

## Research Article

# Nanocomposites with Liquid-Like Multiwalled Carbon Nanotubes Dispersed in Epoxy Resin without Solvent Process

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Liquid-like multiwall carbon nanotubes (MWNTs) were prepared with as-received carboxylic MWNTs-COOH and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-b-PPO-b-PEO) through hydrogen bonding. The sample has liquid-like behavior above 58°C. The MWNTs content is 26.6 wt%. The liquid-like MWNTs nanofluids were incorporated into epoxy matrix with solvent-free process and dispersed well. When the liquid-like MWNTs nanofluids content is up to 1 wt%, the impact toughness of the nanocomposite is 153% higher than the pure epoxy matrix.

## 1. Introduction

Due to their extraordinary electrical, thermal, optical, and mechanical properties, multiwalled carbon nanotubes (MWNTs) have been widely recognized as multifunctional components of next generation composite materials [1]. Owing to the intrinsic van der Waals forces between the tubes with high aspect ratios, MWNTs tend to form clusters and bundles. In the meantime, it is difficult for MWNTs to transfer effective load from the matrix to the MWNTs across their interface due to the weak interfacial bonding. These two reasons prevent the application of MWNTs [2].

In order to overcome these problems, it is of great significance to carry out surface modification of MWNTs. At present, a large amount of research work is centered on the modification of MWNTs to increase their solvability and compatibility with the organic solvents and polymers. Unmodified MWNTs and the majority of functionalized MWNTs are also solids and cannot undergo a solid-to-liquid transition at ambient temperatures [3–5]. Solid MWNTs can flocculate into bundles and agglomerate during mixing with the matrix and in the casting process [6, 7]. It is still difficult to directly process MWNTs on the macroscale to obtain practical composites.

The nanocomposites with liquid-like MWNTs derivatives in the absence of solvent may solve this problem. It is reported that some nanoparticles of TiO<sub>2</sub>, ZnO, DNA, C<sub>60</sub>, nanocarbon tubes, Au, Pt, Ag, and so forth can flow without solvent at ambient temperature [8–19]. It is successful to fabricate liquid-like nano-nanoparticles/polymer composites by solvent-free process. It was reported that covalent attachment of 2,2'-(ethylenedioxy)-diethylamine to multiwalled carbon nanotubes (MWNTs) produced amino-functionalized MWNTs, which behaved like liquids at ambient temperature. These liquid-like MWNTs (l-MWNTs) could be homogeneously dispersed and chemically embedded in an epoxy matrix by solvent-free processing [20]. Texter prepared solvent-free nanofluids with reactive acrylate surface groups that could be incorporated and dispersed in polymer [21]. Li fabricated MWNTs-based nanofluids with cationic organosilanes grafted to the nanoparticle cores, with PEG organic compounds as counterions. They demonstrated that the unique flowability of MWNTs fluids was highly favorable for the homogeneous distribution of MWNTs in polymer matrix [17].

Reactive components were used as canopy for nanofluids, which reactive components canopy functionalization usually improves the dispersion of the inorganic nanoparticle in

an organic polymer matrix. It also improves the mechanical transfer of stress from the matrix to the nanoparticle. However, composites reinforced by liquid-like nanoparticles, especially without reactive component canopy, have not yet been reported to the best of our knowledge.

As we know, the solubility property of the liquid-like MWNTs derivative is improved clearly due to its organic surfactant. The liquid-like MWNTs derivative is soluble well in the good solvent of organic surfactant. We used copolymer, which cannot react with epoxy, as canopy to fabricate solvent-free liquid-like MWNTs and prepared liquid-like MWNTs/epoxy nanocomposites without solvent. Their impact strength, dispersibility, and interfacial behavior were studied by scanning and transmission electron microscopy (SEM and TEM) in conjunction with tensile tests.

## 2. Experimental

Carboxylic MWNTs-COOH (diameter, 20–30 nm; purity  $\geq 95\%$ ) were provided by Shenzhen Nanotech Port Co. Ltd. (NTP), which was used without further purification. The pluronic copolymer, poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) (PEO-b-PPO-b-PEO) ( $M_n = 14600$ , PEO = 82.5 wt%) was obtained from BASF Group. Ethanol and acetone were purchased from Xi'an chemicals Co. Ltd.

200 mg of pluronic copolymer and 20 mg of MWNTs-COOH were put into a 50 mL flask with 20 mL of deionized water and sonicated for 30 min, followed centrifugation at 8000 rpm for 30 min, resulting in a homogeneously black solution. The supernatant liquid was collected, concentrated, and dried at 70°C. In order to remove excess unreacted pluronic copolymer, the residual material was carefully rinsed with water and acetone several times. Finally, the product was dried at 60°C for two days.

The liquid-like MWNTs 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 120°C for 30 min and 140°C for 90 min.

The surface groups on the MWNTs were investigated by Fourier transform-infrared (FTIR) spectrometer (WQF-310) and X-ray photoelectron spectroscopy (XPS). Thermogravimetric analysis (TGA) measurements were taken under  $N_2$  flow by using TGAQ50 TA instrument. Transmission electron microscope (TEM) images were obtained at an accelerating voltage of 100 kV with the Joel H-600 instrument. For this study, a few drops of an aqueous dispersion of MWNTs derivative were placed on a copper grid and evaporated the solvent prior to observation. Rheological properties were studied by using the Rheometer of TA instrument (AR-G2). The moduli  $G'$  and  $G''$  were measured at a constant temperature in the angle frequency range 0.1–1000 rad/s. The strain amplitude  $\gamma_0$  was 20%. All measurements were performed at small enough strains so that the deformations were in the linear-viscosity stage. The scanning electron microscopy (SEM) was examined by AMRAY 1000-B model. The specimen was coated with gold to improve SEM imaging.

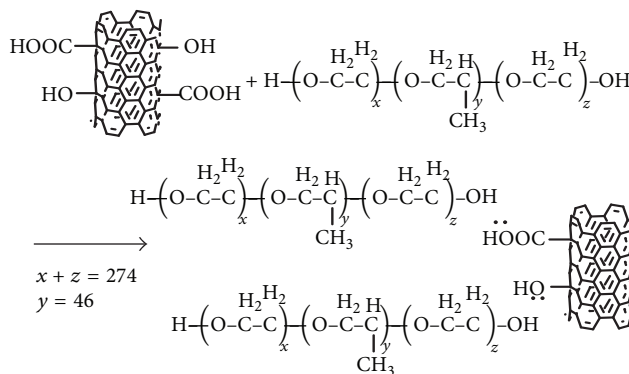


FIGURE 1: The preparation process of liquid-like MWNTs nanofluids.

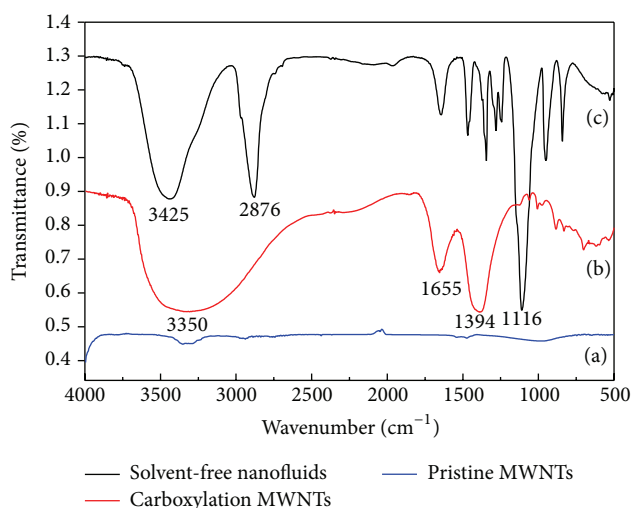


FIGURE 2: FTIR curves of MWNTs and nanofluids MWNTs.

## 3. Results and Discussion

The as-received carboxylic MWNTs have open ends and polar hydrophilic groups ( $-COOH$ ,  $C=O$ , and  $-OH$ ) on the surface. Those groups can react with pluronic copolymer through hydrogen bonding. The modification reaction was shown in Figure 1.

Figure 2 illustrates the FTIR spectra about the modification sequence of MWNTs. There are no obvious peaks in the pristine MWNTs (Figure 2(a)). For the carboxylic MWNTs-COOH, there is a wide peak at 3350  $cm^{-1}$ , attributed to  $-OH$  (Figure 2(b)). The peak at 1655  $cm^{-1}$  indicates that the  $-COO-$  has stayed on the surface of MWNTs-COOH. But after reaction of the MWNTs-COOH with the pluronic copolymer (Figure 2(c)), the FTIR spectra show the characteristic absorption peaks of PEO-b-PPO-b-PEO, such as  $-C-O$  (1109  $cm^{-1}$ ),  $-CH_3$  (1450  $cm^{-1}$ ),  $-CH_2$  (2879  $cm^{-1}$ , 2907  $cm^{-1}$ ), indicating that the pluronic copolymer has been grafted on the surface of MWNTs-COOH. Figure 3 is the XPS curves of MWNTs-COOH. The peak at 289.32 eV is attributed to  $-COO-$ . The peak at 287.90 eV indicates that the  $-C=O$

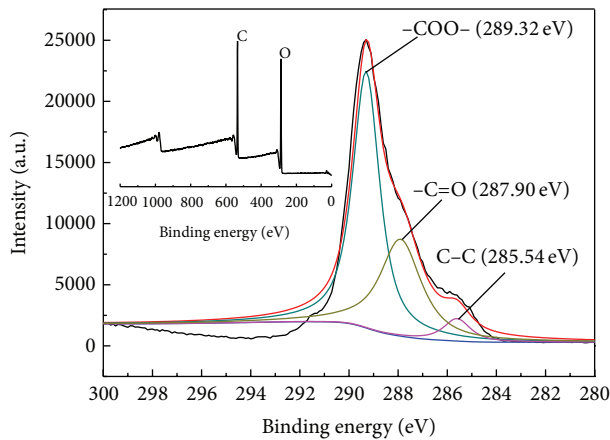


FIGURE 3: X-ray photoelectron spectroscopy of MWNTs-COOH.

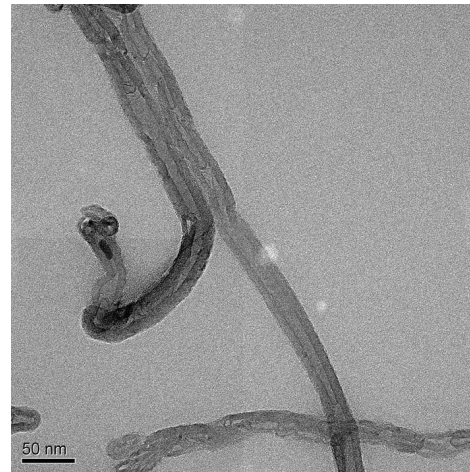
stayed on the surface of MWNTs. There is a peak at 285.54 eV, attributed to C-C.

Figure 4 is the TEM images of the liquid-like MWNTs. It indicates that the MWNTs are well-dispersed hollow tubes with no evidence of aggregation. The thermogravimetric analysis (TGA) is carried out to confirm the thermal stability (Figure 5). There is no weight loss before 180°C, indicating that the sample is virtually solvent-free. There is weight loss between 200°C and 400°C for the pure pluronic copolymer, which is due to decomposition of the organic pluronic copolymer groups (Figure 5(c)). When the pluronic copolymer is grafted on the surface of MWNTs, its decomposition temperature increased up to 300°C (Figure 5(b)). This higher thermal stability could be achieved by employing MWNTs with pluronic copolymer. Figure 5(b) shows that the weight percents of pluronic copolymer and MWNTs are 73.4 wt% and 26.6 wt%, respectively.

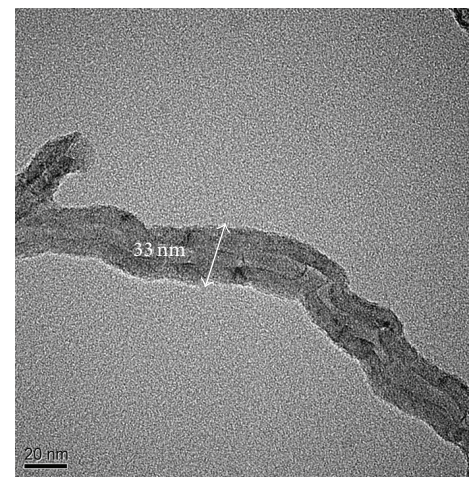
Figure 6 shows the rheology curves at 58°C. Figure 6 indicates that the storage and loss modulus have a transition at 85.53 rad/s. When the frequency is lower than 85.53 rad/s, storage modulus is bigger than loss modulus, indicating that MWNTs-based nanofluids behave in a solid-like manner. When the frequency is bigger than 85.53 rad/s, loss modulus is bigger than storage modulus, indicating that system behaves in a liquid-like manner. This transition, in which the system changes from solid to liquid, is related to the relaxation character of polymer. Because the copolymer has a small molecular weight, its relaxation time is small, indicating that its relaxation time is fast. The shear frequency is so small that it cannot match the fast relaxation time, so the system behaves in a solid-like manner. When the shear frequency increases, it can match the relaxation time; the system becomes liquid-like.

Figure 7 shows that viscosity decreases with the increasing of temperature. When the temperature is below 60°C, the viscosity decreases sharply. Because the system has a low viscosity above 60°C, it is easy for liquid-like MWNTs to disperse well in epoxy resin.

Figure 8 shows representative TEM image of the fabricated composites. 1% MWNTs nanofluids are dispersed homogeneously in the epoxy resin matrix and appear as



(a)



(b)

FIGURE 4: The TEM images of liquid-like MWNTs nanofluids.

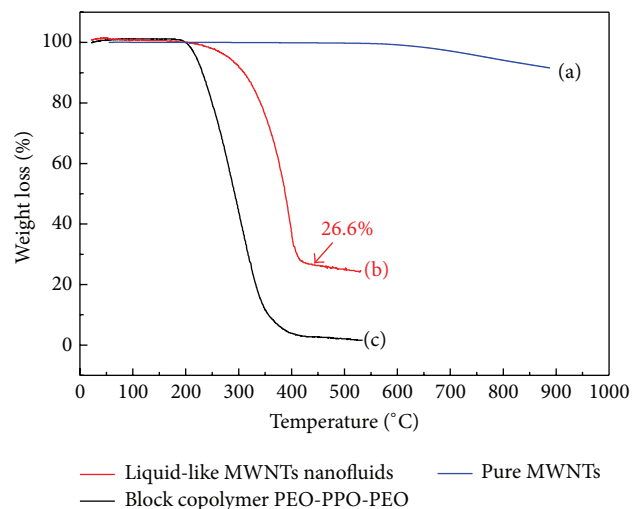


FIGURE 5: TGA curves of pure MWNTs, copolymer, and liquid-like nanofluids.

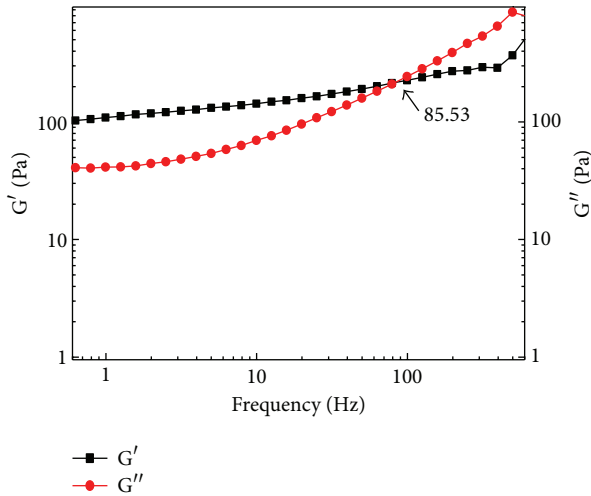


FIGURE 6: Rheology curves of liquid-like MWNTs nanofluids.

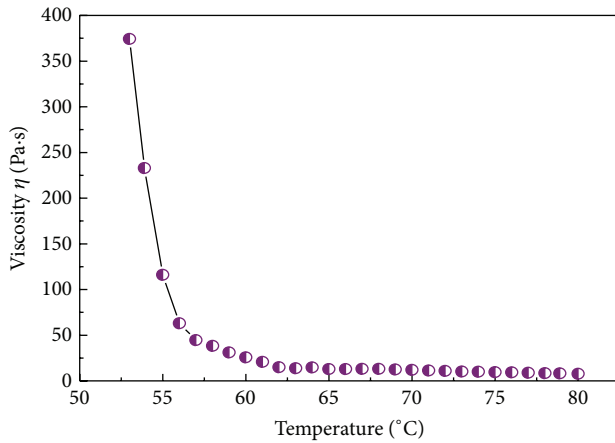
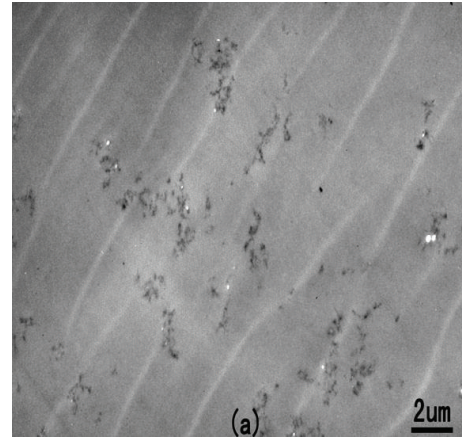


FIGURE 7: The effect of temperature on viscosity of liquid-like MWNTs.

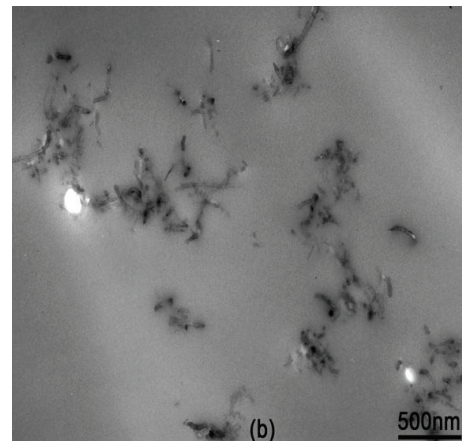
individual tubes with no evidence of aggregation (Figure 8(a)). When the content of MWNTs increased to 1.5%, it is not easy to disperse MWNTs; there are some aggregations in the epoxy resin (Figure 8(b)).

The plots in Figure 9 summarized the features of impact toughness with different weight fraction of liquid-like MWNTs/epoxy nanocomposites. The impact toughness increased with the loading of liquid-like MWNTs increasing. When the liquid-like MWNTs content is 1 wt%, MWNTs disperse well in the epoxy resin; the impact toughness is increased by 153% than pure epoxy resin. When the liquid-like MWNTs content is 1.5%, there is aggregation in the epoxy resin; the impact toughness begins to decrease, but higher than pure epoxy resin.

This improvement on addition of liquid-like MWNTs is important since this composite has a capacity to absorb a large energy at failure [17]. These results indicate that liquid-like MWNTs nanofluids have an evident improving toughness effect for polymeric matrix. When the liquid-like MWNTs content is bigger than 1%, the impact toughness decreased.



(a)



(b)

FIGURE 8: TEM of different MWNTs nanocomposites with 1% and 1.5%.

This is attributed to the high content liquid-like MWNTs aggregation in epoxy resin matrix (Figure 8(b)).

Figure 10 shows SEM images of nanocomposites and fracture surfaces of liquid-like MWNTs/epoxy nanocomposites. For the nanocomposites, there are more river-like lines and new surface formed, indicating that nanocomposite absorb a large energy at failure. It is most probably due to the fact that grafted organic molecules on the surface of MWNTs can act as “plastizer” and deform to absorb more energy at failure [20].

#### 4. Conclusions

Pluronic copolymer was grafted on the surface of MWNTs-COOH via hydrogen bonding. Pluronic copolymer formed a coating and prevented MWNTs aggregation. MWNTs content was 26.6 wt% in the liquid-like MWNTs nanofluids. The copolymer formed a cage through hydroxyl bond. Viscosity of liquid-like MWNTs decreased sharply with the temperature increasing. MWNTs nanofluids behaved in a liquid-like manner and had good dispersion in epoxy resin. Liquid-like MWNTs/epoxy nanocomposite shows the best improvements in impact toughness compared to neat epoxy,

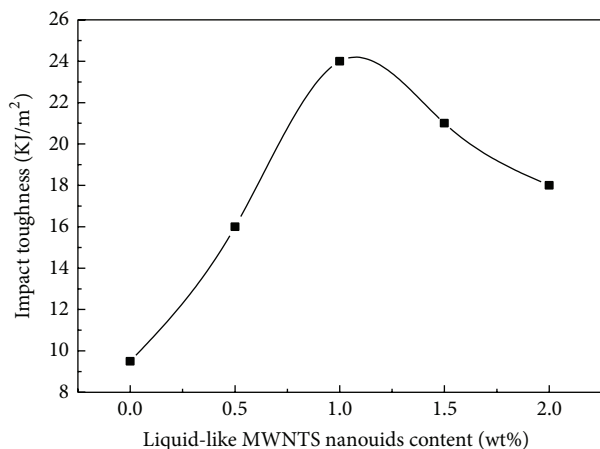
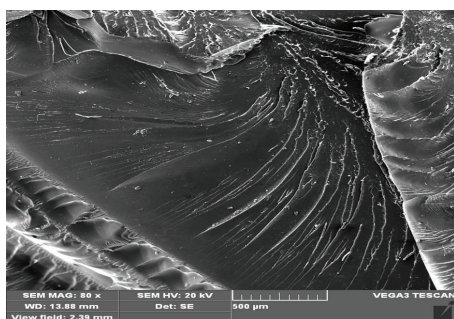
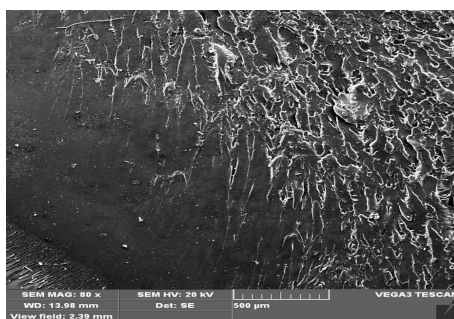


FIGURE 9: The effect of liquid-like MWNTs nanofluids content on the impact toughness of nanocomposites.



(a)



(b)

FIGURE 10: Impact fracture SEM of (a) 1% and (b) 1.5% liquid-like MWNTs/epoxy nanocomposite.

which should be ascribed to the soft organic coating, and the unique flowability of such surface functionalized MWNTs.

### Conflict of Interests

The authors declare that there is no conflict of interests in this paper.

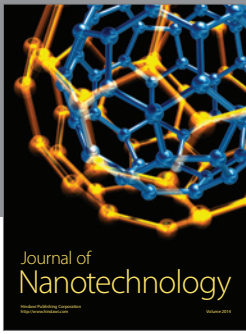
### Acknowledgment

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