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The effect of MWCNTs on molar mass in in situ polymerization of styrene and methyl methacrylate

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ABSTRACT

Two different in situ-polymerization techniques were studied, emulsion polymerization and combined emulsion/suspension polymerization, with styrene and methyl methacrylate in the presence of different multiwalled carbon nanotubes (MWCNTs). Molar masses and molar mass distributions were determined by size exclusion chromatography, and particle size of the emulsions by dynamic light scattering and rotation rheometry. The compatibility of the MWCNTs and monomer affected polymerization and therefore the molar masses. The MWCNTs stabilized the emulsions, and molar mass distributions narrowed with higher amounts of MWCNTs. In emulsion polymerization of styrene, MWCNTs increased the molar mass. The increase of molar mass was based on the compatible molecular structures of MWCNTs and styrene, so that individual nanotubes were covered by monomer clouds when initiator arrived. In combined emulsion/suspension polymerization of styrene, MWCNTs reacted with the initiator and there was less initiator to polymerize the monomer. There is probably a critical surface area of MWCNTs, for which more initiator is consumed in the reaction with MWCNTs than in polymerization of the monomer. In emulsion polymerization of MMA, monomer clouds around MWCNTs do not form due to incompatible molecular structures, and nanotubes do not enhance polymerization of MMA. In combined polymerization, the initiator is reacting with the nanotubes and the tube is acting as a carrier for initiator, and molar masses are higher.

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1. Introduction

Embedding nanoscale particles in polymers offers a means of producing multifunctional polymer composites with enhanced mechanical, electrical, optical, thermal, or magnetic properties. In general, meeting the challenge of controlling and predicting nanocomposite properties requires an understanding about interfacial phenomena between the particles and polymers. Carbon nanotubes (CNTs) have been of major interest during the last decade both in the academic and industrial worlds. The solubility of pure CNTs in either water or organic solvents has been a limitation to the practical use of this unique material [1]. A

lot of effort has been focused on the functionalization of CNTs [2–6] to improve the solubility and dispersion of CNTs aggregates. The challenge has been to achieve nanodispersion of CNTs in the polymer composite with desired electrical conductivity and mechanical properties, which are greatly improved by having the lowest CNTs content possible. Research has been focused on obtaining the homogeneous and fine dispersions of CNTs in polymers [7] using conventional mixing techniques [8–12], in situ-polymerization in the presence of nanotubes [13–16], and combinations of these techniques [17,18].

With in situ-polymerization it is possible to simultaneously obtain a homogeneous dispersion and a strong interface between CNTs and a polymer matrix. However, there are only a few studies on how the polymer affects the properties of the composite or how CNTs are involved

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in the polymerization reactions. The molar mass and crystallinity of the polymer affect mechanical and thermal properties. Kaminsky et al. [19] observed that nanotubes act as nucleating agents and thus increase the crystallization temperature, the rate constant of crystallization and the dimensions of the crystallite growth of polypropylene. Hermant et al. [20] modified molar masses and molar mass distributions of the matrix polymer in CNT composites, and they observed a significant decrease in the percolation threshold upon the introduction of low molar mass polystyrene or poly(methyl methacrylate).

Emulsion polymerization and related methods are some of the most effective polymerization techniques for preparing in situ-polymerized CNT composites [14,21–24]. However, there are no studies on the molar mass growth of a bulk polymer in the presence of CNTs in emulsions. In the studies of emulsion polymerization of styrene and acrylic acid in the presence of carbon black, it has been observed that carbon black inhibits the polymerization of styrene without co-initiator or buffer [25]. It is notable that the electrical charge of the CNT surface varies with the pH of the surrounding medium and the intrinsic surface properties of CNTs are affected by the purification method [26]. Surfactant by itself was not capable of suspending the nanotubes effectively without the aid of vigorous sonication [26], which is normally used to break down CNT aggregates before or at the same time as mixing or in situ-polymerization. The ultrasonic radiation could have ruptured the surfactant, producing radicals and thus serving as an initiator and affecting the molar mass [27].

In this study, we show how CNTs affect the molar mass and molar mass distribution of polystyrene and poly(methyl methacrylate) when different in situ-emulsion and suspension polymerizations techniques, surfactants, and CNT types are used.

2. Materials and methods

2.1. Materials

Styrene (Fluka, >99%) and methyl methacrylate (MMA, Fluka, >99%) were treated with aluminium oxide (Fluka) to remove inhibitor, initiators potassium peroxodisulfate (KPS, Fluka) and azobisisobutyronitrile (AIBN, Fluka), surfactants sodium dodecyl benzene sulfate (DBSA, Fluka) and sodium dodecyl sulphate (SDS, Sigma–Aldrich), buffer sodium hydrogen carbonate (NaHCO_3 , Merck), and thin and thick multi-walled carbon nanotubes (MWCNTs, thin NC7000, Nanocyl, and thick Baytubes C 150 HP, Bayer) were used as received. All water used was distilled.

2.2. Polymerization of styrene

The seed emulsion was prepared ultrasonically. 0–12 wt.% of MWCNTs, 0.5 g surfactant (DBSA, 1.4 mmol/SDS, 1.7 mmol), 0.1 g (1.2 mmol) NaHCO_3 , and 90/100 mL 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 the ultrasonic

horn (Hielscher UP400S) 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 to an oil bath and fitted with a stirrer. The system was deoxygenated with argon. In the case of KPS as an initiator (emulsion polymerization), 0.09 g (0.33 mmol) KPS was dissolved in 10 mL water and the solution was fed into the reactor before monomer feed. Styrene monomer (5 mL, 43.5 mmol) 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), 0.045 g (0.27 mmol) AIBN was dissolved in 5 mL (43.5 mmol) of styrene. Polymerizations were conducted with a stirring rate of 300 rpm under argon atmosphere for 18–19 h at 60 °C with KPS and for 3 h at 80 °C with AIBN.

2.3. Polymerization of methyl methacrylate

The methyl methacrylate polymerizations were carried out using the same basic principle as described for styrene. For the buffer, 0.095 g (1.1 mmol) NaHCO_3 was used. For emulsion polymerizations 0.095 g (0.35 mmol) of initiator (KPS) was used and the polymerization temperature was set to 65 °C. For combined emulsion/suspension polymerizations 0.095 g (0.58 mmol) of initiator (AIBN) was dissolved in 5 mL (46.9 mmol) of methyl methacrylate, the solution was fed into the reactor and the temperature was set to 75 °C. The polymerization time was 20–21 h.

2.4. Characterization

Molar masses (M_w) and molar mass distributions (D) were determined with respect to polystyrene standards by size exclusion chromatography (SEC, The Waters Associates system). The emulsions were dried at 50 °C in an oven overnight. The samples were dissolved in tetrahydrofuran (THF) and THF was used as an eluent. The samples were filtered through polytetrafluoroethylene membrane (0.45 μm , Waters) in order to analyze only pure polymer. The samples were analyzed at room temperature.

The morphology of the dried emulsions and further hot pressed composites was studied with a field emission scanning electron microscope (SEM, JEOL JSM-6335F) and transmission electron microscopy (TEM, Tecnai 12 Bio Twin). SEM samples were coated with platinum and the electron micrographs were taken using an acceleration voltage 5.0 kV. TEM samples were embedded in 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. MWCNTs were analyzed by TEM (Philips/FEI CM200 FEG). The MWCNT samples were prepared by dissolving the MWCNTs in ethanol in an ultrasound bath, dropping the solution onto a grid and drying. The electron micrographs were taken using an acceleration voltage of 200 kV.

The particle sizes of the emulsions were determined using dynamic light scattering (DLS, Zetasizer Nano ZS, Malvern Instruments) using disposable polystyrene cuvettes. The spectrometer operates with a backscatter angle of 173°. The particle size of PS was analyzed from the ori-

ginal emulsion. The PMMA emulsions were diluted (1:100); otherwise the PMMA emulsion was too dark for reliable particle size analysis. The polystyrene latex beads, particle sizes of 100 nm (LB1, Sigma) and 600 nm (LB6, Sigma), and the mixture of latex beads (1:1 by solid content) were tested as references.

The viscosity of emulsions was determined using a rotation rheometer (AR-G2 rheometer, TA Instruments) equipped with a cone-plate geometry at 23 °C. Shear rates of 0.01–1000 1/s were used for shear viscosity studies. In order to confirm that emulsions are stable during the flow test, time sweeps were done before and after the flow test.

3. Results and discussion

In general, the molar masses increased as the MWCNT content in the emulsions increased (Tables 1–4). The compatibility of the MWCNTs and monomer had an effect on the polymerization and molar masses depending on the monomer used. The MWCNTs stabilized the emulsions and molar mass distributions narrowed when MWCNTs were present in the polymerization reaction. The surface area of the thinner NC7000 nanotubes is much larger than that of thicker Baytubes. The difference in the surface areas of the MWCNTs had an effect on molar masses, as the molar mass grew differently with different MWCNTs in the polymerization reaction.

In the emulsion polymerization of styrene with KPS as an initiator, MWCNTs stabilized the emulsion, and thinner nanotubes were more effective than thicker nanotubes, which had lower surface areas. Only 0.5 wt.% of the thinner NC7000 nanotubes had a major impact on the molar mass of polystyrene (Table 1). The stabilization effect is based on the compatible structures of MWCNTs and styrene, in which individual nanotubes are covered by monomer clouds when the initiator arrives. There were no significant differences in molar masses with different surfactants when thick MWCNTs were present in the polymerization

Table 1
The molar masses (M_w) and molar mass distributions (D) of NC7000/PS composites.

| Sample | Initiator | Surfactant | CNT (wt.%) | M_w (g/mol) | D |
|-----------|-----------|------------|------------|---------------|-----|
| S_KDnc0 | KPS | DBSA | – | 380 000 | 5.3 |
| S_KDnc1.5 | KPS | DBSA | 1.5 | 1 270 000 | 3.1 |
| S_KDnc3 | KPS | DBSA | 3 | 1 510 000 | 4.4 |
| S_KDnc6 | KPS | DBSA | 6 | 146 000 | 1.8 |
| S_ADnc0 | AIBN | DBSA | – | 220 000 | 4.4 |
| S_ADnc1.5 | AIBN | DBSA | 1.5 | 630 000 | 4.8 |
| S_ADnc3 | AIBN | DBSA | 3 | 570 000 | 3.7 |
| S_ADnc6 | AIBN | DBSA | 6 | 270 000 | 3.9 |
| S_KSnc0 | KPS | SDS | – | 580 000 | 2.4 |
| S_KSnc0.5 | KPS | SDS | 0.5 | 1 160 000 | 2.0 |
| S_KSnc1.5 | KPS | SDS | 1.5 | 1 200 000 | 1.8 |
| S_KSnc3 | KPS | SDS | 3 | 1 240 000 | 2.0 |
| S_KSnc6 | KPS | SDS | 6 | 1 750 000 | 1.3 |
| S_ASnc0 | AIBN | SDS | – | 350 000 | 2.5 |
| S_ASnc0.5 | AIBN | SDS | 0.5 | 540 000 | 3.5 |
| S_ASnc1.5 | AIBN | SDS | 1.5 | 690 000 | 7.2 |
| S_ASnc3 | AIBN | SDS | 3 | 620 000 | 3.0 |
| S_ASnc6 | AIBN | SDS | 6 | 650 000 | 5.3 |

Table 2

The molar masses (M_w) and molar mass distributions (D) of Baytube/PS composites.

| Sample | Initiator | Surfactant | CNT (wt.%) | M_w (g/mol) | D |
|--------|-----------|------------|------------|---------------|-----|
| S_KD0 | KPS | DBSA | – | 380 000 | 5.3 |
| S_KD3 | KPS | DBSA | 3 | 860 000 | 2.4 |
| S_KD6 | KPS | DBSA | 6 | 1 100 000 | 1.8 |
| S_KD12 | KPS | DBSA | 12 | 1 360 000 | 1.7 |
| S_AD0 | AIBN | DBSA | – | 220 000 | 4.4 |
| S_AD3 | AIBN | DBSA | 3 | 440 000 | 5.3 |
| S_AD6 | AIBN | DBSA | 6 | 650 000 | 5.8 |
| S_AD12 | AIBN | DBSA | 12 | 920 000 | 2.3 |
| S_KS0 | KPS | SDS | – | 580 000 | 2.4 |
| S_KS3 | KPS | SDS | 3 | 870 000 | 2.2 |
| S_KS6 | KPS | SDS | 6 | 1 080 000 | 2.0 |
| S_KS12 | KPS | SDS | 12 | 1 540 000 | 1.6 |
| S_AS0 | AIBN | SDS | – | 350 000 | 2.5 |
| S_AS3 | AIBN | SDS | 3 | 770 000 | 2.3 |
| S_AS6 | AIBN | SDS | 6 | 920 000 | 2.0 |
| S_AS12 | AIBN | SDS | 12 | 460 000 | 3.3 |

Table 3

The molar masses (M_w) and molar mass distributions (D) of NC7000/PMMA composites.

| Sample | Initiator | Surfactant | CNT (wt.%) | M_w (g/mol) | D |
|-----------|-----------|------------|------------|---------------|-----|
| M_KDnc0 | KPS | DBSA | – | 144 000 | 3.7 |
| M_KDnc1.5 | KPS | DBSA | 1.5 | 155 000 | 2.2 |
| M_KDnc3 | KPS | DBSA | 3 | 145 000 | 2.8 |
| M_KDnc4.5 | KPS | DBSA | 4.5 | 159 000 | 2.7 |
| M_KDnc6 | KPS | DBSA | 6 | 160 000 | 3.6 |
| M_KDnc10 | KPS | DBSA | 10 | 217 000 | 3.7 |
| M_KSnc0 | KPS | SDS | – | 263 000 | 2.4 |
| M_KSnc3 | KPS | SDS | 3 | 373 000 | 3.1 |
| M_KSnc6 | KPS | SDS | 6 | 597 000 | 3.6 |
| M_ADnc0 | AIBN | DBSA | – | 235 000 | 2.3 |
| M_ADnc1.5 | AIBN | DBSA | 1.5 | 412 000 | 2.4 |
| M_ADnc3 | AIBN | DBSA | 3 | 486 000 | 2.3 |
| M_ADnc4.5 | AIBN | DBSA | 4.5 | 461 000 | 2.2 |
| M_ADnc6 | AIBN | DBSA | 6 | 395 000 | 2.5 |
| M_ADnc10 | AIBN | DBSA | 10 | 500 000 | 2.4 |

Table 4

The molar masses (M_w) and molar mass distributions (D) of Baytubes/PMMA composites.

| Sample | Initiator | Surfactant | CNT (wt.%) | M_w (g/mol) | D |
|--------|-----------|------------|------------|---------------|-----|
| M_KD0 | KPS | DBSA | – | 144 000 | 3.7 |
| M_KD3 | KPS | DBSA | 3 | 152 000 | 2.8 |
| M_KD6 | KPS | DBSA | 6 | 504 000 | 2.8 |
| M_KD15 | KPS | DBSA | 15 | 661 000 | 2.9 |
| M_KS0 | KPS | SDS | – | 263 000 | 2.4 |
| M_KS3 | KPS | SDS | 3 | 397 000 | 2.7 |
| M_KS6 | KPS | SDS | 6 | 469 000 | 3.8 |
| M_KS15 | KPS | SDS | 15 | 1438 000 | 2.5 |
| M_AS0 | AIBN | SDS | – | 235 000 | 2.3 |
| M_AS3 | AIBN | SDS | 3 | 455 000 | 2.7 |
| M_AS6 | AIBN | SDS | 6 | 487 000 | 2.8 |
| M_AS15 | AIBN | SDS | 15 | 493 000 | 2.9 |

reaction (Table 2). However, when thinner nanotubes were used with SDS as a surfactant, molar masses were slightly lower and the molar mass distributions were narrower and independent of the amount of nanotubes.

In the combined emulsion/suspension polymerization of styrene with AIBN as an initiator, molar masses were clearly lower than in emulsion polymerizations. One rea-

son for the difference in molar masses with different initiators was the difference in feeding. In combined polymerization, the initiator was fed with the monomer and therefore there were more radical entries. The other reason was the reactions between nanotubes and AIBN. It has been observed that AIBN reacts with MWCNTs [28,29], and there were probably fewer pure polystyrene chains in combined polymerizations to determine with SEC. The polymer chains, which were covalently bonded to the MWCNTs, were mostly filtered out before SEC analysis. There is probably a critical surface area of MWCNTs for which more initiator is consumed in the reaction with nanotubes than in the polymerization of styrene. When there was 12 wt.% of the thinner NC7000 nanotubes in the combined polymerization of styrene, no polymer was observed. With 12 wt.% of the thicker Baytubes, the molar mass dropped when SDS was used as a surfactant. Benzene rings of DBSA covered better the surface of the nanotubes due to π -stacking, and this decreased the reactions between initiator and MWCNTs, preventing a drop in molar mass for 12 wt.% Baytubes with DBSA.

In the emulsion polymerization of MMA with KPS as an initiator, nanotubes did not affect the polymerization of MMA in the same extent as in the case of styrene, due to the incompatible structures of the monomer and MWCNTs (Tables 3 and 4). The addition of thin MWCNTs to the emulsion had only a minor effect on the molar mass, and a significant amount of MWCNTs, over 6 wt.%, was needed before the effect was seen (Table 3). However, a small amount of thin nanotubes stabilized the emulsion and the molar mass distributions narrowed. When the MWCNT content was further increased, the molar mass distribution broadened. In combined polymerization, the initiator AIBN reacted with the nanotubes, the nanotubes acted as a carrier for the initiator, and the molar mass increased as the amount of MWCNTs increased, with the molar mass distribution remaining constant. When thicker nanotubes were used the effect of nanotubes was even smaller (Table 4). The molar masses increased when the amount of nanotubes increased, but the difference between the initiators was not as pronounced as for thin nanotubes.

The surfactant did not cause the increase of molar mass even though there is a need to consume more surfactant to disperse increased amount of MWCNTs and less surfactant is left to form polymer particles in the emulsion. However, the amount of surfactant was high in comparison with the amounts of MWCNTs and monomers that the difference in consumptions was negligible. Otherwise there should be higher molar masses, when thinner MWCNTs were present in the polymerization reaction, as they need more surfactant for dispersion. It seems that DBSA was better dispersant for the nanotubes by giving more stable molar mass distributions and, at the same time, covering the surface of the nanotubes so fewer nanotubes participated in the polymerization reaction.

Covalently bonded polymer chains are preferred in composites, where good adhesion between components and the mechanical properties of the composite should be optimized. SEC was used to determine the molar mass of pure polymers and the effect of MWCNTs on the polymerization reaction. However, there were covalently

bonded polymer chains, which were filtered out before SEC analysis. Even though the amount of grafted polymer was small, based on the weights of the filtered residue and the original SEC sample before the filtering, the presence of grafted polymer chains on the surface of MWCNTs is a significant factor when trying to improve adhesion between a matrix polymer and MWCNTs. Therefore dried emulsions were analyzed by SEM.

Both polymerization methods formed polymer beads that can be seen in the SEM images from the dried emulsions (Figs. 1 and 2). Without MWCNTs, there were less agglomerated polymer beads in the emulsions. The size of PS beads was clearly bigger than the size of PMMA beads. The same behavior was seen in the molar masses of the polymers, PS had higher molar masses compared with PMMA regardless of the polymerization method. The PS beads seemed also to form agglomerates more easily compared with the PMMA beads. With MWCNTs, the size distribution of the PS beads was higher, especially when the combined polymerization method was used. In the combined polymerization, the initiator can form additional bonding with MWCNTs, therefore some PS beads were tightly attached to the MWCNTs (Fig. 1b). On the other hand, without strong interactions between a polymer and MWCNTs, small PMMA beads filled the space around MWCNTs and fused together (Fig. 2b). Therefore, both polymers improved the stable dispersion of MWCNTs by preventing the agglomeration of MWCNTs effectively. TEM images from the composites, which have been melt processed after drying the emulsions, confirmed that in situ-emulsion polymerization provides the stable dispersion of the high concentrations of MWCNTs after mild ultrasound treatment (Fig. 3). The effects of MWCNTs and the molar masses on the electrical and mechanical properties of the composites are discussed elsewhere [30].

The molar masses and beads of the polymers were analyzed from the treated emulsions. However, the sample handling can affect the original properties of the material. Therefore, DLS was used to analyze the particle size in the original emulsions, where both types of polymer chains and beads, free and bonded, were present. Based on the SEM images, there were single beads, agglomerated beads, and large particles, in which the single and agglomerated beads were bonded on the surface of the MWCNTs. Therefore, reference PS beads and their mixture were analyzed in order to control the results of the wide particle size dispersion of the emulsions. DLS gave the information of the number of particles, as the curves show the size classes and the associated mean relative percentage of particles in each class based on the volume occupied.

DLS was used to analyze also, how the particle size changed during the monomer feed and polymerization, because the monomers were fed drop by drop and not at once as a batch. The samples for DLS analysis were taken from the polymerization reactor during the reaction. In order to get the data of the prevailing particle size of the emulsion, reaction was stopped by adding 5 μ l hydroquinone solution into the 1.5 ml of the sample solution. Without MWCNTs in the seed emulsions, small 2 nm diameter surfactant micelles were observed. These micelles disappeared when monomer feeding was started. The

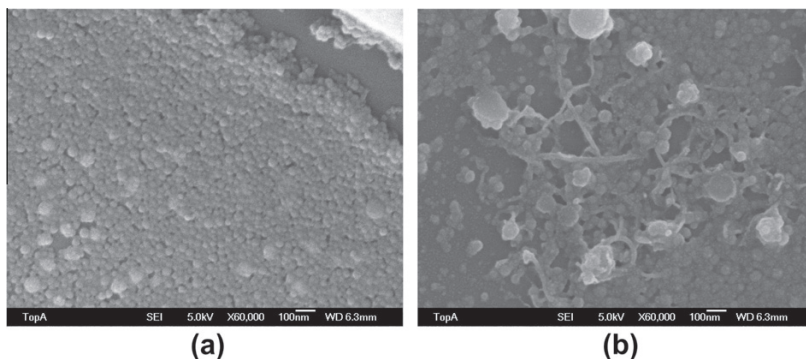


Fig. 1. SEM images of dried PS emulsions; combined polymerization with DBSA and (a) without nanotubes, (b) 3 wt.% of Baytubes.

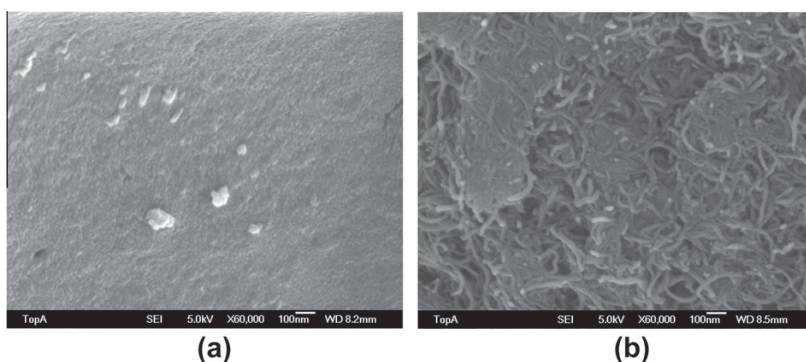


Fig. 2. SEM images of dried PMMA emulsions; emulsion polymerization with DBSA and (a) without nanotubes, (b) 15 wt.% of Baytubes.

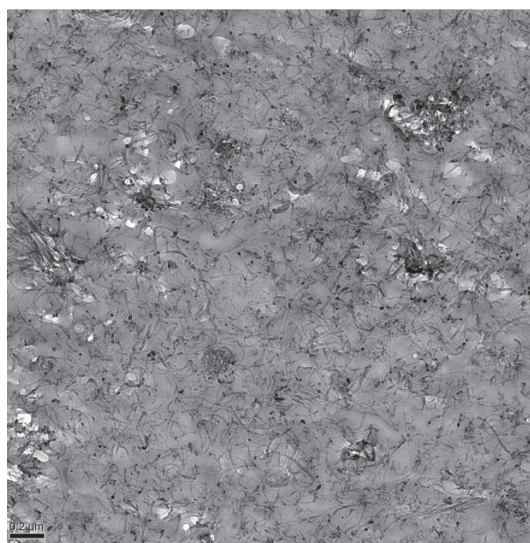


Fig. 3. TEM images of PMMA/MWCNTs composites; emulsion polymerization with DBSA and 15 wt.% of Baytubes.

feeding continued nearly three hours, and the polymerization reaction already started during monomer feed. Therefore, instead of large monomer particles, there were polymer particles containing the monomer in the emulsion. The particle size of the emulsion remained constant after 3 ml of 5 ml monomer was fed (Fig. 4). With MWCNTs in the seed emulsions, pure surfactant micelles did not form. However, after the monomer feed was started, the changes in the particle size of the emulsion with MWCNTs followed the changes in the emulsions without MWCNTs.

The size of the polymer beads was in the same range observed with SEM. This kind of similarity between particle sizes analyzed by SEM and DLS was seen in the study of emulsion polymerization of styrene with an enzyme-catalyst redox initiator [31]. DLS measures the hydrodynamic radius of the particle. Therefore, the particle size determined by DLS is slightly larger than the one determined by SEM. The diameter of polystyrene particles was 20–40 nm and the number of pure polystyrene particles decreased when the amount of MWCNTs increased in the emulsion (Fig. 5). Based on the DLS measurements of reference PS beads and their mixture, the DLS results were accurate when the particle size distribution of the emulsions was narrow, which was the case of the emulsions without MWCNTs. On the other hand, with the large parti-

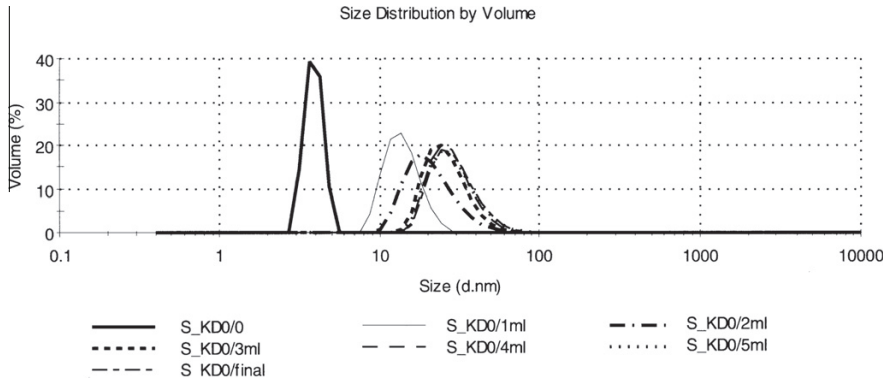


Fig. 4. The change in particle size distributions during styrene monomer feed and after total polymerization time. Emulsion polymerization with DBSA and without nanotubes.

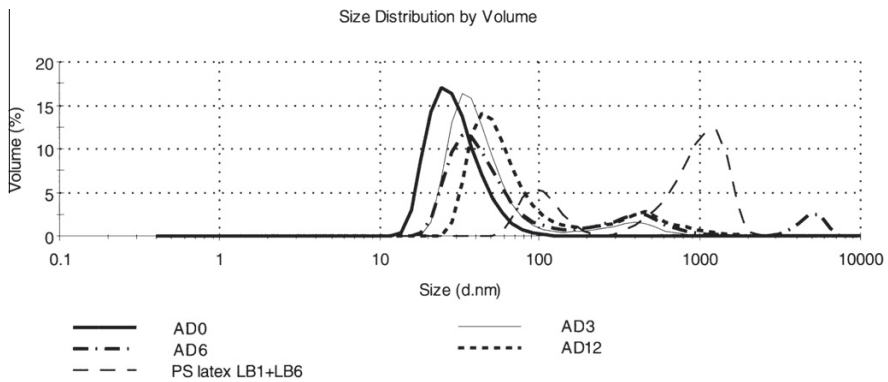


Fig. 5. Particle size distributions of PS emulsion samples with DBSA and 0–12 wt.% of Baytubes after combined polymerization. PS latex is the mixture of latexes that consist beads of 100 and 600 nm diameter.

cle size distribution of the emulsions, the smaller set of particles, diameter under 200 nm, were detected precisely. However, with the larger particle size distribution of the emulsions, the results of larger set of particles, diameter

above 200 nm, were only approximate. When the amount of thicker MWCNTs increased in the emulsion, particles of 500 nm diameter was detected by DLS. When AIBN was used as an initiator, there were slightly more distin-

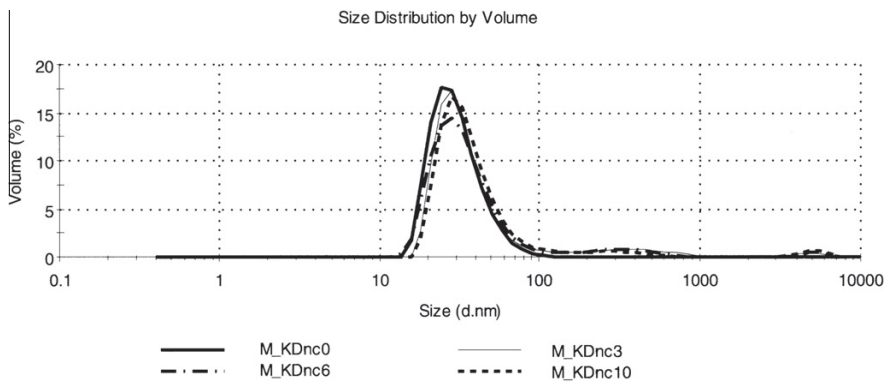


Fig. 6. Particle size distributions of PMMA emulsion with DBSA and 0–10 wt.% of NC7000 nanotubes after emulsion polymerization.

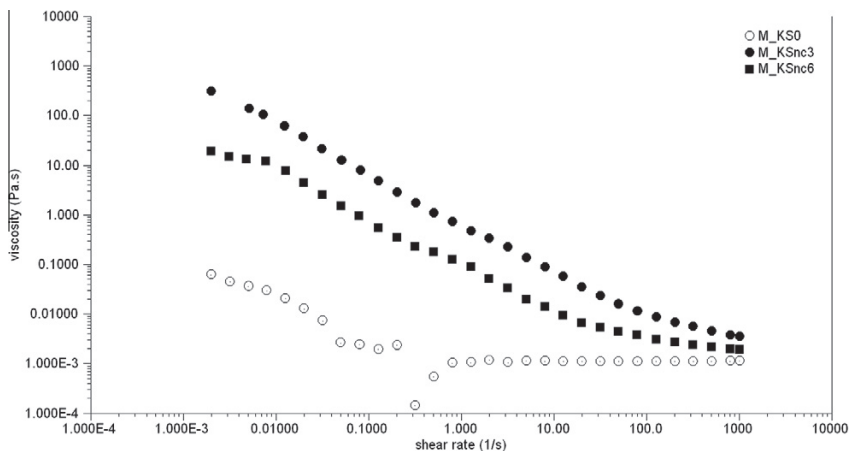


Fig. 7. The viscosity of PMMA emulsions; emulsion polymerization with SDS.

guish set of 500 nm particles (Fig. 5). However, when thinner MWCNTs were used, only the polymer particles of diameter under 100 nm were observed. As thinner MWCNTs have more surface area to adsorb styrene, the size of the aggregated particles including agglomerated polystyrene beads and nanotubes was out of the measuring range of DLS. There was the set of larger particles of 5 μm diameter that can be pointed to the aggregates of MWCNTs and polymer beads attached to MWCNTs according to SEM images.

When MMA was used as a monomer, formed PMMA beads were slightly smaller than PS beads. In general, the particle size distribution of PMMA was similar with PS but the particle size changed differently during the monomer feed and as the amount of MWCNTs increased. When KPS was used as an initiator and DBSA as a surfactant, the particle size distribution was independent of the amount of MWCNTs and thinner MWCNTs showed more distinguish sets of particles (Fig. 6). The similar results were ob-

served in molar masses of PMMA, which were independent of the amount of thinner MWCNTs.

Based on the measurements of molar masses by SEC, the amount of surfactant was not the main reason for the increase of molar mass. DLS results are in line with SEC results. Thinner MWCNTs consume more surfactant during dispersion, but the amount of surfactant was so high that it affected only partly to the size of particles i.e. there would be less surfactant and the size of polymer particles would grow due to that. Otherwise the increase of MWCNTs in the polymerization reactions would increase the particle size more strongly and decrease the number of smaller particles, which was not detected in the DLS results.

As DLS detects the polymer beads rather than the set of polymer beads attached to MWCNTs, the rheology of the emulsions was measured. The viscosity of the emulsions was low due to the dilute solution and at higher shear rates the viscosity was close to each other for all the emulsions

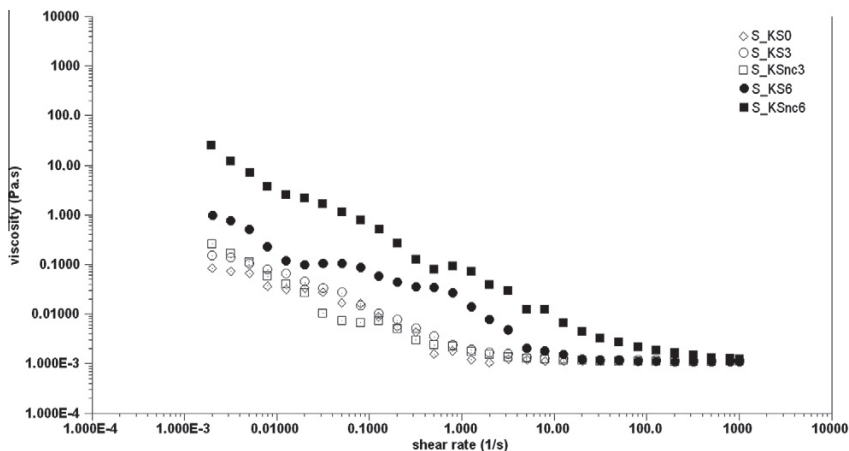


Fig. 8. The viscosity of PS emulsions; emulsion polymerization with SDS.

independently from the amount of the MWCNTs. At lower shear rates the MWCNTs increased the viscosity, as the particle sizes and molar masses increased. The rheology results of the PMMA emulsions supported the conclusions that thinner MWCNTs were not affected the polymerization reaction. The viscosity of the emulsion increased when the amount of MWCNTs increased but the distribution of particle sizes in the emulsions did not change, as the shape of curves was similar with different MWCNT contents (Fig. 7). The same result was seen from DLS data. On the other hand the viscosity of PS emulsions varied as the amount of MWCNTs changed. The particle size distributions in emulsions become narrower when the amount of MWCNTs increased in the emulsions, which can be seen as change in the slope of the curves (Fig. 8). The curvature of these curves is sharper, which indicates the narrower distribution. The rheology results confirm the stabilization effect of MWCNTs, which provides the increase of molar mass of PS.

4. Conclusions

Using in situ-polymerization it is possible to simultaneously obtain a homogeneous dispersion and a strong interface between carbon nanotubes (CNTs) and a polymer matrix. Two different in situ-polymerization techniques were studied, emulsion polymerization and combined emulsion/suspension polymerization with styrene and methyl methacrylate in the presence of different multi-walled carbon nanotubes (MWCNTs). The compatibility of the MWCNTs and monomer affected polymerization. Therefore, the molar masses of the polymers were affected. The MWCNTs stabilized the emulsions, and molar masses increased with higher amounts of MWCNTs. The results showed that molar mass and molar mass distribution can be tailored by choosing the particular combinations of MWCNTs, the initiator, and the surfactant. Based on the interactions between the monomer, the initiator, and the nanotubes, the role of the nanotubes in the polymerization reaction varies. The nanotubes act as a carrier for the initiator and stabilize the emulsion, or they can inhibit polymerization by reacting with the initiator themselves. Based on the effect that the nanotubes have on the polymerization reaction, the surface area and quality of the nanotubes are both to be considered when the properties of the final composites are designed.

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