Effect of SWCNT Dispersion on Epoxy Nanocomposite Properties

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In nanocomposites containing single wall carbon nanotubes (SWCNTs), the final properties strongly depend on the dispersion quality of these fillers. Various methods have been used to improve the dispersion of nanofillers; however, one of the most effective ways is to functionalize carbon nanotubes (CNTs) with covalent and noncovalent functional groups. In this work, the dispersion of SWCNTs in an epoxy system was studied by using surfactants, acid (COOH), and ester groups (PGE)-modified CNTs. Rheological and scanning electron microscopy analysis showed that functionalization of CNTs helped in improving the dispersion of fillers in the epoxy matrix. Systems with surfactant modified SWCNTs (1 wt%) exhibited the highest storage modulus at low frequencies after 5-min sonication. This behavior is associated to a stronger network of fillers as a result of a good dispersion. However, longer sonication times lowered the storage modulus, corresponding to a degradation of the tubes. The effect of the dispersion quality on mechanical properties was also studied using a three-point bending set-up. POLYM. COMPOS., 33:582–588, 2012. © 2012 Society of Plastics Engineers

INTRODUCTION

Polymer matrices reinforced with carbon nanotubes (CNTs) have gained an enormous interest in research and industry. Composites with CNTs show improved thermal, mechanical, and electrical properties compared with the traditional composites. However, because of their nanometric size, CNTs create agglomerations and decrease the quality of the dispersion. This problem must be overcome in order to utilize the unique properties of nanotubes and develop high performance CNT-based materials. Therefore, there have been many studies in developing approaches for effective and reproducible dispersions of CNTs [1–3]. For instance, Advani et al. studied the storage modulus (G'), loss modulus (G''), and complex and steady shear viscosities for multiwalled nanotubes (MWCNT)/epoxy suspensions with different dispersion states, aspect ratios, concentrations, network structures, and orientation states. They reported that a good MWCNT dispersion, high aspect ratio, and high concentrations aided in the formation of a stronger MWNT network as indicated by higher G' and complex viscosity values [4].

There are two main approaches for dispersing CNTs: mechanical methods and chemical methods. Mechanical dispersion methods, such as ultrasonication [5], centrifugation [6], and high shear mixing [7], not only can help to separate bundles of nanotubes but also can shorten the tubes, decreasing their aspect ratio. Chemical methods are designed to alter surface characteristics of the nanotubes, either physically (noncovalent functionalization) [8, 9] or chemically (covalent functionalization) [10, 11]. Chemical methods include surface functionalization of CNTs to improve their compatibility with polymers or solvents. In general, functionalization provides wetting enhancement and reduce the tendency of the CNTs to agglomerate. However, strong acids and aggressive chemical procedures may create structural defects, resulting in poor properties for the nanotubes. On the other hand, noncovalent functionalization methods, such as surfactants, give opportunities of adsorbing various groups on the CNT surface without disturbing the π system of graphene sheets [7, 12].

The main goal of this study was to understand and evaluate the problems associated with the dispersion of CNTs in polymeric systems. Different mechanical and chemical techniques, such as sonication, addition of surfactants, and covalent functionalization, were evaluated, and the quality of the sample dispersion was assessed by the constancy of the storage modulus with the frequency in the low-frequency range. Furthermore, the effect of dispersion qualities on mechanical and morphological properties of SWCNT/epoxy composites was discussed. A good dispersion SWCNT in a polymeric material is critical, because a wide range of applications depends on the final properties of the system. Such applications range

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from sensors and bioscience applications to polymer nanocomposites and electronic devices.

EXPERIMENTAL

Materials

SWCNTs were obtained from a commercial source (Shenzen Nanotech Port, China). The nanotubes were produced by chemical vapor deposition, and contained ∼10 wt% impurities, consisting primarily of amorphous carbon and transition metals. The diameter range for the SWCNTs was <2 nm; the length range was 5–15 μm.

During this work, Epon 828 epoxy was used in combination with a polyether triamine hardener (Jeffamine T-403, Huntsman) to prepare the composites. Nonionic polyoxyethylene octyl phenyl ether (Triton X-100) was used as a surfactant agent. Tetrahydrofuran (THF), sulfuric acid (H_2SO_4), nitric acid (HNO_3), and hydrochloric acid (HCl; Fisher Scientific) were used as received during the oxidation procedure.

Process

Functionalization of SWCNTs. In this study, CNTs were oxidized based on a process reported before [13]. According to the procedure, 1 g of SWCNT was dispersed in 250 mL of 3:1 H_2SO_4 (98%)/HNO_3 (70%). This solution was sonicated for 1 h followed by 3 h of stirring at room temperature. These conditions were selected to achieve moderate oxidation and maintain a high aspect ratio. After exhaustive washes with deionized water, HCl was added to facilitate the formation of carboxylic acid groups —COOH. The solution was washed again with deionized water until a constant pH value around 5–6 was achieved. The acid-treated CNTs were obtained after centrifugation of the aqueous suspensions and dried overnight in a vacuum oven at 90°C. The TGA analysis showed that 8.6 wt% organic groups were attached onto the SWCNTs. The existence of acid groups was proved with further FTIR analysis [13].

After the acid treatment, the nanofillers were esterified following the procedure below. Triphenylphosphine (TPP; 0.2 mole per mole of epoxy groups) was used as a catalyst to attach the functional group PGE onto the acidified fillers. Oxidized nanotubes (1 g), PGE (molar ratio PGE/COOH = 3), and TPP were dispersed in 200 ml of THF. The esterification reaction was refluxed in an oil bath heated to 90°C for 96 h.

After the treatment, the fillers were thoroughly washed with THF, centrifuged, and dried in a vacuum oven at 90°C for 24 h. These esterified nanotubes were denoted as type of filler plus PGE.

Noncovalent functionalization of SWCNTs was developed by adding the nonionic polyoxyethylene octyl phenyl ether (Triton X-100) surfactant agent (amount of surfactant agent was calculated as 1 wt% of the CNT concentration in the suspension). These fillers were denoted as SWCNT-$S_{t\,=\,x}$, where "x" indicates the total sonication time.

Preparation of SWCNT/Epoxy Composites

Epoxy nanocomposites were synthesized by employing different concentrations of unmodified (pristine-SWCNT), acidified (SWCNT-COOH), esterified (SWCNT-PGE), and surfactant-assisted (SWCNT-S) single wall nanotubes. The nanotubes were dispersed in THF, sonicated for 5 min, and left to homogenize for 1 week. Samples were also prepared with suspensions sonicated for 30 min and 120 min for surfactant assisted SWCNT systems. Afterward, the epoxy was added, and the suspension was mixed for 2 h and placed overnight in a vacuum oven at 80°C to allow solvent evaporation. Finally, a stoichiometric amount of hardener was added, followed by further mixing (2 min) and degasification (10 min). The solution was cast into a polytetrafluoroethylene (PTFE) mold and cured at 75°C for 3 h, with a postcuring process at 125°C for 3 h.

Techniques

Rheological analysis was used to explore the state of nanotube dispersion. The rheological response of the epoxy matrix without a curing agent was characterized as a Newtonian liquid; thus, all of the viscoelastic and nonlinear behaviors of the suspensions were caused by the addition of SWCNTs [4, 14, 15].

The rheological properties of the epoxy/nanotube suspensions (without hardener) were determined using a commercial strain controlled rheometer (AR-G2, TA Instruments). A cone-plate geometry (diameter 60 mm and 27 μm truncation) was used to register the viscoelastic response of the CNTs/epoxy suspensions. Viscoelastic properties of all samples were measured at 25°C temperature. Dynamic strain sweep at a constant frequency (1 Hz) was used to find the linear viscoelastic region in which G' and G'' were independent of the strain amplitude. For all samples, 1% strain was chosen in the linear viscoelastic region, and a linear viscoelastic response characterized at the entire range of frequency was used in this work (100 to 0.01 rad/s). During the sample loading procedure, 5-min rest time was used to eliminate the effect of loading history.

The mechanical response of the different types of SWCNT epoxy nanocomposites was evaluated. Samples were tested with a three-point bending set-up using a dynamic mechanical analysis machine (RSA3, TA Instruments) tool following the ASTM D790M standard. The flexural modulus was calculated by using the equation: $E = (L^3 {*} m)/(4 {*} b {*} d^3)$, where E is the modulus of elasticity in bending mode (MPa), L is the supportive span length (which is 10 mm in this study), b is the width of the beam tested (mm), and m is the slope of the tangent to

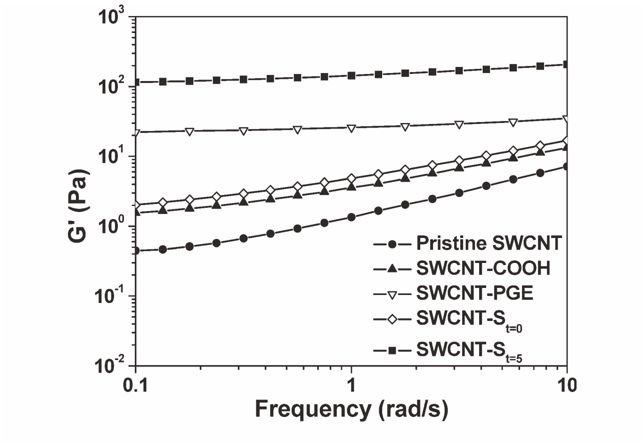

FIG. 1. Effect of functionalization on G' (Pa).

the initial straight-line portion of the load-deflection curve (N/mm of deflection).

Scanning electron microscopy (SEM, Zeiss EVO 50) was used to observe the fractured surfaces of the nanocomposites prechilled in liquid nitrogen. Samples were sputter-coated with gold prior to SEM observation.

RESULTS AND DISCUSSION

Dispersion Quality

Effect of Chemical and Mechanical Modification. In this study, viscoelastic data of 1 wt% SWCNTs with surfactant (SWCNT-S$_{t\,=\,0}$), acidified SWCNTs (SWCNT-COOH), and esterified SWCNTs (SWCNT-PGE) were compared with those obtained from 1 wt% pristine SWCNTs (for surface-modified nanotubes or nanofibers, the weight refers to the neat nanotube or nanofiber calculated from thermal gravimetric analysis). Ultrasonication was also applied in order to improve the dispersion of SWCNTs with surfactant (SWCNT-S$_{t\,=\,5}$). Results are shown in Fig. 1.

At low frequencies, the storage modulus (G') flattened out to a constant value. Both SWCNT-S$_{t\,=\,0}$ and SWCNT-S$_{t\,=\,5}$ showed a higher storage modulus than the pristine SWCNT system. The storage modulus of the SWCNT-S$_{t\,=\,0}$ system increased by 358% at 0.1 rad/s. After applying ultrasonication, the storage modulus of SWCNT-S$_{t\,=\,5}$ had a value 100 times (263,805%) higher than the pristine SWCNT system at low frequencies. In the SWCNT-COOH system, the storage modulus at low frequencies increased 245%, compared with pristine SWCNTs.

The aggregated pristine SWCNTs behaved more like a particle suspension, and when the frequency was applied, the suspension showed lower flow resistance (lower viscosity and so G') when compared with the SWCNTs with surfactant. On the other hand, surfactants are adsorbed on the nanotube surface by hydrophobic or π–π interactions. In a typical dispersion procedure, further ultrasonication helps surfactants debundle (or exfoliate) nanotubes by Columbic or hydrophilic interactions. Therefore, the rubbery plateau for the SWCNTs-S$_{t\,=\,5}$ showed higher a storage modulus compared to the other suspensions. In the case of chemically modified SWCNTs, the chemical groups provide repulsion forces, which separate the SWCNTs in the suspension. The presence of acid groups provides steric stabilization of SWCNTs, which lowers their tendency to create aggregations and help them form uniform dispersions. Therefore, the shear resistance (viscosity and G') was boosted by adding functionalized SWCNTs into the suspension. For the SWCNT-PGE system, the reason for the higher increase in storage modulus (4,900%) was due to the strong interaction of PGE groups with the epoxy matrix.

Effect of Aspect Ratio and Filler Concentration. Advani et al. suggested that CNT separation refers to the separation of individual CNTs from the aggregates, and CNT interconnection addresses the interconnections between the CNT aggregates and separated CNTs [4]. It is expected that a different rheological behavior between these two structures will be observed. If a Newtonian plateau of G' develops at low frequencies, it is an indication of the development of an entanglement or network in the suspension [4]. By comparing the rheological properties of SWCNT epoxy suspensions with different sonication times (0, 5, 30, 120 min), the effect of the SWCNT network structure on the dispersion of 1 wt% SWCNTs was evaluated (Fig. 2).

In this figure, the higher storage modulus value was observed for the system with a 5-min sonication process, and the lower storage modulus value was observed for the 120-min sonication time. This indicates that aggregated CNTs were separated by using a longer sonication time, producing weaker interconnections between the CNTs and structural damage in the CNTs, which created a considerable decrease in the aspect ratio of the tubes.

Table 1 shows the ultimate sonication time for different concentrations of nanofillers. It was observed that the highest storage modulus obtained for 0.25, 0.5, and 1 wt% of SWCNTs with surfactant was with 5-min

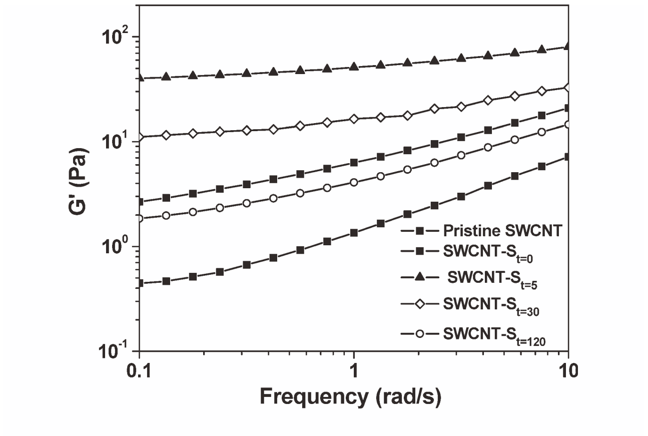

FIG. 2. Effect of sonication time on G' (Pa).

TABLE 1. Amount of increase in storage modulus at 0.1 rad/s for different sonication times and concentrations of surfactant-assisted SWCNTs.

Time (min)	0.25 wt%	0.5 wt%	1 wt%	1.5 wt%
0	0	0	0	0
5	894	237	1,885	1,220
30	668	143	1,266	1,480
120	6	142	11	1,076

sonication. For the 1.5 wt%, the highest storage modulus value was found at sonication time of 10 min. The reason for the longer sonication time at higher concentrations was that the interaction between nanotubes increased at higher concentrations, and more energy was required to separate the aggregated bundles of nanotubes.

Figure 3 shows the viscoelastic data of SWCNTs with surfactant at different concentrations. It was observed that as the concentration increases, the storage modulus (G') increased. When the concentration increases in a well-dispersed system, the distance between the individual tubes shortens and the interaction between the tubes becomes stronger. This reduces the mobility and increases the suspension's resistance to flow. After a critical concentration, where the nanotubes form a 3D network, the suspension shows a solid-like behavior characterized by a fixed storage modulus (G') and loss modulus (G'') with the frequency. This critical concentration is called the "percolation threshold," and in this study, as the concentration reached 0.5 wt%, it was observed that the suspension showed a rubbery plateau at low frequencies, which suggests the formation of a network exhibiting solid-like behavior.

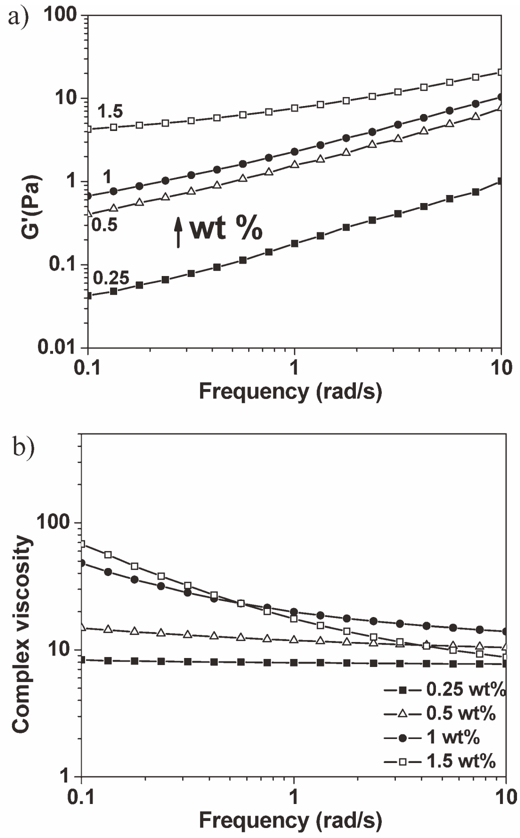

FIG. 3. Effect of concentration on: a) Storage modulus (G'), b) Complex viscosity.

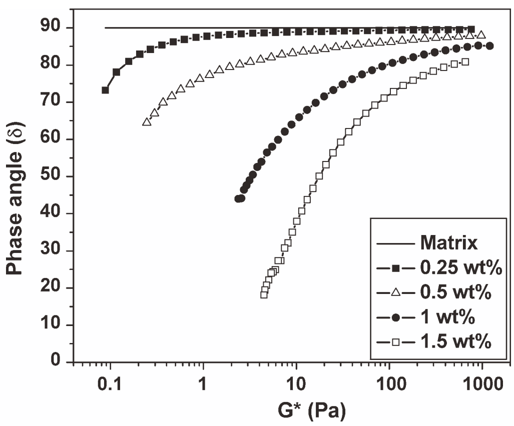

FIG. 4. Phase angle (δ) vs. complex storage modulus (G*) plot for different concentrations.

It was also observed that the complex viscosity increased sharply in the whole frequency range from 0.25 to 1 wt% CNT loading (Fig. 3b), being more significant in the range of low frequency. The curves present a plateau at high frequencies without a clear trend in the viscosity values. The sample with 1.5 wt% of CNT presents lower complex viscosity at high frequencies than the sample of 1 wt%. This effect could be associated to dispersion problems of the CNT in the epoxy matrix.

In order to obtain a better understanding of the transition from the liquid-like to the solid-like behavior, a phase angle (δ) versus complex storage modulus (G^*) plot was evaluated for the surfactant assisted system (Fig. 4). This plot can be used to detect the rheological percolation because the phase angle is very sensitive to the fluid–solid transition of a viscoelastic fluid. A typical liquid system shows a delta degree of 90°, whereas a typical solid system shows a delta degree of 0°. Below the percolation threshold, the phase angle tends to be $\sim 90°$ at low G^*, consistent with a behavior dominated by the viscous flow. At and beyond the percolation threshold, the phase angle decreases significantly with the modulus, in agreement with an increasing elastic behavior. In this case, it was observed that the system showed a pronounced solid-like behavior close to the 0.5 wt% of CNT.

Several studies have also focused on the percolation threshold of CNT-reinforced polymer nanocomposites. Pothschke et al. [16] found the percolation threshold value to be 2% by weight for MWCNTs systems. Du et al. [17] found it to be 0.12% by weight, while Kinloch et al. [18] found it to be around 0.5% by volume. The reason for different percolation threshold values is that research groups might use different aspect ratio CNTs and suspend the fillers in different systems. However, all these

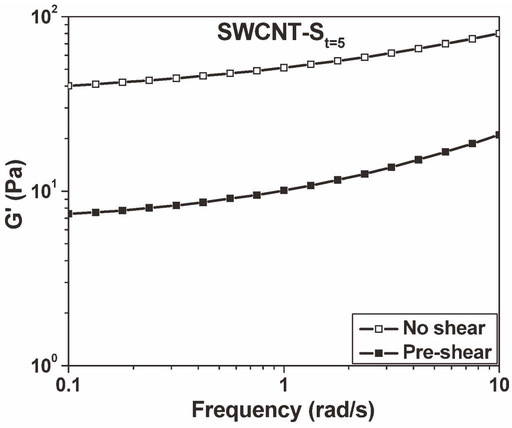

FIG. 5. Effect of orientation on G' (Pa).

studies showed that the viscosity of the suspension increased by the concentration, and that the viscosity was strongly related to the percolation threshold concentration.

Effect of Orientation. Figure 5 shows the effect of the preshear process on the storage modulus of the SWCNT-$S_{t = 5}$ system. In order to study the effect of the orientation, all samples were tested before and after 20 s^{-1} shear rate for 30 min. It was observed that the storage modulus decreased 80% after the preshear period, indicating that the preshear process aligned the SWCNTs in the shear direction and decreased the flow resistance. It was already mentioned that the 5-min sonication developed a good CNT network, and the preshear process, which may break down this network, produced a sharp decrease in the storage modulus (from 40 to 7.5 Pa).

The use of high shear flow aligns the nanotubes in the shear direction, and this aligned suspension shows a lower viscosity and G' than randomly orientated fiber suspensions as it experiences lower resistance to flow. At the same time, higher shear flows may break down the 3D network formed by the filler, producing a decrease in the viscosity.

Mechanical and Morphological Analysis

There are two main factors that affect the mechanical properties of nanocomposites: the interfacial adhesion/interaction between the filler and the matrix, and the CNT dispersion quality. Improved dispersion of CNTs creates a larger interfacial area that is available to transfer load. In this study, the effect of the dispersion quality on the mechanical properties was measured by flexural experiments. The results are shown in Table 2. It can be observed that the flexural modulus of the epoxy matrix improved after adding SWCNTs into the system.

TABLE 2. Flexural modulus of SWCNT/Epoxy nanocomposites.

Filler	Flexural modulus (GPa)	Improvement (%)
Matrix	2.2 ± 0.29	–
Pristine SWCNT	2.53 ± 0.11	15
SWCNT-COOH	2.62 ± 0.07	19
SWCNT-$S_{t = 0}$	3.05 ± 0.10	39
SWCNT-$S_{t = 5}$	3.26 ± 0.13	48

TABLE 3. Effect of SWCNTs with surfactant on the flexural modulus (5-min sonication).

SWCNT-S (wt%)	Flexural Modulus (GPa)	Improvement (%)
0	2.2 ± 0.29	–
0.25	2.71 ± 0.01	23
0.5	2.83 ± 0.01	29
1	3.26 ± 0.13	48

For both covalent and noncovalent systems, the better dispersion provided higher mechanical properties. Surfactant-assisted systems provided the hydrophobic segment of the surfactant that interacted with the carbon, while the hydrophilic segment interacted with epoxy through hydrogen bonding. Thus, using a surfactant improved the wettability of the CNTs. Besides improved adhesion, steric repulsion forces between the CNTs improved the dispersion so that CNTs overcame the van der Waals attractive forces. On the other hand, besides improving the dispersion, covalently functionalized nanotubes provided a better adhesion between the nanotubes and the matrix, which increased the load transfer efficiency from the matrix to the filler.

The effect of the concentration on the mechanical properties of the nanocomposites is shown in Table 3. It was observed that the increase in the amount of SWCNT led to improved flexural modulus of nanocomposites. Adding 1 wt% of nanotube improved the flexural modulus 48% compared to the epoxy matrix. As more nanotubes are added into the system, the distance between the tubes decreases. This provides stronger interaction between the nanotubes and an increase in the flexural modulus confirming the results obtained by rheology.

The effect of sonication time on the mechanical properties is shown in Table 4. The results from flexural experiments followed the same trend as was observed for rheological experiments. Although the improvement in the modulus was around 48% for the 5-min sonication system, compared with the matrix, the improvement for the 120-min sonication system was only 7%. Suave et al. [19] also studied the sonication effect on the mechanical properties of CNT/Epoxy nanocomposites. The highest tensile

TABLE 4. Effect of sonication time on the flexural modulus (1 wt% of SWCNT-S).

Sonication time (min)	Flexural modulus (GPa)	Improvement (%)
Matrix	2.2 ± 0.29	–
0	3.05 ± 0.11	39
5	3.26 ± 0.14	48
30	3.03 ± 0.27	37
120	2.36 ± 0.09	7

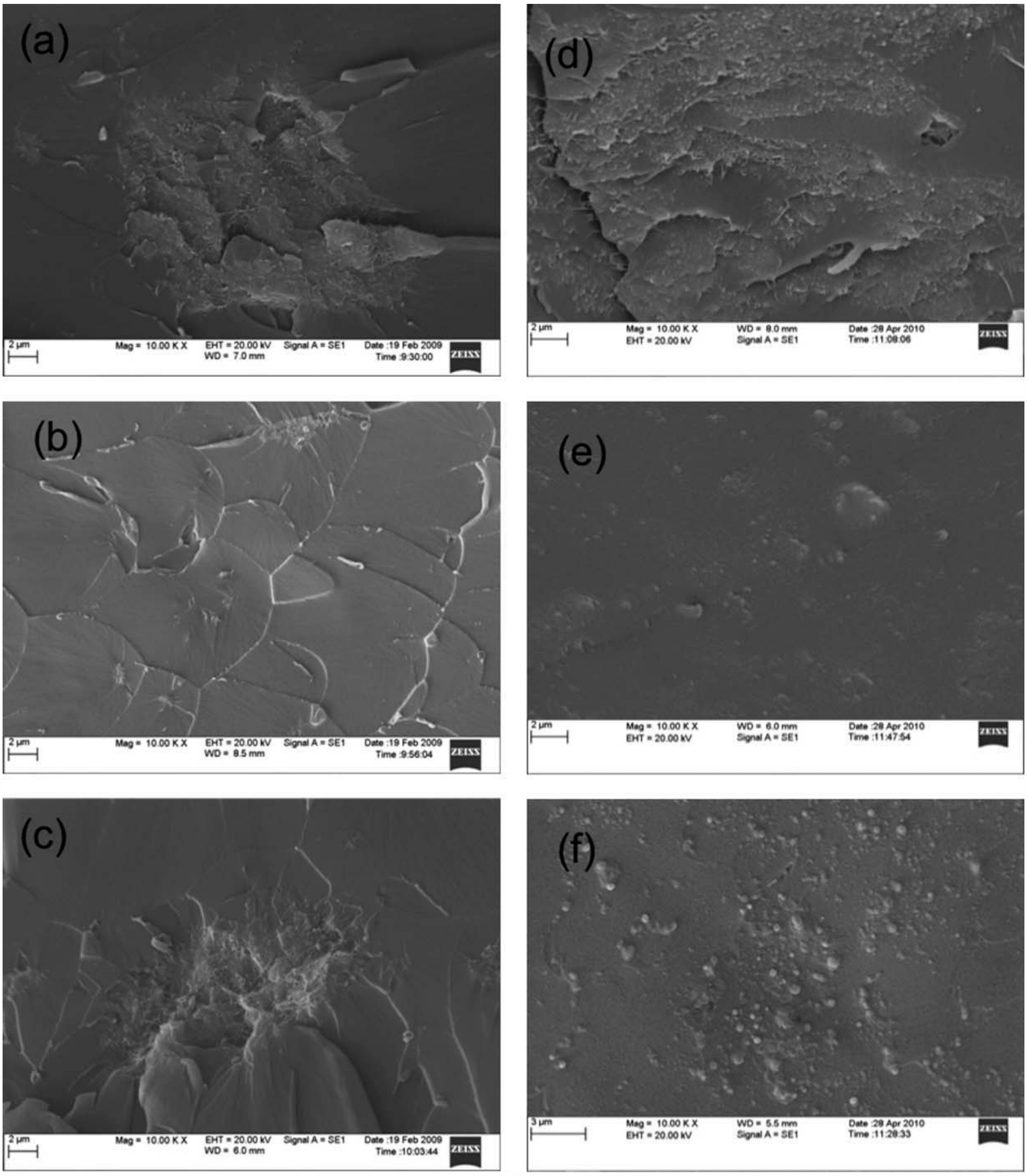

FIG. 6. SEM images of the epoxy nanocomposites of (a) Pristine SWCNT, (b) SWCNT-COOH, (c) SWCNT-PGE, (d) SWCNT-$S_{t\,=\,0}$, (e) SWCNT-$S_{t\,=\,5}$, (f) SWCNT-$S_{t\,=\,120}$.

strength of CNTs was observed at 20 min of sonication. As they increased the sonication time to 40 min, they observed a 22% decrease in the Young's modulus.

The observations after the rheological experiments helped give an idea about how the mechanical properties would be affected by different sonication times. It is expected that a better dispersion system will yield a higher modulus. These results proved that the longer sonication time caused weaker interactions between the tubes, and in addition, a structural damage on tube walls.

The dispersion of the nanotubes was also shown through SEM images of 1 wt% SWCNTs sample's fracture surface that was broken in liquid nitrogen (Fig. 6). These images showed that nanotubes were more uniformly distributed in the polymer matrix after covalent and noncovalent functionalization. A considerably smoother surface was observed for the SWCNT-COOH and SWCNT-$S_{t\,=\,5}$ systems (Fig. 6b and e, respectively). In Fig. 6f (SEM image of SWCNT-$S_{t\,=\,120}$), separated nanotubes were observed. The SEM images confirmed the better dispersion quality of the functionalized SWCNT systems compared to pristine SWCNT. However, large bundles were observed for esterified SWCNTs systems, even though the systems showed an increase in storage modulus from rheological analysis. Initially, the system with esterified SWCNTs was expected to possess better dispersion due to the similar functional group with epoxy. Instead, an increase in the bundling of SWCNT-PGE compared with unmodified and COOH-modified nanotubes was an unexpected result. A possible explanation is the occurrence of a polymerization-induced phase separation. Starting from a good dispersion of SWCNT-PGE in epoxy precursors, at a certain conversion in the polymerization reaction, the solution becomes metastable mainly due to the decrease in the entropic contribution in the free energy, and phase separation takes place, leading to domains rich in SWCNT-PGE.

CONCLUSIONS

Using a combination of techniques, an attempt was made to characterize single wall CNT/epoxy systems. Several dispersion techniques were chosen, such as covalent and noncovalent functionalization and ultrasonication. The quality of the dispersion was evaluated through rheological studies. The highest storage modulus (G') value, which indicates a better dispersion, was observed for SWCNTs with surfactants after 5-min sonication.

The effect of carbon the nanotubes' concentration on the dispersion quality was also studied. It was observed that as the CNT concentration increased, the suspension showed a noticeable transition between a liquid-like to solid-like behavior (percolation concentration). The percolated threshold concentration was estimated to be $\sim$0.5 wt% of SWCNTs, where the storage (G') and loss (G'') moduli and the viscosity increased several orders of magnitude, compared with the unreinforced system.

It was also observed that the sonication time produced a considerable effect on the final dispersion of the fillers. The G' value increased as the sonication time increased, indicating a better disentanglement of the SWCNTs bundles. However, at longer sonication times, the storage modulus (G') decreased because of the weaker interconnection between the CNTs and possible degradation of the final structures. The effect of the orientation on the storage modulus was also discussed. The orientation of SWCNTs in the suspension decreased the resistance to flow, and thus decreased the storage modulus of the suspensions.

Finally, the mechanical properties of SWCNT epoxy nanocomposites were investigated. It was observed that the highest flexural modulus was obtained for a sonication process followed by a surfactant-assisted SWCNT epoxy system, which had a better dispersion quality, compared with the other systems. Furthermore, the effect of the concentration on the flexural modulus was analyzed, and it was noted that as the concentration increases, the flexural modulus of the composite system increases. The dispersion quality was also discussed through SEM analysis.

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