

Preparation and rheological behavior of polystyrene/multi-walled carbon nanotube composites by latex technology

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Abstract

Polystyrene/multi-walled carbon nanotube (PS/MWCNT) composites were prepared by the use of latex technology. The monodisperse PS latex was synthesized by an emulsifier-free emulsion polymerization from styrene/potassium persulfate/water system in the presence of ethanol. The MWCNTs were first treated with acid mixture to eliminate impurities, dispersed in deionized water driven by ultrasonicator, and then mixed with the PS latex. From these mixtures, PS/MWCNT composites were prepared by freeze-drying and subsequent compression molding. In the small-amplitude oscillatory shear experiments, both complex viscosity and storage modulus increased with increasing MWCNT content. A pronounced effect of MWCNT content was observed, resulting in larger storage modulus and stronger yield behavior at low frequencies when compared to unmodified PS. It showed a transition from viscous to elastic behavior with increasing MWCNT content. Over the MWCNT content of 3 wt%, the storage modulus was higher than the loss modulus across all frequencies.

Keywords : multi-walled carbon nanotube composite, monodisperse polystyrene particle, emulsifier-free emulsion polymerization, latex technology, rheological behavior

1. Introduction

Carbon nanotubes (CNTs) have received a great deal of attention due to unique properties, such as a high elastic modulus, good electrical conductivity and thermal stability (Treacy *et al.*, 1996; Yu *et al.*, 2007). These unique properties make CNTs a preferred candidate to be used as fillers into various polymer matrices to enhance the performance of polymers. In the field of polymer/CNT composites, a lot of works have shown some promising results, such as improvement in thermal conductivity (Kim *et al.*, 2001), electrical conductivity (Sandler *et al.*, 1999) and mechanical properties (Gorga and Cohen, 2004) of polymers. However, it has been well known that as-produced CNTs are very difficult to be dispersed in polymer matrices as CNTs have large aspect ratio and surface area and possess large van der Waals forces between themselves, which can lead to the formation of aggregates or bundles that are tightly bound. Therefore, the dispersion of CNTs and incorporation of CNT individuals into polymer matrices is one of the most important tasks to optimize the effective utilization of polymer/CNT composites. The incorporation of CNTs into polymer matrices has frequently been achieved by solution blending (Safadi *et al.*, 2002), *in situ*

polymerization (Kim *et al.*, 2007) and melt mixing (Zhang *et al.*, 2006).

In recent studies, the use of latex technology has been proposed to incorporate CNTs in polymer matrices (Regev *et al.*, 2004; Yu *et al.*, 2007). They demonstrated that the latex technology can successfully be applied to prepare polymer/CNT composites with good dispersion of CNTs, but any information related to the uniformity of colloidal particles was not described. Successful applications of this technology must be strongly dependent on the availability of colloidal particles with highly monodisperse state. Among various colloidal particles, polystyrene (PS) colloids have potential uses in biomedical and drug delivery because the highly monodisperse PS colloids can be easily synthesized by emulsion polymerization techniques. An approach to fabricate the self-assembly multi-walled carbon nanotube (MWCNT)/PS latex nanocomposites by emulsion polymerization using sodium dodecylsulfate emulsifier was reported (Wu and Chen, 2008). However, the effect of CNT content on rheological properties of the composites prepared by latex technology has not yet been investigated.

In this study, we prepared the PS/MWCNT composites by the use of latex technology and investigated their rheological properties since rheology could be used as a tool to quantify from a global average of the degree of dispersion across the whole sample (Krishnamoorti and Yurekli, 2001). The mon-

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odisperse PS latex without surfactants such as sodium dodecylsulfate was synthesized by an emulsifier-free emulsion polymerization in the presence of polar solvent. Acid-treated MWCNTs were dispersed in deionized water and then mixed with the PS latex using ultrasonication process. From these mixtures, PS/MWCNT composites were prepared by freeze-drying and subsequent compression molding. In the small-amplitude oscillatory shear experiments, complex viscosity, storage modulus and loss modulus were analyzed.

2. Experimental

2.1. Synthesis of monodisperse PS latex

The monodisperse PS latex was synthesized by an emulsifier-free emulsion polymerization from styrene/potassium persulfate/water system in the presence of polar solvent. It is reported that the particle size of microspheres was decreased with increasing of the addition amount of polar solvent in emulsifier-free emulsion polymerization (Ou *et al.*, 2001). In this study, ethanol was selected as a polar solvent and a suitable amount of ethanol was introduced to design monodisperse PS microspheres with diameter of 500 nm. Styrene monomer was purified by a vacuum distillation method before use. At first, potassium persulfate (0.3676 g) as an initiator was dissolved in deionized water (50 ml). A specified amount of styrene (40 ml), ethanol (43.2 ml) and deionized water (310 ml) were added into the potassium persulfate solution and followed by stirring the mixture at the rate of 300 rpm for 20 min under N_2 atmosphere. Finally, emulsifier-free emulsion polymerization was carried out in a 3-neck double-jacketed Pyrex reactor at 70°C for 24 h while keeping the agitation speed of 300 rpm.

2.2. Preparation of PS/MWCNT composites

The MWCNTs (Iljin Nanotech, Korea) synthesized by a thermal chemical vapor deposition were acid-treated in 300 ml of H_2SO_4 and HNO_3 (1:3 by volume) at 140°C for 60 min under a reflux process, not only to eliminate impurities of MWCNT such as metallic catalysts and amorphous graphitic materials but also to introduce carboxylic groups on the surface of MWCNT. Fig. 1 shows a schematic diagram for acid treatment of as-received MWCNTs. Quantitative analysis on the effect of acid treatment was not performed in this study, but one can find a literature describing that the purity of as-received MWCNT was 97% and that of acid-treated MWCNT was 99% using thermogravimetric analysis (Park *et al.*, 2005), where they used the same MWCNT as this study. The acid-treated MWCNTs were dispersed in deionized water driven by an ultrasonicator with a probe of 13 mm in tip diameter (VCX 500, Sonics, USA). Ultrasonication was imposed for 30 min. In order to prevent the temperature rise of the suspension, the beaker was placed in an ice bath during sonication pro-

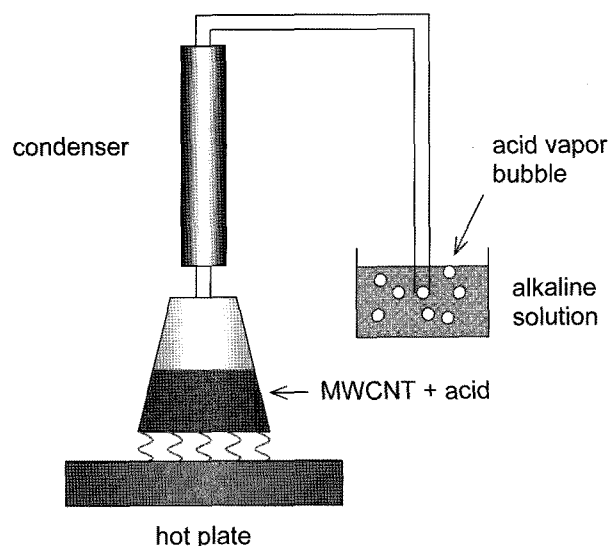


Fig. 1. Schematic diagram of acid treatment of MWCNTs.

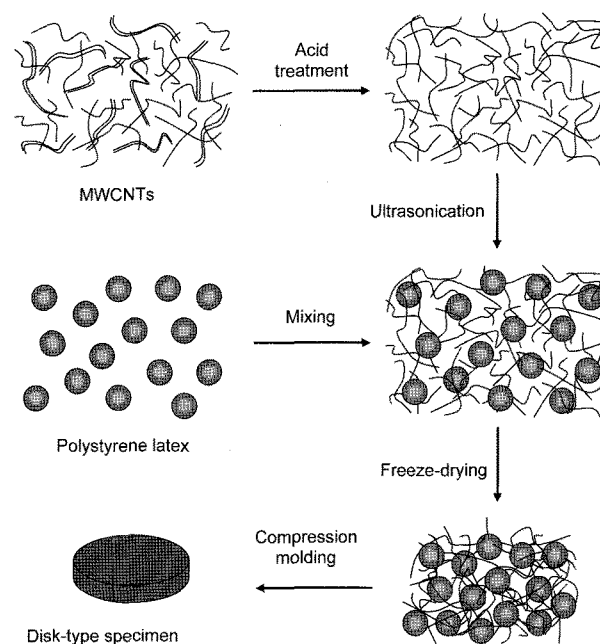


Fig. 2. Schematic procedure for preparation of PS/MWCNT composite by latex technology.

cess. After the sufficient dispersion has been achieved, the MWCNT suspension was homogeneously mixed with suitable amount of PS latex while keeping ultrasonication for 30 min and then abruptly frozen with liquid nitrogen. The aqueous moiety in the frozen mass was removed with a freeze-dryer (FD-1000, Eyela, Japan). Lastly, the PS/MWCNT composite so obtained was compressed into 1–2 mm thick disk-type samples with diameter of 25 mm at 180°C for 5 min using a hot press. The samples were used for subsequent rheological measurements. Schematic procedure for the preparation of PS/MWCNT composites by latex technology is shown in Fig. 2.

2.3. Characterization and measurements

The molecular weight and the molecular weight distribution of PS latex were determined by using a gel-permeation chromatograph with refractive index detector (Waters, USA), where tetrahydrofuran was used as carrier solvent. The particle size of PS latex and the morphology of freeze-dried PS/MWCNT composite powder were observed by using scanning electron microscopy (SEM: JSM 5200; FE-SEM: JSM 6700F, Jeol, Japan). The rheological properties of the composite samples were investigated with a stress-controlled rotational rheometer (MCR 300, Paar Physica, Germany) in a small-amplitude oscillatory shear mode using a parallel plate geometry. Frequency sweeps between 0.03 and 100 rad/s were carried out at specified strain. The strain amplitude was imposed to 3% throughout the measurements, after confirming that the amplitude was within the range of linear viscoelasticity from strain sweep tests. All measurements were conducted at a constant temperature of 210°C under nitrogen atmosphere. Specimens were placed between the preheated plates in a thermostating chamber and were allowed to equilibrate for about 5 min prior to each frequency sweep test.

3. Results and discussion

3.1. Morphology

Fig. 3 shows an SEM microphotograph of the PS particles synthesized by an emulsifier-free emulsion polymerization in the presence of ethanol. Though ethanol is a polar solvent, the polarity of ethanol is lower than that of water. Thus the polarity of the dispersion medium is reduced with the addition of such a polar solvent. The reduction of polarity enhances the solubility of styrene monomer in water and followed by increasing the formation of primary particles at the early stage of polymerization (Ou *et al.*, 2001). Consequently, it leads the polymerization system to form higher number of primary par-

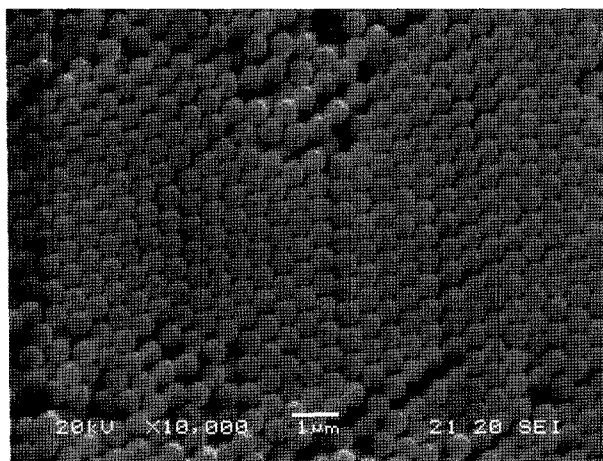


Fig. 3. SEM micrograph of PS particles prepared by emulsifier-free emulsion polymerization in the presence of ethanol.

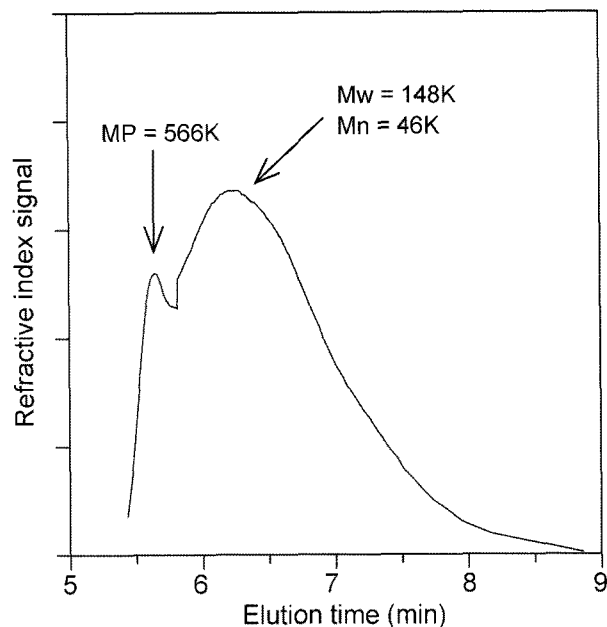


Fig. 4. Molecular weight distribution of the PS latex prepared by emulsifier-free emulsion polymerization in the presence of ethanol (Mw: weight-average molecular weight; Mn: number-average molecular weight; MP: molecular weight at peak).

ticles so that smaller microspheres are produced. As can be seen in Fig. 3, the PS particles synthesized in this study show spherical shape and are arranged in well-ordered two-dimensional hexagonal patterns, indicative of monodisperse particle formation. The number-average diameter of PS particle was about 510 nm. In the case that acetone was used as a polar solvent that is less polar than ethanol, smaller particles than this size were produced (the result not shown here).

The molecular weight distribution of the PS latex is shown in Fig. 4. It is found that two peaks comprised of number-average molecular weights of 10 K–100 K and above 100 K. In the emulsifier-free emulsion polymerization based on styrene/potassium persulfate/water system, the nucleation mechanism follows micellar nucleation (Goodall *et al.*, 1977; Ou *et al.*, 2001). The coalescence of the primary particles favors the formation of polymers having higher molecular weight during the nucleation period. As conversion proceeds, the formation of higher molecular weight polymers is restricted and the main molecular weight polymers of 10 K–100 K are increased. On the other hand, in the system of higher water solubility and low surfactant concentration, the nucleation mechanism follows homogeneous nucleation (O'dian, 1991). When ethanol is introduced into the styrene/potassium persulfate/water system as in this study, styrene monomer becomes more soluble in mixture solvent than in water medium, which in turn favors homogeneous nucleation. As the amount of ethanol used in this study is about 12 vol% of water content, the nucleation mechanism is likely to follow both micellar nucleation and homogeneous nucleation.

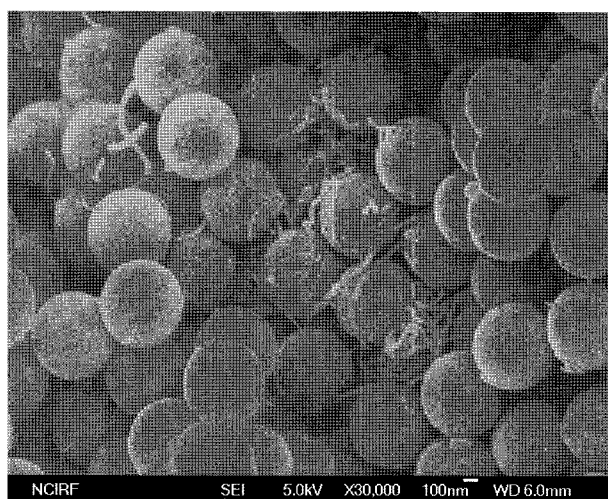


Fig. 5. FE-SEM micrograph showing the dispersion state of MWCNTs in PS/MWCNT 1% composite powder.

Further efforts have to be made to more properly explain why the molecular weight distribution curve of the PS latex has two peaks.

Fig. 5 shows an FE-SEM microphotograph of freeze-dried PS/MWCNT composite powder with the MWCNT content of 1 wt%. It shows the resulting nanocomposite is composed of spherical and tube-like morphology that represents PS particles and MWCNTs, respectively. It is reported that the formation mechanism of PS/MWCNT nanocomposites is believed to involve possible interactions between negative charges of PS latex and slightly positive charges of MWCNT with sodium dodecylsulfate using ultrasonication process (Wu and Chen, 2008). In this study, however, the PS/MWCNT composites composed of pristine MWCNTs without surfactant and bare PS particles were used to exclude any other variables which may affect the properties of the composites. The zeta-potential value of pristine MWCNT is known to have a linear relationship with pH from around -32 mV at pH 8 to $+38$ mV at pH 3 (Sun and Gao, 2003), and that of bare PS particle to be -41.8 mV for 550 nm in diameter (Lee *et al.*, 2007). It seems that bare PS latex and pristine MWCNT in neutral conditions cannot have interactions between them, but the MWCNTs used in this study are acid-treated so that they may give positive effect on interactions between PS latex and MWCNT. Furthermore, ultrasonication can assist to disperse MWCNTs from bundles and prevent re-aggregation of MWCNTs by electrostatic repulsion. The aqueous mixture of PS particles and MWCNTs dispersed under ultrasonication followed by sudden freezing in liquid nitrogen is expected to get better dispersion, but some aggregated MWCNT bundles are still found within the PS particles as can be seen in Fig. 5.

3.2. Rheological properties

Rheological properties such as complex viscosity, storage modulus and loss modulus would give a measure

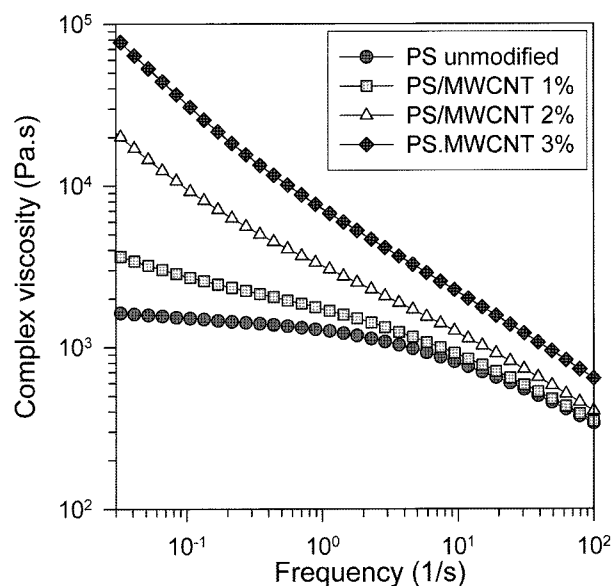


Fig. 6. Effect of MWCNT content on complex viscosity of PS/MWCNT composites prepared by latex technology.

of the dispersion of nanotubes in polymer matrix. The complex viscosities η^* of unmodified PS and PS/MWCNT composites are shown in Fig. 6. The unmodified PS shows typical flow behavior of shear thinning polymer melts, revealing a Newtonian plateau at low frequencies and shear thinning at high frequencies. The complex viscosity strongly increases with the MWCNT content at low frequencies and diminishes with increasing frequency due to shear thinning. At lower frequencies, as MWCNTs may form a nanoscale network, the rheological behavior exhibits solid-like resulting in strong yield stress. On the contrary, the rheological properties at higher frequencies will be mainly determined by the polymer matrix because the attractions between MWCNTs are getting weaker due to high shear and the orientation of tube-like fillers leads to lower viscosities. At high frequencies, therefore, regardless of the MWCNT content tested in this study, the rate at which the complex viscosity decreases with frequency is nearly identical to that of unmodified PS melt.

The storage modulus G' and the loss modulus G'' gradually increase with increasing frequency as shown in Figs. 7 and 8. The effect of MWCNT content is much higher at lower frequencies than at high frequencies, and the increase of modulus at low frequencies is more pronounced in the storage modulus than in the loss modulus. According to Shenoy (1999), it is described that a highly agglomerated system would show the existence of yield and high storage modulus at low frequencies, which varies minimally with frequency giving more solid-like response and lower loss tangent. In a similar manner, as the MWCNT content increases, the network-like structure is formed due to greater interactions between nanotubes, and as a result, the storage modulus at low frequencies shows dramatic

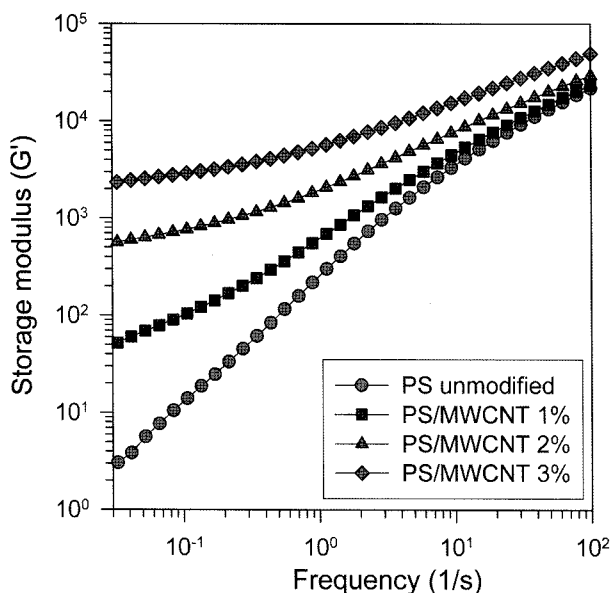


Fig. 7. Effect of MWCNT content on storage modulus of PS/MWCNT composites prepared by latex technology.

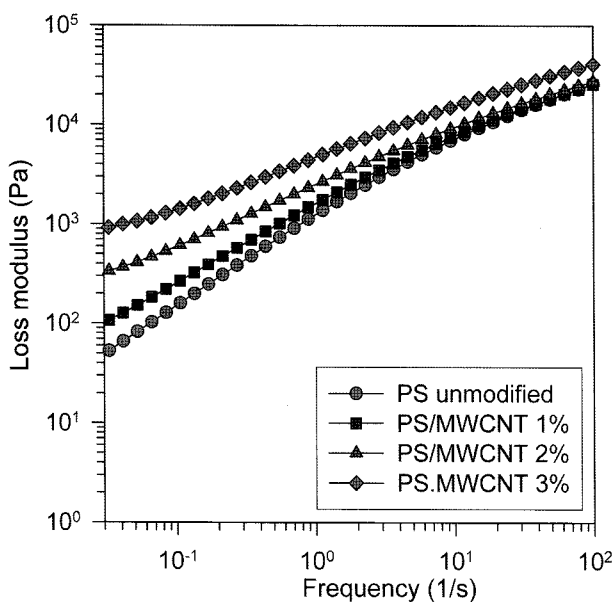


Fig. 8. Effect of MWCNT content on loss modulus of PS/MWCNT composites prepared by latex technology.

increase and the slope becomes less steep. Thus, it can be said that the unique rheological response of the PS/MWCNT composites is dominated by the degree of the formation of nanotube network-like structure.

A plot of storage modulus versus loss modulus analogous to Cole-Cole plots is often used to monitor morphological evolution with temperature in the microstructure of polymers (Han *et al.*, 1989; Lee and Han, 2003). In multiphase systems, such plots can be used in a similar way to indicate structural differences between the matrix and filled systems at a given temperature (Kim and Lee, 2008; Potschke

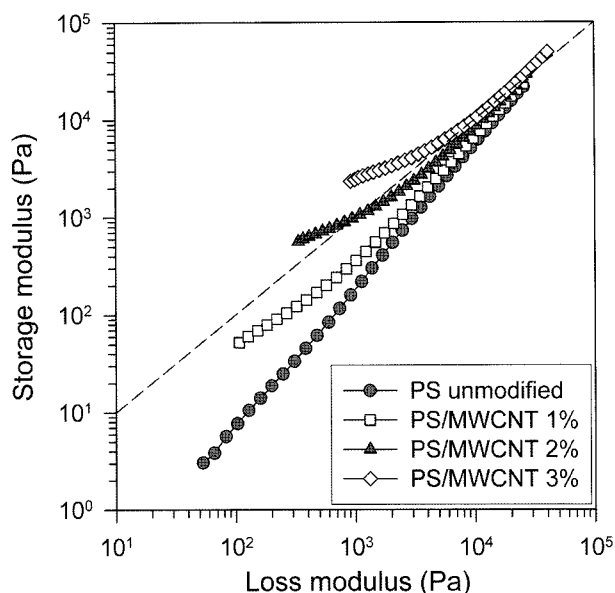


Fig. 9. Effect of MWCNT content on storage modulus vs. loss modulus of PS/MWCNT composites prepared by latex technology.

et al., 2002). Fig. 9 shows log G' versus log G'' plots for the PS/MWCNT nanocomposites at the MWCNT content of 0, 1, 2 and 3%. The short dash line in the graph stands for the line that shows G' and G'' are equal. The storage modulus increases significantly with increasing content of MWCNTs. The slope of log G' versus log G'' plots decreases with increasing content of MWCNTs. The shift and the change in slope of log G' versus log G'' plots indicate that the microstructure of the PS/MWCNT composites changes significantly with the addition of MWCNTs. The microstructural change is getting remarkable as the MWCNT content increases. However, all the plots seem to be nearly superimposed as frequency increases, *i.e.*, as the plots go toward the upper right-side direction. This is because the polymer matrix governs the rheological properties at high frequencies as mentioned previously. In the plot of the PS/MWCNT 3%, interestingly, the storage modulus lies above the loss modulus across all frequencies conducted in this study. The PS/MWCNT composites containing the MWCNT content of 3% and above seem to follow a pattern that represents a network-like structure similar to a percolated structure which means the number density of nanotubes is higher than the percolation threshold. Zhao *et al.* (2005) performed a tremendous amount of rheological measurements for polystyrene-clay nanocomposites and categorized the speculated rheological response into four classes to the increase in the number of clay particles per unit volume. Pure polystyrene gives a typical terminal relaxation behavior for polymer ($G' \sim \omega^2$, $G'' \sim \omega$), the response of which belongs to Class 1. Incorporation of particles into the polymer belongs to Class 2, which results in a change of the spectrum in the terminal relaxation regime (G' ,

$G'' \sim \omega$). As the number density of particles increases, both moduli show more solid-like behavior, especially at low frequencies ($G' > G''$, $G'' \sim \omega^0$), which belongs to Class 3. Further increase in the number density of particles belongs to Class 4, which produces a response where $G' > G''$ across all frequencies, indicating a percolated network structure. Based on this classification, the PS/MWCNT 3% composite is thought to be near the rheological threshold, representing the rheological behavior of the composite changes from melt-like to solid-like.

4. Conclusions

The PS/MWCNT composites were prepared via latex technology, and their rheological properties were investigated. Monodisperse PS particles with diameter of 510 nm were synthesized by emulsifier-free emulsion polymerization from styrene/potassium persulfate/water/ethanol system. The molecular weight distribution of PS particles showed a curve having two peaks comprised of 10 K ~ 100 K and above 100 K. The PS particles were mixed with acid-treated MWCNTs using ultrasonic process and then freeze-dried. The PS/MWCNT composite powder so obtained was molded into disk-type specimens for rheological measurements. In the small amplitude oscillatory-shear experiments where the linear viscoelastic region holds, a pronounced effect of MWCNT incorporation was observed, resulting in larger storage modulus and stronger yield behavior at lower frequencies when compared to unmodified PS. In the composite containing MWCNT 3%, particularly, the storage modulus lay above the loss modulus across all frequencies tested in this study. In the vicinity of this content, it is speculated that the rheological behavior of the composite changes from melt-like to solid-like due to the formation of nanotube network-like structure.

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