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Chemical Modification of Carbon Nanotubes and Preparation of Polystyrene/Carbon Nanotubes Composites

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Abstract: Single-walled carbon nanotubes (SWNTs) have been chemically modified through the formation of carboxylic acid functionalities or by grafting octadecylamine and polystyrene onto them. We purified SWNTs with nitric acid to remove some remaining catalysts and amorphous carbon materials. After purification, we broke the carbon nanotubes and shortened their lengths by using a 3:1 mixture of concentrated sulfuric acid and nitric acid. During these purification and cutting processes, carboxylic acid units formed at the open ends of the SWNTs. Octadecylamine and amino-terminated polystyrene were grafted onto the cut SWNTs by condensation reactions between the amine and carboxylic acid units. The cut SWNTs did not disperse in organic solvents, but the octadecylamine-grafted and polystyrene-grafted SWNTs dispersed well in dichloromethane and aromatic solvents (e.g., benzene, toluene). Composites were prepared by mixing polystyrene with the octadecylamine-grafted or polystyrene-grafted SWNTs. Each composite had a higher dynamic storage modulus than that of a pristine polystyrene. The composites exhibited enhanced storage moduli, complex viscosities, and unusual non-terminal behavior when compared with a monodisperse polystyrene matrix because of the good dispersion of carbon nanotubes in the polystyrene matrix.

Keywords: carbon nanotubes, composite, chemical modification.

Introduction

There have been great interests in carbon nanotubes (CNTs), since Iijima discovered them in 1991.[1] Many applications of CNTs were suggested because of their unique electronic, mechanical properties with chemical stability.[2-4] CNTs are considered as a brilliant filler of polymer composites due to their outstanding mechanical properties.[5] Theoretical predictions have suggested that the Youngs modulus of individual CNTs is higher than 1 TPa.[6] The combination of CNTs with polymers may offer an attractive possibility to enhance the mechanical properties of polymer composites. The CNTs and polymer composites were initially reported by Ajayan and co-workers, where they mechanically mixed the purified CNTs with epoxy resin.[7] Many efforts to prepare carbon nanotubes/polymer composites were still reported.[8-10,23]

Preliminary arrangement to make CNTs/polymer composites with solution blending method is the preparation of stable organic solution of CNTs. A celebrated procedure for this is the chemical modification of CNTs.[11-14] The efficient utilization of CNTs in composite applications depends on the ability to disperse the CNTs homogeneously throughout the matrix and the compatibility between CNTs and the matrix. These two factors are important in the utilization of fillers in polymer composites as well as CNTs. Even in the polymer/layered silicate nanocomposites, exfoliated structure of layered silicate were preferred rather than intercalated structure in a viewpoint of mechanical improvement of the composites, because of the dispersibility of layered silicate in the composites. Mitchell and co-workers, investigated the effect of chemical modification of CNTs on the dispersion state of CNTs in the polymer matrix.[15] In this paper, we report the preparation of composites of polystyrene and chemically modified carbon nanotubes.

Experimental

Materials. Triton X-100^{TM}, toluene, benzene, hydrochloric acid, nitric acid, and sulfuric acid were purchased from Aldrich and used as received. THF, DMF, and thionyl chloride were distilled from and stored in molecular sieves. The single-walled carbon nanotubes (SWNTs) containing raw soot (50 to 70 vol% purity, purchased from Carbolex Inc.) was prepared by the modified electric-arc discharge technique. Major impurities are carbon nanospheres and carbon-

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encapsulated catalyst nanoparticles. Amino-terminated polystyrene (NH_2-Polystyrene, $M_w = 2,880$, PDI = 1.15, and functionality of amine group = 0.98) was purchased from Polymer Source Inc.. Octadecylamine ($C_{18}H_{39}NH_2$) was from Fluka. Polystyrene ($M_w = 290,000$, PDI = 1.05), the matrix polymer in the composites, was purchased from Pressure Chemical Inc.. SWNTs were purified by refluxing in nitric acid solution.[16] Purified SWNTs (PurSWNTs) were cut into shortened SWNTs (CutSWNTs) with acid solution (HNO_3 and H_2SO_4 mixed 1:3) for 10 hrs and then filtered and washed thoroughly with ultra pure water.

Chemical Modification of SWNTs. 100 mg of CutSWNTs were stirred in 50 mL of $SOCl_2$ (containing 1 mL of DMF) at 70 ºC for 24 hrs. After reaction, the solvent was distilled out. The remaining sample (SWNT-COCl) was dried in vacuum for 5 hrs at 90 ºC. The SWNT-COCl, DMF (1 mL), and amino-terminated polystyrene in benzene (4 g) (or octadecylamine) were charged into a flask and stirred at 90 ºC under nitrogen for 5 days. The mixture was then washed with benzene and centrifuged for several times to remove free polystyrene (or octadecylamine) molecules. Amino-terminated polystyrene (or octadecylamine) can be grafted to the SWNTs by amide formation reaction between the terminal amine group and the acid chloride groups.

Preparation of Polystyrene/Chemically Modified SWNTs. Octadecylamine-grafted single-walled carbon nanotubes (ODASWNTs) or polystyrene-grafted single-walled carbon nanotubes (PSSWNTs) were mixed with polystyrene in benzene (1 or 3 wt% SWNTs). The mixture was then cast into a culture dish and the benzene was allowed to evaporate. And it was dried in vacuum oven for 7 days at 90 ºC to remove the solvent completely.

Measurements. Transmission electron microscopy analysis was conducted on a 200 kV Phillips CM-20, and 300 kV Jeol JEM-3010 TEM. IR spectroscopy, NMR, and XPS analysis were used to characterize the chemical modification by Biorad FT-IR spectrometer, 600 MHz Bruker DMX 600 spectrometer, and VG scientific Ltd. ESCALAB MK-II. Thermogravimetric analyses (TGA) were carried out with a PerkinElmer thermobalance by heating from room temperature to 800 ºC with the scan rate of 10 ºC/min under N_2 atmosphere. Tanand storage modulus (E') were obtained by a Rheometric Scientific DMTA4 with Rectangular tension/compression mode from 30 to 160 ºC with a heating rate of 4 ºC/min under 0.01% of deformation at 1 Hz of frequency. Samples were molded in 12 × 25 × 1 mm size at 130 ºC for 3 min under 3,000 psi of pressure. Glass transition temperatures, T_g, of the composites and pure polymer were determined from the maximum values in the tanvs temperature scan. Rheology measurements of composites were performed on an Advanced Rheometric Expansion System (ARES) in oscillatory mode with a parallel plate geometry using 25 mm diameter plates of 1 mm gap size at 180 ºC. Samples for melt rheology were molded in a disk shape by compression. All the experiments were performed under nitrogen atmosphere to minimize the oxidation of specimens.

Results and Discussion

Figure 1 provides representative TEM images of purchased SWNTs (APSWNTs), PurSWNTs, CutSWNTs. Many catalysts and amorphous carbons were removed from SWNTs during purification procedure. But some still remained in them. According to the TEM image of CutSWNTs, SWNTs were cut into the length of about 490 nm. But residual catalysts and broken small pieces of SWNTs are shown. Peaks according to the carboxylic acid and its derivatives were shown at 1719, 1640, and 1575 cm^{-1} in the FT-IR spectra of PurSWNTs and CutSWNTs (not shown here).

After the chemical modification of CutSWNTs, amino-terminated polystyrene and octadecylamine were grafted. In the ^1H NMR spectra of ODASWNTs, the peak shift during chemical modification was observed (not shown here). Peak from methyl group in octadecylamine at 2.6 ppm shifted downward as the amide functionality formed, and broadened due to grafting to huge and stiff SWNTs compared to free octadecylamine.[11,12,17] But in the case of ^1H-NMR of PSSWNTs, the methyl functionality neighboring with the amide functionality was too small to be detected in FT-IR spectra.

The XPS spectra of PSSWNTs are shown in Figure 2. The dotted lines in both spectra show decomposed C_{1s}, and N_{1s} peaks which are summarized in Table I.[18] There are five distinct carbon bands in the decomposed spectrum of carbon C_{1s}, and three nitrogen bands in the decomposed spectrum of nitrogen N_{1s}. The band at 287.5 eV in C_{1s} originates from the carbon with amide functionality. Unexpectedly, the highest peak area of C-C bond is just 86.2%. This value is lower than that expected. The reason may be explained in following ways. During purification, and cutting procedure, ends of SWNTs were opened, and many defects were made in the side wall of SWNTs.[19] Then, many carboxylic acid groups were formed there, and they could act as reaction sites during amino-terminated polystyrene grafting reaction. The decomposed spectra of nitrogen N_{1s} show that the amide functionality was formed. And, they also show that there are free amine and protonated amine in the PSSWNTs. It means that free amino-terminated polystyrene still exists. 37.4% of amine is protonated, because the byproduct of the chemical reaction is hydrochloric acid and they are expected to graft to the SWNTs with ionic interaction between carboxylate group and protonated amine.[20] Octadecylamine-grafted SWNTs (ODASWNTs) have almost the same XPS feature.

Thermal gravimetric analysis (TGA) of CutSWNTs, octadecylamine, Amino-terminated polystyrene, ODASWNTs and PSSWNTs in a nitrogen atmosphere (at 10 ºC/min^{-1}) was performed. SWNTs were known that they were not

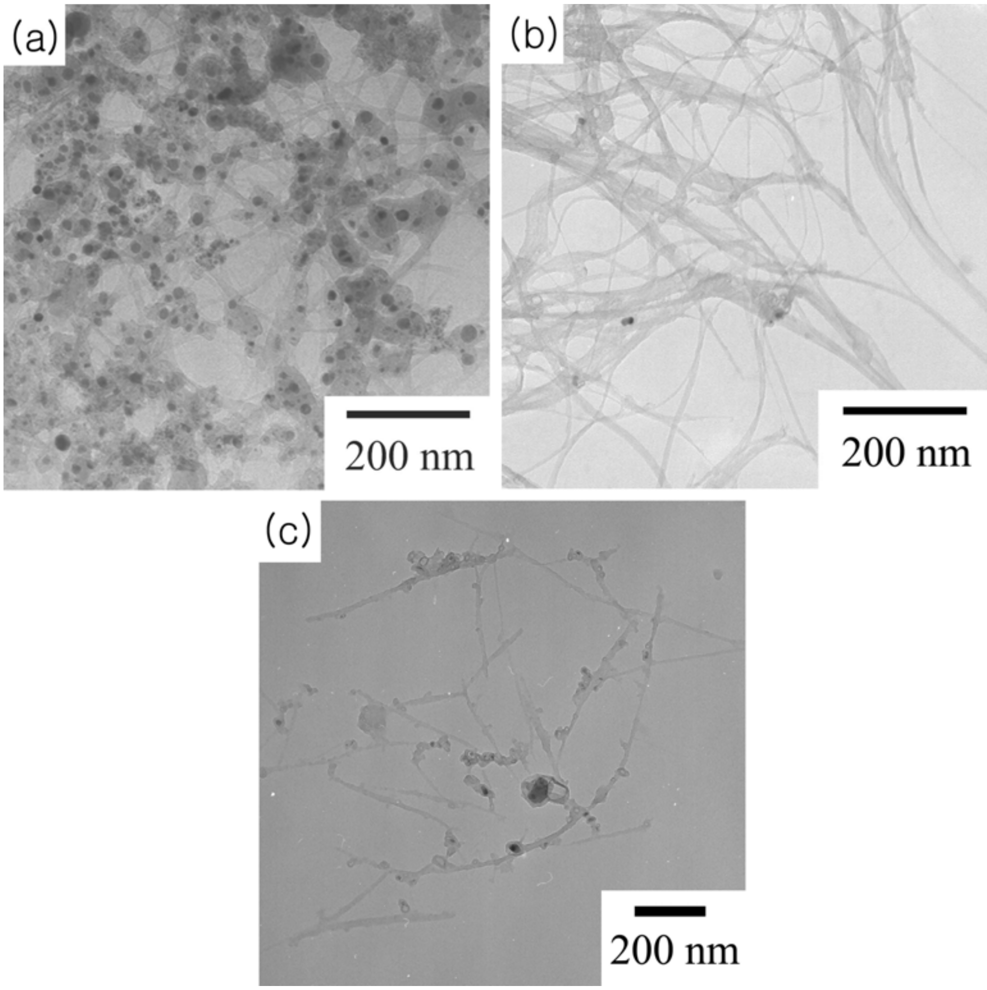

Figure 1. Transmission electron micrographs of (a) APSWNTs, (b) PurSWNTs, and (c) CutSWNTs.

Table I. Binding Energies (BE) of X-ray Photoelectrons and Related Area Percentages

Peak		BE (eV)	Area %	
			ODASWNTs	PSSWNTs
C_{1s}	C-C (alkyl chain and tubes)	284.6	85.1	86.2
	C-N (amine and amide)	286.0	5.8	5.0
	C=O (carbonyl)	286.3	4.4	4.3
	N-C=O (amide)	287.5	3.0	3.2
	COO (carboxylic acid)	288.8	1.7	1.3
N_{1s}	$-NH_2$ (amine)	398.9	24.3	17.0
	CONH (amide)	399.9	29.1	45.6
	$-NH_3^+$ (protonated amine)	401.3	46.6	37.4

decomposed at 600 °C in a nitrogen atmosphere. In this result, the residue of CutSWNTs at 600 °C was 78 wt%. Thermal decomposition of SWNTs at low temperature happened due to the residual impurities and the weakness of CutSWNTs for acid oxidation. The thermal decomposition of octadecylamine, and Amino-terminated polystyrene occurs about 150-250 and 370-470 °C, as shown in Figure 3. At 600 °C, the residue reaches the weight percentage 44% of ODASWNTs and 63% of PSSWNTs. The calculated portions of alkyl chain in the chemically modified SWNTs were about 34 and 15 wt% of ODASWNTs and PSSWNTs, respectively. The difference in the portion of alkyl chain between two samples is considered as the difference in the reactivity due to the main chain mobility during reaction.

CutSWNTs didnt disperse in any solvents including water, even though they had many carboxylic acid functionalities. But, PSSWNTs and ODASWNTs were dispersed well in chloroform, and aromatic solvents (benzene, toluene). In Figure 4, the dispersions are transparent (their actual color was brown). But, they are transparent. PSSWNTs and ODASWNTs do not precipitate over a month. And their TEM images prepared by scooping up the solution with grid. Both PSSWNTs and ODASWNTs dispersed randomly, but still existed in rope, not separated every tube. The small spherical particles shown in the TEM images are residual

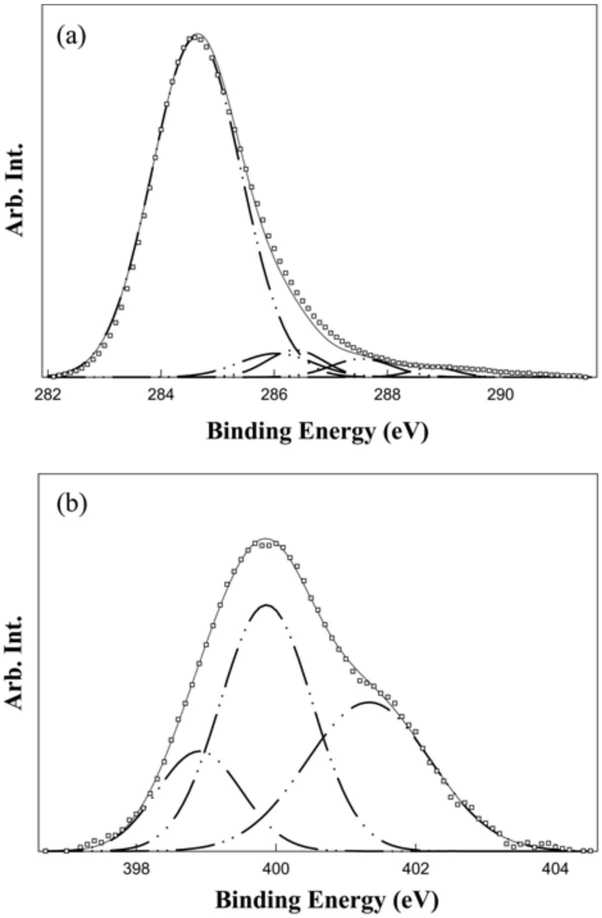

Figure 2. Curve fitting for XPS spectra of (a) C_{1s} of PSSWNTs and (b)N_{1s} of PSSWNTs.

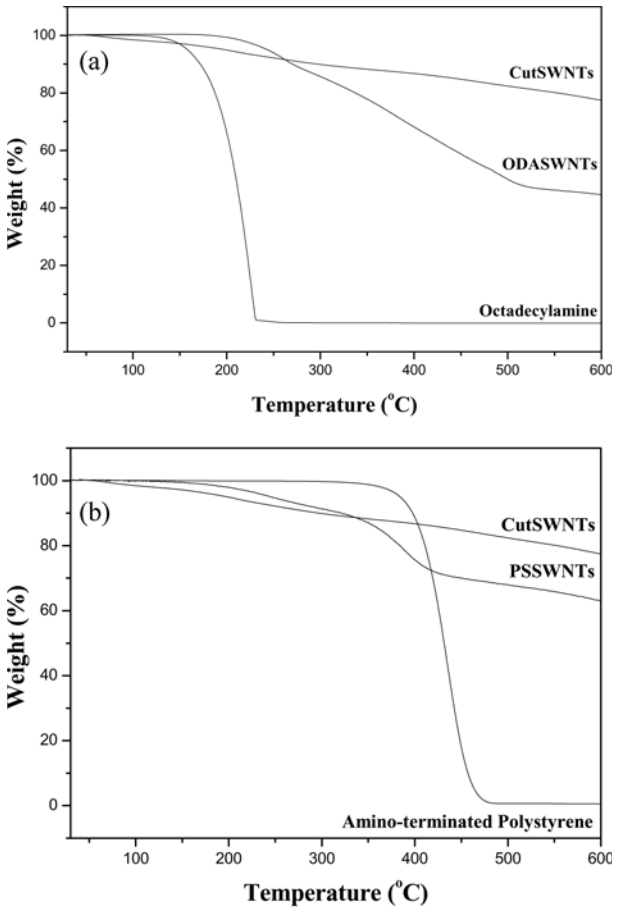

Figure 3. TGA thermograms for (a) CutSWNTs, ODASWNTs, ODA, and (b) CutSWNTs, PSSWNTs, amino-terminated polystyrene.

catalysts wrapped up in short SWNTs, as shown in Figure 1.

Figure 5(a) exhibits the storage moduli, E', of PS, and the composites containing 1 wt% chemically modified carbon nanotubes. At 40 °C, the storage moduli of the composites are 2.42×10^9 Pa for CutSWNTs1/PS, 2.39×10^9 Pa for ODASWNTs1/PS, 3.17×10^9 Pa for PSSWNTs1/PS, 2.58×10^9 Pa for CutSWNTs3/PS, 3.10×10^9 Pa for ODASWNTs3/PS, and 4.73×10^9 Pa for PSSWNTs/PS composite. The storage modulus of homo polymer, PS, is 2.42×10^9 Pa. The storage moduli of the composites increase 131% for 1 wt% and 195% for 3 wt% of PSSWNTs relative to the homo matrix polymer. CutSWNTs did not disperse well in the matrix polymer, PS as well as in the solvent during preparation of the composite. CutSWNTs do no have specific interaction with matrix polymer PS. Many functional groups added on the outside of SWNTs during purification and cutting hinder the adhesion of matrix polymer to CutSWNTs. PSSWNTs show a higher storage modulus of the composite than ODASWNTs, because PSSWNTs are more compatible with the matrix polymer, PS. The styrene group of PSSWNTs causes the compatibility of SWNTs with matrix polymer.

Glass transition temperature, T_g, of each nanocomposite is obtained from the maximum temperature of tan δ in Figure 6. It does not show the difference from that homo polymer, PS. It reveals that the relaxation behavior of the matrix polymer, PS, in the composites, does not affect with the filler, chemically modified CNTs. The mechanical property of the composites depends on the dispersion state and the compatibility of the fillers.

Figure 7 shows the storage moduli and complex viscosity of the homo polymer and the composites with 3 wt% fillers. The storage modulus of CutSWNTs3/PS becomes smaller when compared to the homo polymer. The CutSWNTs did not disperse and aggregated in the matrix, and the compatibility of CutSWNTs with PS was bad. So, Slippage could happen at the interface between CutSWNTs coagulum and polymer matrix. PSSWNTs show a higher storage modulus of the composite than ODASWNTs, because the amino-terminated polystyrene group grafted on SWNTs has a higher compatibility with PS than the octadecylamine group. In the low frequency region, the storage moduli of the ODASWNTs3/PS and PSSWNTs3/PS composites show non-terminal

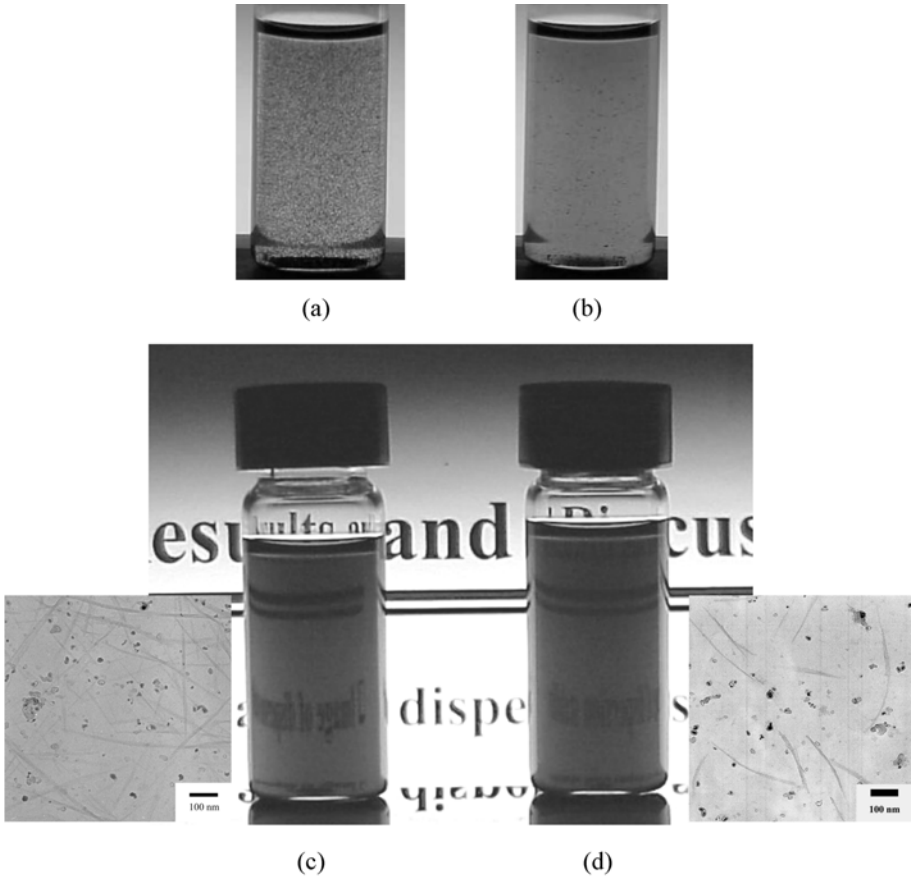

Figure 4. Pictures of (a) CutSWNTs dispersion, (b) CutSWNTs and polystyrene dispersion, (c) PSSWNTs dispersion, and (d) ODASWNTs dispersion in benzene. All samples were prepared to make the total amount of solutes/solvent to 1 mg/4 mL. The TEM images are PSSWNTs and ODASWNTs dispersions.

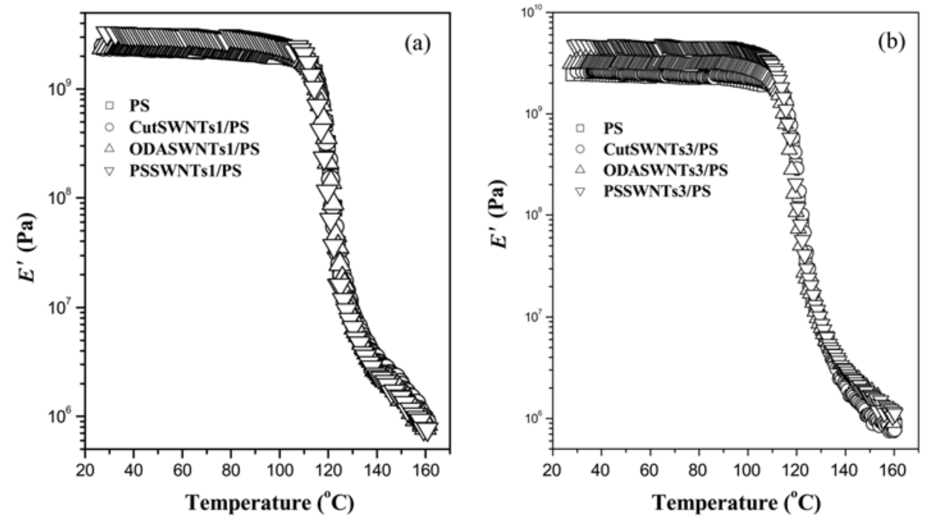

Figure 5. Dynamic storage moduli (E') of the polystyrene/chemically modified carbon nanotubes composites s (a) with 1 wt% of fillers and (b) with 3 wt% of fillers.

behavior. This phenomenon is characteristic of layered-silicate/polymer nanocomposites.[21,22] It happens due to the interaction between the nanoscale fillers when the fillers are well dispersed in matrix.

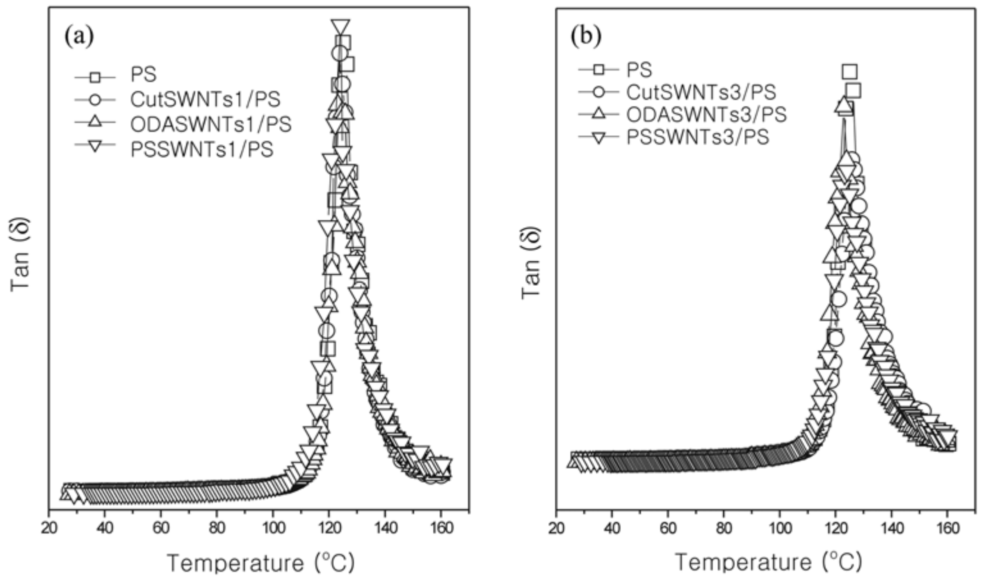

Figure 6. Tan δ of the polystyrene/chemically modified carbon nanotubes composites (a) with 1 wt% of fillers and (b) with 3 wt% of fillers.

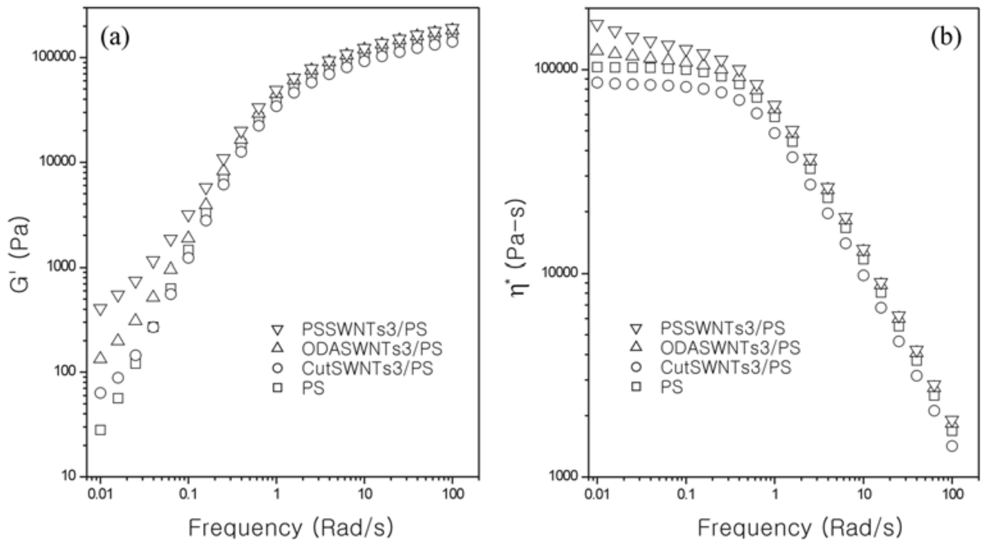

Figure 7. (a) Storage moduli (G'), and (b) complex viscosity (η^*) of polystyrene/chemically modified carbon nanotubes composites with 3 wt% of fillers.

Figure 8 gives plots of log G' versus log G'' for the monodisperse polystyrene and nanocomposites. The slope of monodisperse polystyrene is very close to 2 in the terminal region. The log G' versus log G'' slopes of the nanocomposites with 3 wt% filler have a slope less than 2 in the terminal region. It shows that the elastic property of the nanocomposites was increased due to the chemically modified SWNTs. But in the high G' value region, the G' value of CutSWNTs3/PS was lower than PS. It reveals that the compatibility of CutSWNTs with PS was low, as we mention in Figure 7.

Figure 9 is the TEM image of the PSSWNTs3/PS composites. It reveals that carbon nanotubes are well dispersed in the matrix.

Conclusions

In this experiment, octadecylamine and amino-terminated polystyrene were grafted on the surface and end of carbon nanotubes during chemical modification of carbon nanotubes. ODASWNTs and PSSWNTs showed dispersion stability in the dichloromethane, benzene, toluene, etc. The composite containing 3 wt% of PSSWNTs had a twice higher dynamic

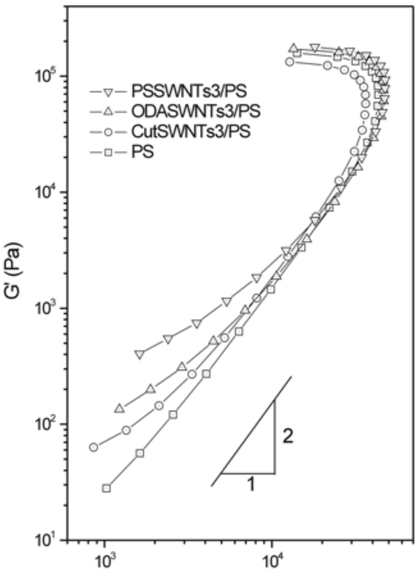

Figure 8. Plots of log G' versus log G'' for the monodisperse polystyrene and the polystyrene/chemically modified carbon nanotubes composites with 3 wt% of fillers.

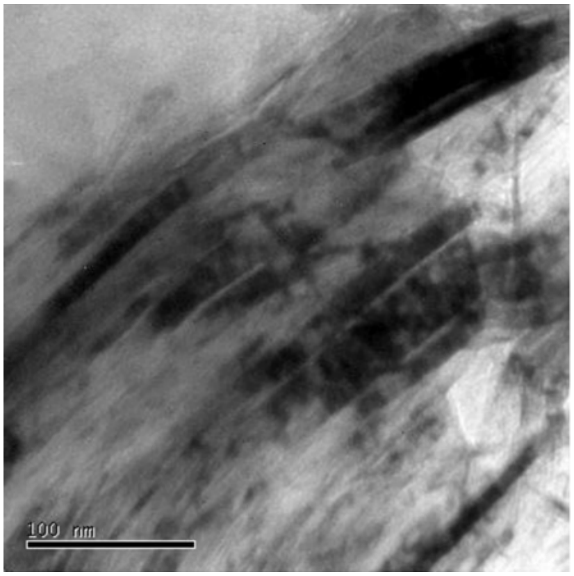

Figure 9. Transmission electron micrographs of polystyrene/PSSWNTs composites with 3 wt% of fillers.

storage modulus than homo polymer. Dispersion state of carbon nanotubes in the polymer matrix and the compatibility of between carbon nanotubes and matrix affected the mechanical and rheological properties of the composite. The storage modules of ODASWNTs/PS and PSSWNTs/PS composites showed non-terminal behavior.

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