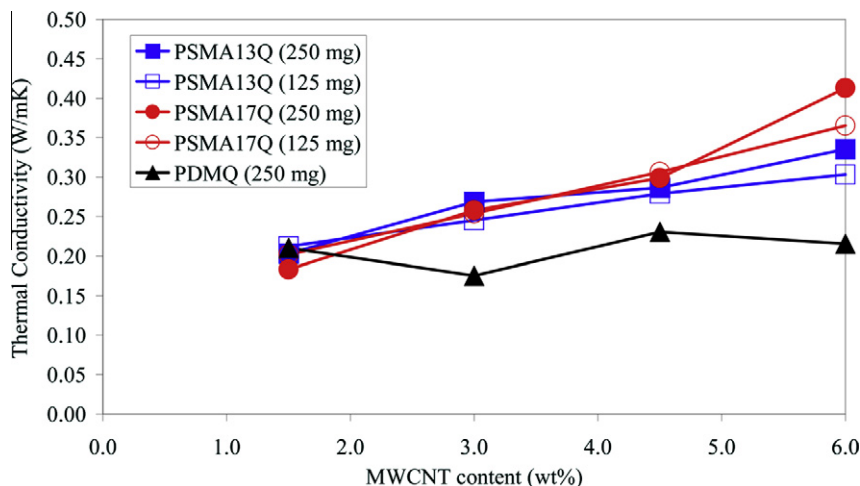


Fig. 7. Thermal conductivities for MWCNT/PMMA composites.

higher concentration of amphiphilic copolymer, which is the opposite of what was observed for electrical conductivity. The *in situ* polymerization method used, where the MWCNTs are individually dispersed in the polymer matrix, is not optimal for good thermal conductivity. Unlike electrical conductivity, thermal conductivity requires very close proximity or preferably physical contact between MWCNTs. In contrast, electricity can “hop” over short distances. With the dispersal system used, the MWCNTs were near, but not actually touching, each others even at high (6.0 wt.%) CNT loading. This was most likely one reason for the relatively low thermal conductivity. As with electrical conductivity, the CNT length is a critical factor for thermal conductivity, with short CNTs having significantly lower thermal conductivity than long ones. The diameter of CNTs, on the other hand, does not have a notable influence on thermal conductivity. Thick MWCNTs have been reported to have thermal conductivities that are equal to or even better than those of thin SWCNTs [25,26]. The PSMA17Q (17 mol% of SMA) gave higher thermal conductivities than PSMA13Q, especially at higher MWCNT loading, which might correspond to having slightly better dispersion and a different orientation capability at the higher SMA content. The thermal conductivity of the composite with quaternized homopolymer (PDMQ) as a surfactant was also tested, but the thermal conductivity did not improve at all even at high MWCNT loading (6 wt.%). The PDMQ could not disperse the MWCNTs properly, leading to a composite with agglomerated MWCNTs as “islands” in the polymer matrix. The electricity could pass through this kind of structure, but for thermal energy 6 wt.% MWCNTs was not enough. With cationic copolymers the thermal conductivity increased up to 110% (6 wt.% load), which was comparable to thermal conductivity results reported with non-polymeric, or traditional, surfactants [27]. In short, the thermal conductivity of polymer-based composites can be improved by CNTs, but the magnitude of the improvement is small when compared to expectations based on the extremely high thermal conductivities of CNTs.

#### 4. Conclusions

A method to produce MWCNT/poly (methyl methacrylate) composites via *in situ* polymerization using novel amphiphilic copolymers was developed. All steps in the composite production chain, such as *in situ* polymerization, the use of pristine unmodified MWCNTs, the use of water as a medium, a simple drying process for the end-product, etc., were chosen to keep the polymerization procedure as simple and inexpensive as possible. Novel amphiphilic copolymers (poly[(stearyl methacrylate)-*stat*-([2-(methacryloyloxy)ethyl] trimethyl ammonium iodide)]) were used to disperse the MWCNTs. The dispersion of MWCNTs into the poly (methyl methacrylate) matrix was good, with no aggregates detected in the composites by TEM, even at high MWCNT loadings (6 wt.%). The adding of MWCNTs in the polymerization using amphiphilic copolymers as dispersant did not affect molecular weights of the composites significantly, so improvements in mechanical properties were due to the addition of MWCNTs. The pristine Nanocyl NC7000 MWCNTs were short, and possibly slightly shortened by the initial ultrasound treatment. This was reflected in electrical and thermal conductivities of the composites. Despite good dispersion of the MWCNTs, the percolation threshold for electrical conductivity was 3.0–4.0 wt.%. Thermal conductivity was improved by 110% (0 vs. 6.0 wt.% of MWCNTs), but absolute values for composites were low (<0.5 W/mK). The concentration of amphiphilic copolymer also played a role in determining the composite properties. Only a limited amount of amphiphilic copolymer could participate in polymerization and dispersion processes; too much amphiphilic copolymer started to degrade the composite properties. The optimal amount of amphiphilic copolymers was not determined. The surfactant concentration needed for successful dispersion of MWCNTs was lower than with traditional surfactants like SDS and DBSA, which had a positive influence, especially on mechanical properties. The amphiphilic copolymers used had relatively high molecular weights; optimization of molecular weights might give still better

dispersion capability. Besides cationic copolymers, PDMQ homopolymer was used as a reference. This homopolymer did not work well, and the dispersion capability was almost non-existent, which was reflected by the poor composite properties, especially for electrical and thermal conductivities.

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