Journal of Applied Polymer Science

A Liquid-Like Multiwalled Carbon Nanotube Derivative and Its Epoxy Nanocomposites

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ABSTRACT: Multiwall carbon nanotubes (MWCNTs) with liquid-like behavior at room temperature were prepared with sulfonic acid terminated organosilanes as corona and tertiary amine as canopy. The liquid-like MWCNT derivative had low viscosity at room temperature (3.89 Pa s at 20°C) and exhibited non-Newtonian shear-thinning behavior. The weight fraction of MWCNT in the derivative was 16.72%. The MWCNT derivative showed very good dispersion in organic solvents, such as ethanol and acetone. The liquid-like MWCNT derivative was incorporated into epoxy matrix to investigate the mechanical performance of the nanocomposites and the distribution of MWCNTs in the matrix. When the liquid-like MWCNT derivative content was up to 1 wt %, the flexural strength and impact toughness of composites were 12.1 and 124% higher than the pure epoxy matrix, respectively. Transmission electron microscope (TEM) confirmed the very good dispersion of the liquid-like MWCNT derivative in epoxy matrix. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 2217–2224, 2013

KEYWORDS: composites; nanotubes; graphene and fullerenes; rheology; viscosity and viscoelasticity; mechanical properties

Received 16 February 2013; accepted 11 April 2013; Published online 20 May 2013
DOI: 10.1002/app.39398

INTRODUCTION

Multiwall carbon nanotubes (MWCNTs) have been widely recognized as next generation filler due to their novel electrical, mechanical, and chemical properties.[1–3] Some works focused on this aspect in MWCNT/polymer composites.[4–8] However, MWCNTs can easily entangle due to the one-dimensional nature and ultrahigh aspect ratio.[9,10] For this reason, it is difficult for obtaining the homogeneous dispersion of the MWCNTs in polymer matrix.[11] This kind of entanglement deteriorates the performance of the composites and limits its application. Besides, the MWCNTs are not compatible with all solvents because of their chemical inertness.

Typically, there are two ways to realize good dispersion of MWCNTs in the matrix, including melt compounding and solution processing technique. Both of them have disadvantages. The Melt compounding processing often yields poorly dispersion of MWCNTs since the viscosity of the MWCNT/polymer mixture is very high.[12,13] And the solution processing technique, with expensive organic solvent and complex post-treatment, induces defects and hampers the mechanical property of composites.[14]

A new route was developed to prepare nanocomposites with liquid-like MWCNT derivative in the absent of solvent. The synthesizing liquid-like MWCNT derivative in the absence of solvent has been reported by several works. When MWCNTs are modified with polyethylene glycol (PEG) chains, the MWCNT derivative could melt reversibly at 35°C.[15] Robert[16] prepared a MWCNT derivative by radical-based reaction. In addition, liquid-like MWCNT derivative could also be obtained through hydrogen bonds and steric effect with pluronic copolymer.[17] The material was in waxy solid state at room temperature, which melted and behaved liquidly at 45°C. Our group also synthesized a series of liquid-like MWCNT derivatives.[17–19]

Many works reported on preparing the nanocomposites with solid MWCNTs.[4–8] However, the solid MWCNTs flocculated into bundles and agglomerated in the matrix during mixing and casting process.[20,21] The nanocomposite with liquid-like MWCNT derivatives in the absent of solvent may solve this problem. Yang[22] reported that the liquid-like MWCNT derivative improved the tensile property of the epoxy. The Young's modulus, tensile strength, failure strain, and toughness of epoxy nanocomposites with 0.5 wt % liquid-like MWCNT derivative are increased by 28.4, 22.9, 24.1, and 66.1%, respectively, whereas those of the epoxy composites with 0.5 wt % solid MWCNT are improved by only 10, 11.1, 7.4, and 25.4%, respectively. In contrast, with 0.5 wt % pristine MWCNTs, the tensile strength, failure strain, and toughness of neat epoxy decreased by 4.4, 9.3, and 12.9%, respectively. The scanning electron microscope (SEM) images indicated that the liquid-like MWCNT derivative dispersed well in epoxy and had stronger interfacial force with epoxy resin. Li used the liquid-like

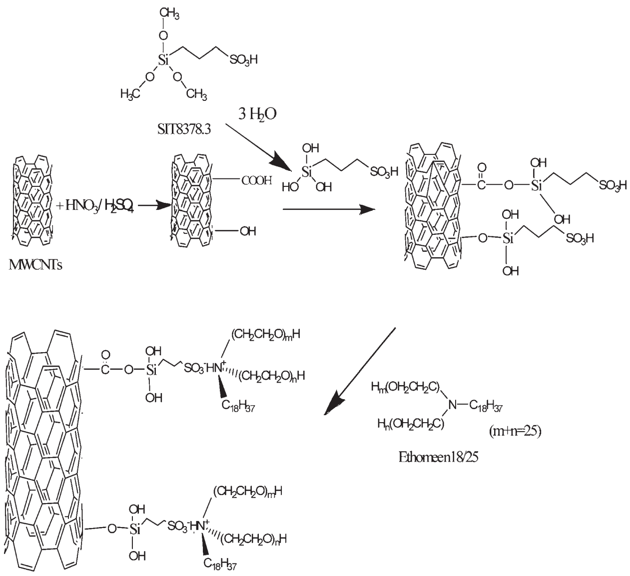

Figure 1. Reaction scheme of liquid-like MWCNT derivative.

MWCNT derivative to prepare liquid-like MWCNT/PA11 composites and tested their tensile modulus and elongation.[23] It revealed that the fracture elongation of the liquid-like MWCNT/PA11 composites was maintained within the range of 140–260%. In contrast, the fracture elongation of the MWCNT/PA11 system decreased down to a very low level of less than 30% as the loading of raw MWCNTs increases. The tensile modulus of liquid-like MWCNT/PA11 composites increased gradually at low liquid-like MWCNT derivative loadings and then come to an invariant level. At the highest point (around 0.8 wt %), the tensile modulus of the liquid-like MWCNT/PA11 composite are increased by about 22%. SEM images of the MWCNT/PA11 composites confirmed that the MWCNTs dispersed well in the matrix.

In this article, we prepared a liquid-like MWCNT derivative by modifying MWCNTs with sulfonic acid terminated organosilanes (SIT8378.3) as corona and tertiary amine surfactant (Ethomeen18/25) as canopy. The liquid-like MWCNT derivative showed perfect dispersion in organic solvents, such as ethanol and acetone. The derivative exhibited non-Newtonian shear-thinning behavior. The viscosity of the liquid-like MWCNT derivative (3.89 Pa s at 20°C and 0.34 Pa s at 65°C) was much lower than those of the MWCNT derivative reported by Li (360 Pa s at 20°C and 180 Pa s at 65°C) and Yang (31 Pa s at 20°C).[23,24] It is highly favorable to obtain good dispersion of MWCNT derivative in polymer matrix, which was confirmed by TEM. The flexural strength and the impact toughness of liquid-like MWCNT derivative/epoxy nanocomposites with 1 wt % liquid-like MWCNT derivative were 12.1 and 124% higher than the pure epoxy matrix, respectively.

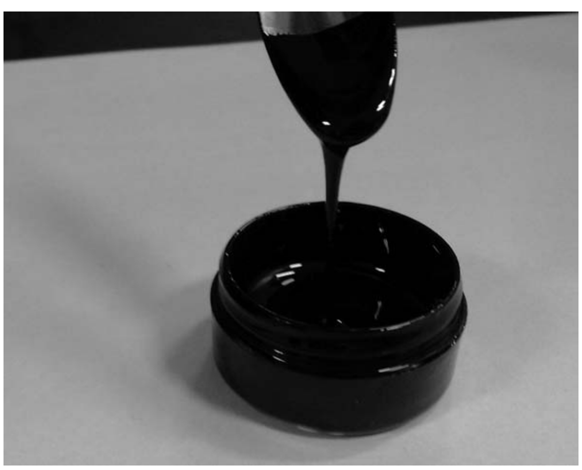

Figure 2. Picture of the liquid-like MWCNT derivative at room temperature.

EXPERIMENTAL

Materials and Preparation

The MWCNTs (diameter 20–40 nm, length 5–15 μm), provided by Chengdu organic chemicals Co., were synthesized by chemical vapor deposition (CVD) method. The SIT8378.3 [$(CH_3O)_3Si(CH_2)_3HSO_3$] and Ethomeen18/25 ($(C_{18}H_{37})N[(CH_2CH_2O)_mH][(CH_2CH_2O)_nH]$, $m + n = 25$) were produced by Gelest Inc. and Feixiang Chemicals, respectively. Methyl tetrahydrophthalic anhydride (METHPA) was from GuangZhou Weibo Chemistry Co. 2,4,6-Tri(dimethylaminomethyl) phenol (DMP-30) was bought from Aladdin Chemistry Co. Other analytical grade chemicals were sodium hydroxide solution (NaOH), $NaHCO_3$, H_2SO_4, HNO_3, ethanol, and acetone.

To begin with, MWCNTs (1 g) were modified with H_2SO_4/HNO_3 (250 mL, volume ratio 3 : 1) for 3 h at 60°C. The product, called carboxylic MWCNTs, was washed by the deionized water to remove residual acid. In the second step, the carboxylic MWCNTs (0.5 g) and SIT8378.3 water solution (1.667 g, weight fraction 30%) were mixed with 50 mL deionized water and have been stirred for 20 min. Then NaOH solution (0.1 mol/L) was added drop-wise until the pH was

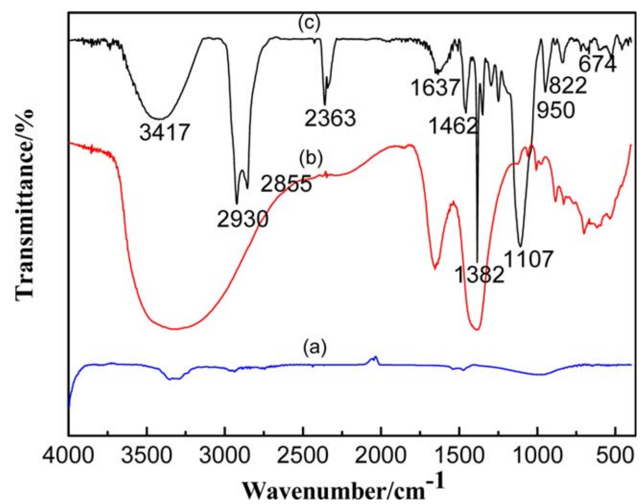

Figure 3. FTIR curves of (a) pristine MWCNTs; (b) carboxylic MWCNTs; (c) liquid-like MWCNT derivative (MWCNT + SIT8378.3 + Ethomeen18/25). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

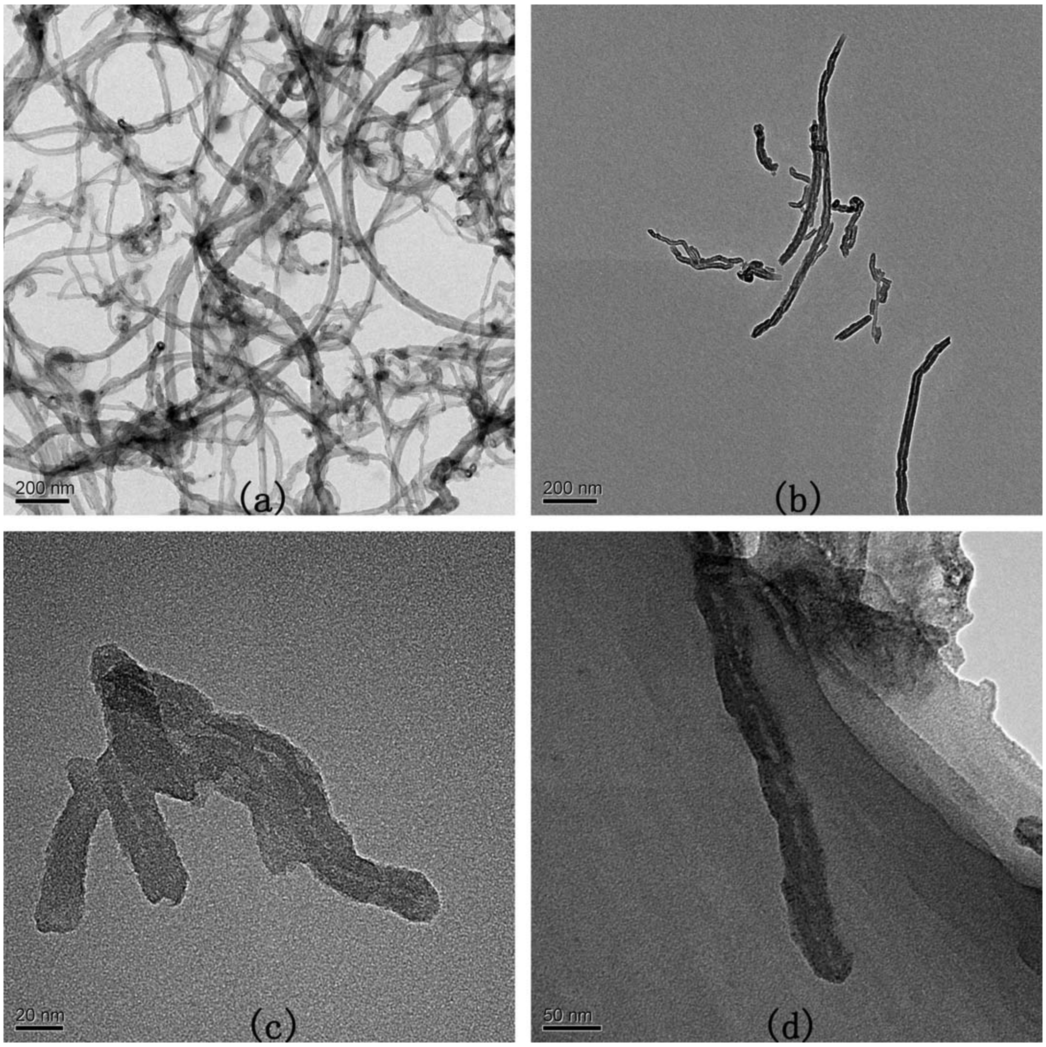

Figure 4. The TEM images of (a) pristine MWCNTs; (b) and (c) carboxylic MWCNTs; (d) liquid-like MWCNT derivative.

about 7. After that the solution was reacted at 60°C for 24 h in a three-necked flask. In order to remove the residual SIT8378.3, the product was dialyzed by dialysis tube (Spectra/Por RC Biotech Membrane, 15000 MWCO, 16 mm flat width) for 48 h while the water was changed every 8 h. Then the product (0.5 g) was dispersed in 50 mL deionized water and Ethomeen18/25 ethanol solution (15 g, weight fraction 10%) was added. The reaction proceeded under magnetic stirring at 60°C for 24 h. After that the water was removed at 100°C. The product was disolved and centrifugated at 6000 rpm for 15 min, resulting in a homogeneously black solution. Finally, the supernatant liquid was collected, concentrated and dried at 70°C to obtain the resulting liquid-like MWCNT derivative.

The liquid-like MWCNT derivative was added into the epoxy resin CYD-128(Sinopec) at 65°C and sonicated for 30 min. The mixture was cured in the vacuum oven with METHPA as curing agent and DMP-30 as accelerating agent. The system was cured at 90°C for 90 min, followed by 100°C for 30 min, 110°C for 30 min, 120°C for 30 min, and 140°C for 90 min.

Characterization

The surface groups on the MWCNTs were investigated by Fourier transform-infrared spectrometer (FTIR; Model: WQF-310) using KBr pellets. Transmission electron microscope (TEM) images were obtained at an accelerating voltage of 100 kV with the JEM-2100 instrument. For this study, a few drops of an aqueous dispersion of hybrid material were placed on a copper grid and evaporated the solvent prior to observation. Differential scanning calorimetry (DSC) traces were collected using a Q1000 TA instrument at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) measurements were taken under N_2 flow with a heating rate of 5°C/min by using TGAQ50 TA instrument. The sample was annealed at 110°C for 48 h before testing. Rheological properties were studied by the rheometer of TA instrument (AR-2000). The cone–plate geometry was 40 mm of cone diameter and 2° of cone angle. Steady flow tests of the derivative and Ethomeen18/25 were carried out at 25 and 10°C, respectively. Then temperature ramp test of the liquid-like MWCNT derivative was carried out at the shear rate of 10 s^{-1} in order to investigate the relationship between viscosity and temperature. After that, frequency sweep test was carried

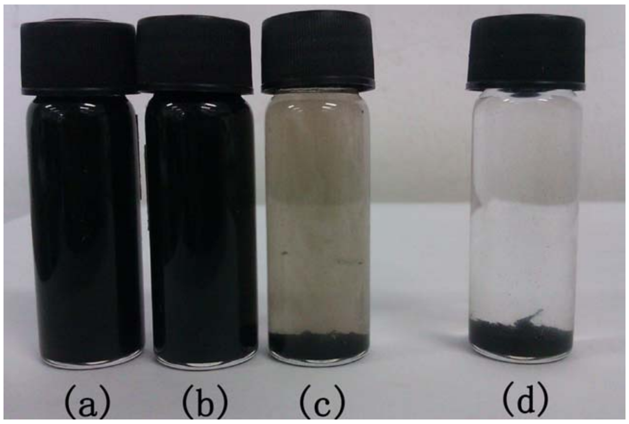

Figure 5. Solubility of liquid-like MWCNT derivative in (a) ethanol; (b) acetone; (c) water; and (d) solubility of MWCNTs in ethanol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

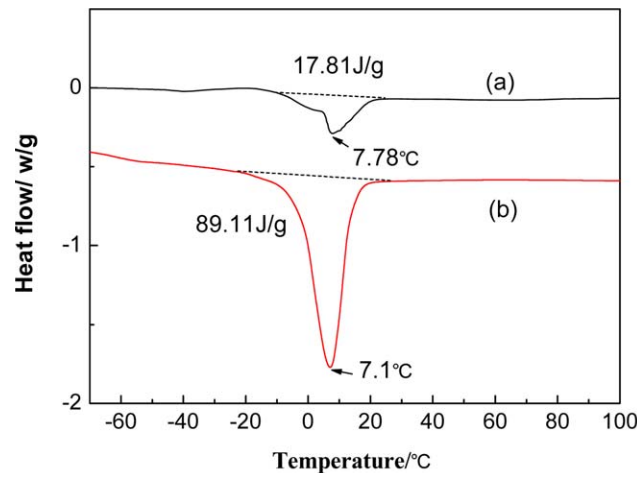

Figure 7. DSC curve of (a) the liquid-like MWCNT derivative; (b) Ethomeen18/25. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

out at 25°C with constant strain of 1%. Finally, the temperature sweep test was performed at 10 s^{-1} with constant strain of 1%. Flexural strength and impact toughness of the nanocomposites with different weight fraction of MWCNT derivative were tested on the universal testing machine (CMT-5105). The TEM images of the MWCNT derivative/epoxy nanocomposites were obtained in order to study the dispersion of MWCNT derivative in epoxy matrix. The SEM pictures of facture surface were obtained to study the facture pattern of the nanocomposites.

RESULTS AND DISCUSSION

Characterization of the Liquid-Like MWCNT Derivative

The liquid-like MWCNT derivative was synthesized through three reaction steps (Figure 1). The picture (photo) of the product at room temperature is shown in Figure 2.

The groups on surface of the liquid-like MWCNT derivative were studied by FTIR spectra (Figure 3). For the FTIR spectra of the carboxylic MWCNT [Figure 3(b)], the absorption peak at 3307 cm^{-1} is for hydrogen bonding of hydroxyl (–OH). The one at 1700 cm^{-1} relates to the formation of hydrogen bonding between the carbonyl and the hydroxyl among carboxyl groups. These absorption peaks indicate that the carboxyl groups (–COOH) has been successfully grafted onto the surface of the MWCNTs. From Figure 3(c), there is an absorption peak of –Si–O– at 950 cm^{-1}, which indicates that SIT8378.3 has been grafted. Meanwhile, the absorption peak at 1107 cm^{-1} is assigned to the asymmetric stretching vibration of $–CH_2–O–CH_2–$, suggesting that Ethomeen18/25 has also been grafted onto the surface of MWCNTs. The absorption peaks at 674 and 2363 cm^{-1} represent $–SO_3^-$ and R_3NH^+, respectively. It reveals that electrostatic interaction takes place between SIT8378.3 and Ethomeen18/25.

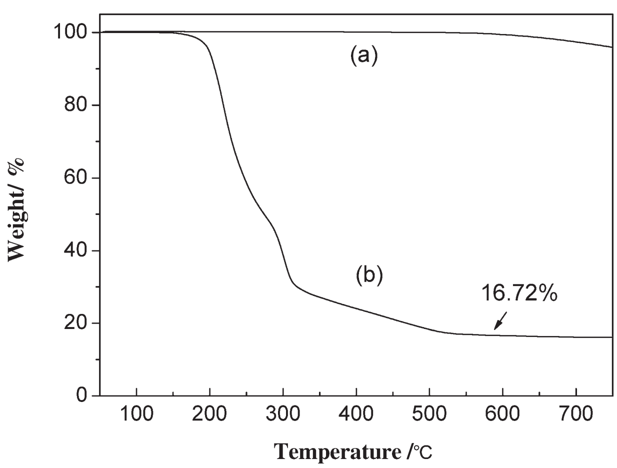

Figure 6. The TGA curves of (a) pristine MWCNTs and (b) liquid-like MWCNT derivative.

The TEM images of the pristine MWCNTs, carboxylic MWCNTs, and liquid-like MWCNT derivative were shown in Figure 4. Compared with the pristine MWCNTs [Figure 4(a)], the carboxylic MWCNTs [Figure 4(b,c)] are much shorter, suggesting that the carboxylation procedure incises MWCNTs effectively.

Figure 5 shows the solubility of the liquid-like MWCNT derivative in solvent after stewing for 3 months. The concentration of the solution is 10 mg/mL. As we know, the MWCNTs are insoluble in organic solvent, such as ethanol [Figure 5(d)]. However, the solubility property of the liquid-like MWCNT derivative is improved clearly due to its organic surfactant. The liquid-like MWCNT derivative is soluble well in the solvent of Ethomeen18/25 and SIT8378.3, such as ethanol [Figure 5(a)] and acetone [Figure 5(b)]. Unfortunately, it is still insoluble in water [Figure 5(c)], which is non-solvent for surfactants. There is a large-scale agglomeration in water after 10 min.

The TGA curve of the liquid-like MWCNT derivative [Figure 6(b)] shows there is almost no weight loss at the temperature below 150°C. It means that the sample is nearly void of any conventional solvent, such as water and acetone. The weight loss above 150°C is due to the decomposition of the surfactants on the surface of the MWCNTs. The decomposition of MWCNTs starts from 580°C [Figure 6(a)]. The content of MWCNTs in liquid-like MWCNT derivative is about 16.72 wt %.

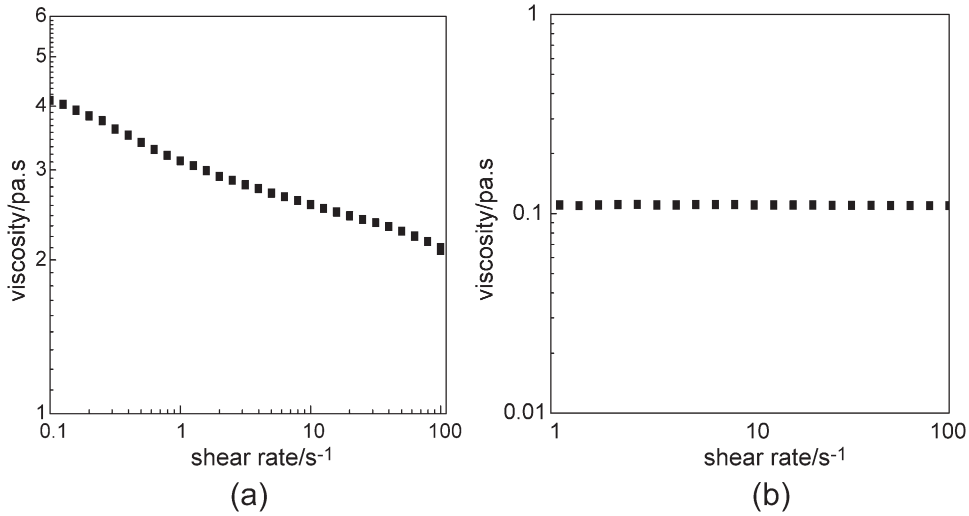

Figure 8. Viscosity versus shear rate of (a) the liquid-like MWCNT derivative at 25°C; (b) Ethomeen18/25 at 10°C.

As we know, there are many $–CH_2CH_2O–$ (EO) units in Ethomeen18/25. The DSC trace [Figure 7(b)] of the Ethomeen18/25 shows a large endotherm at 7.1°C. The fusion heat of EO crystalline units is 89.11 J/g. The DSC trace of the liquid-like MWCNT derivative [Figure 7(a)] shows a much smaller endotherm at 7.78°C, and the fusion heat of EO crystalline units is 17.81 J/g. It means that the crystallinity percentage decreases from 100% of Ethomeen18/25 to 19.98% of the liquid-like MWCNT derivative. It is highly possible that MWCNTs confined the crystal of EO unit. The same conclusion were reported by Rodriguez and Warren.[25,26]

Rheological Property of the Liquid-Like MWCNT Derivative

Steady flow test results [Figure 8(a)] shows that Ethomeen18/25 exhibits Newtonian behavior. The liquid-like MWCNT derivative, nevertheless, has shear-thinning (pseudoplastic) non-Newtonian behavior [Figure 8(b)], which is completely different from the observed Newtonian ones in EG/TiO_2[27] and propylene glycol/Al_2O_3[28] nanoparticle-based fluids. But Hojjat[29] reported that carboxymethyl cellulose (CMC)/Al_2O_3, CMC/TiO_2, and CMC/CuO nanoparticles-based fluids had shear-thinning behavior. This phenomenon appears because the liquid-like MWCNT derivative reorientates themselves in the direction of flow, which can break agglomeration of MWCNTs derivative. As a consequence, the viscosity of the system decreases with the increase of the shear rate.[30] When we fabricate nanocomposites with this liquid-like MWCNT derivative, we can simply reduce its viscosity by increasing the shear rate. In this case, it is easy for MWCNTs to get good dispersion in polymer matrix.

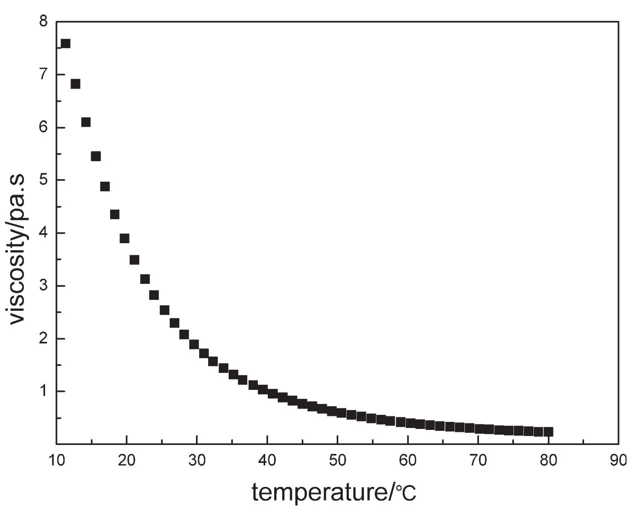

Figure 9. Viscosity of liquid-like MWCNT derivative versus temperature at 10 s^{-1}.

The viscosity of the liquid-like MWCNT derivative decreases dramatically with the increase of temperature (Figure 9). To be exactly, the viscosity decreases from 7.58 Pa s (11.3°C) to 0.23 Pa s (80°C). This feature makes it possible for future application of the liquid-like MWCNT derivative in fabricating MWCNT/polymer composite. When the temperature is 65°C, the viscosity of the liquid-like MWCNT derivative is 0.34 Pa s. It is so low that the liquid-like MWCNT derivative can disperse homogeneously in polymer matrix. As a result, the processability of the nanocomposites should be improved obviously.

Figure 10(a) shows the variation of the storage modulus G' and the loss modulus G'' with temperature. The liquid-like MWCNT derivative shares the same characteristic as liquid material since G'' is always higher than G' over the temperature range from 20°C to 80°C. As we know, G' denotes the elastic behavior of materials, which is the driving force for molecule deformation. G'' represents the consumption energy of viscous deformation for materials. Because the liquid materials have permanent deformation with flowing and exhibit viscous behavior, G'' is higher than G'. Figure 10(b) gives the relationship between the storage modulus G' and loss modulus G'' as a function of the frequency. Both of them increase with the increase of frequency. This reveals that the increase of the temperature and the decrease of the frequency have the similar effect on the movement of the molecule.

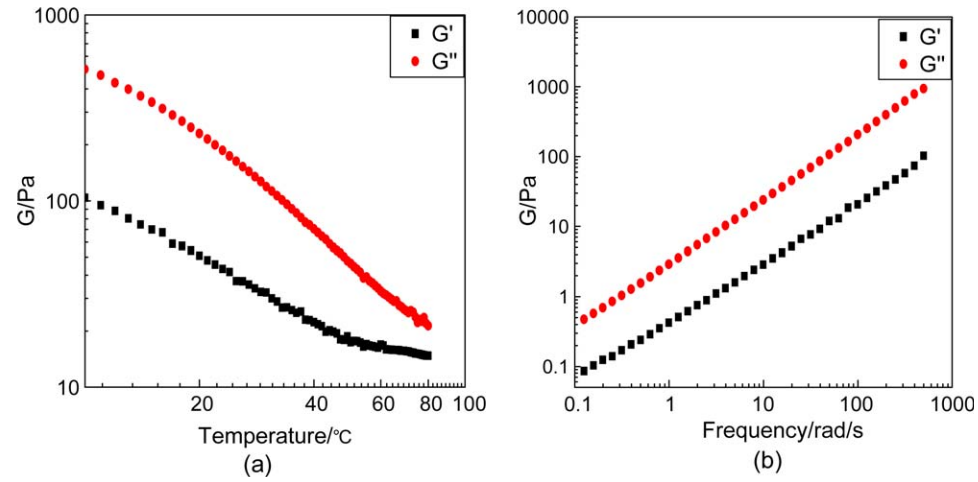

Figure 10. (a)The modulus versus temperature at 10 s^{-1}; (b) the modulus versus frequency at the temperature of 25°C of the liquid-like MWCNT derivative. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Properties of Liquid-Like MWCNT Derivative/Epoxy Nanocomposites

The mechanical property of liquid-like MWCNT derivative/epoxy and solid MWCNT/epoxy nanocomposites were investigated. Adding the solid MWCNTs and the liquid-like MWCNT derivative can improve the mechanical property of epoxy (Figure 11). For the solid MWCNT/epoxy nanocomposites with 1 wt % MWCNTs, the flexural strength is increased by 7.2%. Meanwhile, for liquid-like MWCNT derivative/epoxy nanocomposites with 1 wt % liquid-like MWCNT derivative, the flexural strength is improved 12.1%, indicating that liquid-like MWCNT derivative leads to good reforcement effect in polymer matrix.

The impact toughness of solid MWCNT/epoxy nanocomposites with 1 wt % MWCNT is increased by 51.7%. However, that of liquid-like MWCNT derivative/epoxy nanocomposites with 1 wt % liquid-like MWCNT derivative is increased by 124% (Figure 12). This drastic improvement of the impact toughness in the liquid-like MWCNT derivative/epoxy nanocomposites is also comfirmed by SEM images (Figure 13). For the ductile fracture of the pure epoxy resin, it appears smooth surface with little river lines. In the case of MWCNT/epoxy nanocomposites, it displays more river lines, indicating that more impact energy can be dissipated through these new surfaces. The liquid-like MWCNT derivative/epoxy nanocomposites sample has more and finer lines than the solid MWCNT/epoxy one. In the crack expansion process, materials absorb corresponding energy, leading to the improvement of overall energy absorption and the toughness. Much more impact energy can be dissipated through these new surfaces, resulting in that the impact strength of the liquid-like MWCNT derivative/epoxy composites is improved obviously.

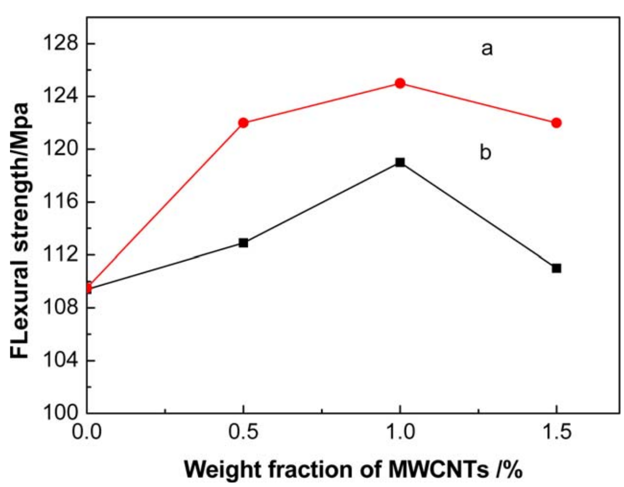

Figure 11. Flexural strength of (a) liquid-like MWCNT derivative/epoxy nanocomposites and (b) MWCNT/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

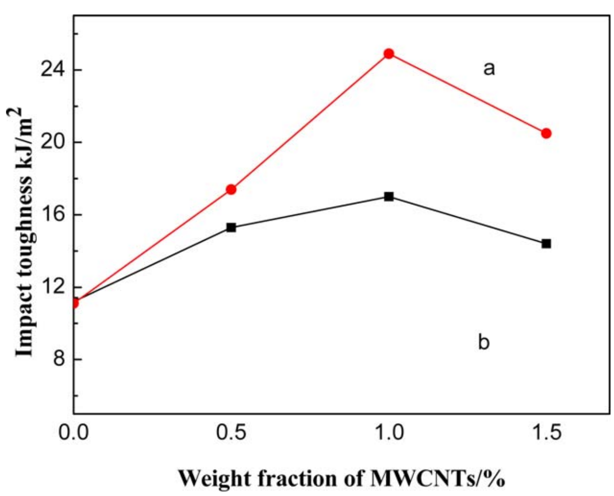

Figure 12. Impact toughness of (a) liquid-like MWCNT derivative/epoxy nanocomposites and (b) MWCNT/epoxy nanocomposites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

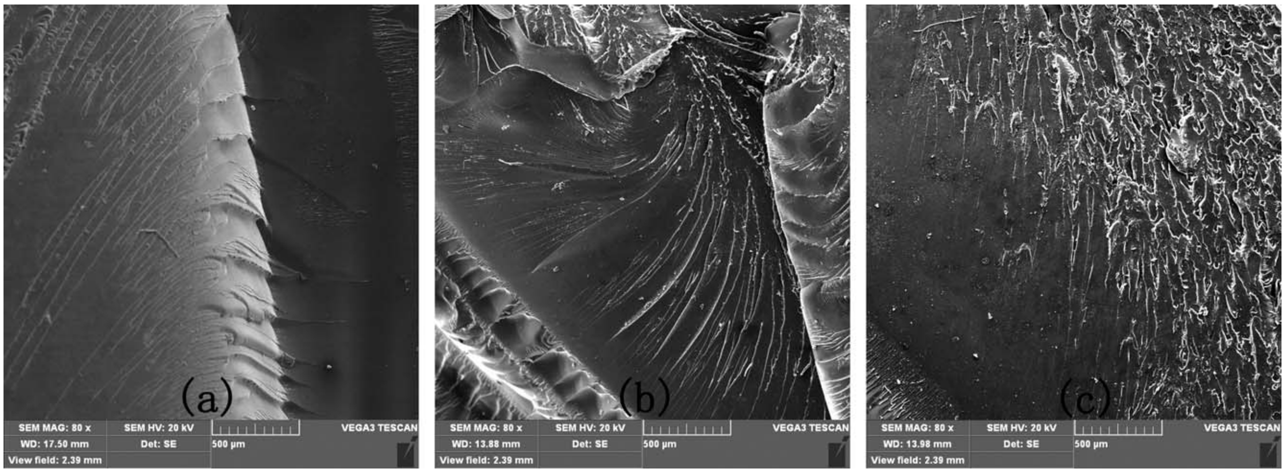

Figure 13. SEM picture of the facture surface of (a) epoxy; (b) MWCNT/epoxy nanocomposites; (c) liquid-like MWCNT derivative/epoxy nanocomposites.

This improvement is due to the organic surfactant shell, which has plasticization effect. When the liquid-like MWCNT derivative was fabricated, Ethomeen18/25 and SIT8378.3 were attached on the surface of MWCNTs. The liquid-like MWCNT derivative has an organic shell consisting of long flexible chain, which can act as plasticizer and improve compatibility of nanoparticles and matrix.[31,32] Besides, in the liquid-like MWCNT derivative, there are some Ethomeen18/25 and SIT8378.3 that were not attached on the MWCNTs. These surfactants can also acted as plasticizer and improve the toughness of the composite. The interfacial adhesion between the liquid-like MWCNT derivative and epoxy might be remarkably improved due to the organic shell, which has hydrogen bond and reacts with the epoxy.

Yang[22] and Li[23] reported that the pristine MWCNTs dispersed poorly in polymer matrix. However, the TEM images of the liquid-like MWCNT derivative/epoxy nanocomposites (Figure 14) reveal the good dispersion of MWCNTs in epoxy without agglomeration. The good dispersion of the liquid-like MWCNT derivatives in epoxy should be due to the long and flexible organic surfactant shell. The canopy of liquid-like MWCNT derivative, which was made up by Ethomeen18/25, consists of many EO units. These EO units can improve compatibility of liquid-like MWCNT derivative in epoxy matrix. Moreover, the long and flexible organic surfactant shell can bridge the MWCNTs, which makes it harder for MWCNTs to entangle.

As we know, the dispersion of nanometer-sized particles in the polymer matrix has a significant impact on the mechanical properties of nanocomposites.[33] Therefore, the good dispersion of MWCNTs in epoxy improves the impact toughness and flexural strength of liquid-like MWCNT derivative/epoxy nanocomposites.

CONCLUSIONS

The multiwall carbon nanotubes (MWCNTs) with liquid-like behavior at room temperature were prepared with sulfonic acid

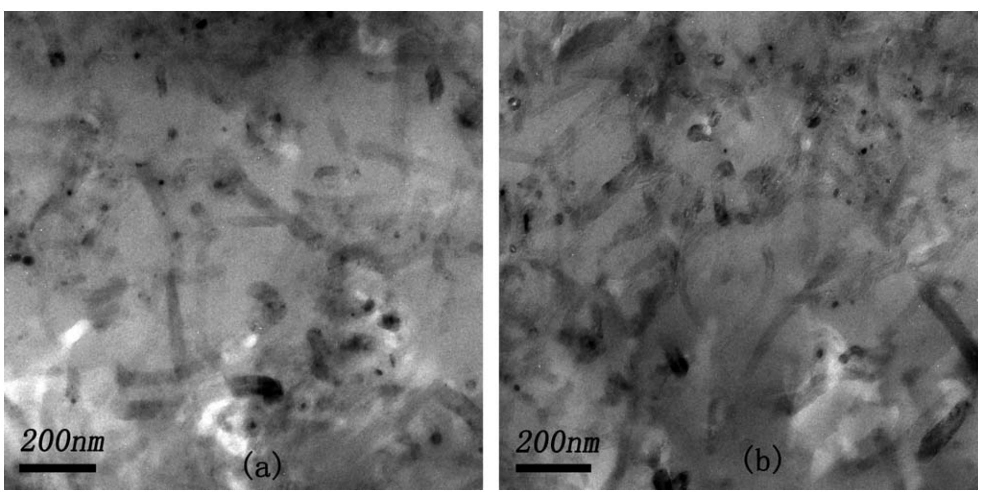

Figure 14. TEM picture of the MWCNT derivative/epoxy nanocomposites.

terminated organosilanes as corona and tertiary amine as canopy. The liquid-like MWCNT derivative has a low viscosity (3.89 Pa s at 20°C) and exhibits non-Newtonian shear-thinning behavior. The product shows liquid-like behavior at room temperature and has 16.72 wt % MWCNTs. The liquid-like MWCNT derivative improves the mechanical property of the epoxy. The flexural strength and impact toughness of nanocomposites with 1 wt % liquid-like MWCNT derivative are increased by 12.1 and 124% regard to the pure epoxy matrix, respectively. The TEM images reveal the good dispersion of the liquid-like MWCNT derivative in epoxy matrix. The solvent-free nature and good dispersion property of the liquid-like MWCNT derivative provide an effective way to fabricate high performance nanocomposites.

ACKNOWLEDGMENT

This study is supported financially by the National Natural Science Foundation of China (51073129) and the graduate starting seed fund of Northwestern Polytechnical University (Z2013164).

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