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Figure 1

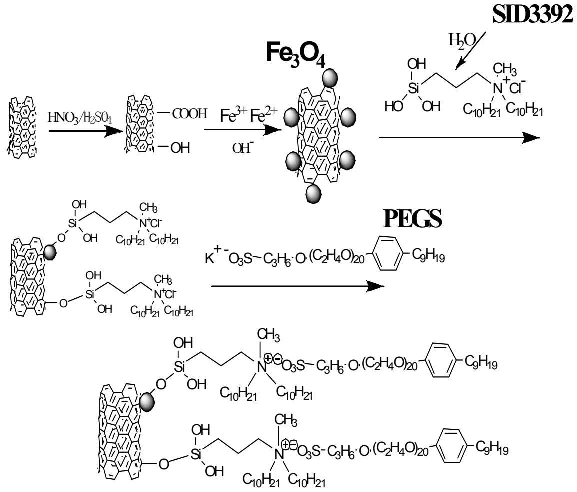

Figure.1 Reaction scheme of liquid-like MWCNT derivative

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Figure 2

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

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Figure 3

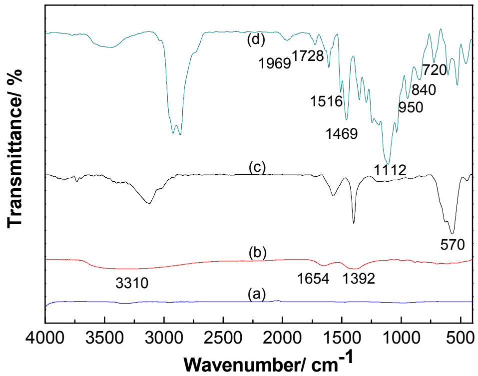

Figure.3 FTIR curves of (a) pristine MWCNT, (b) carboxylic MWCNT

(c) MWCNT/Fe_3O_4 (d) the liquid-like MWCNT derivative

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Figure 4

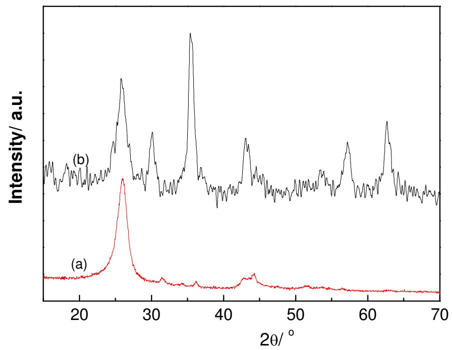

Figure.4 XRD curves of (a) pristine MWCNT (b) MWCNT/Fe_3O_4

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Figure 5

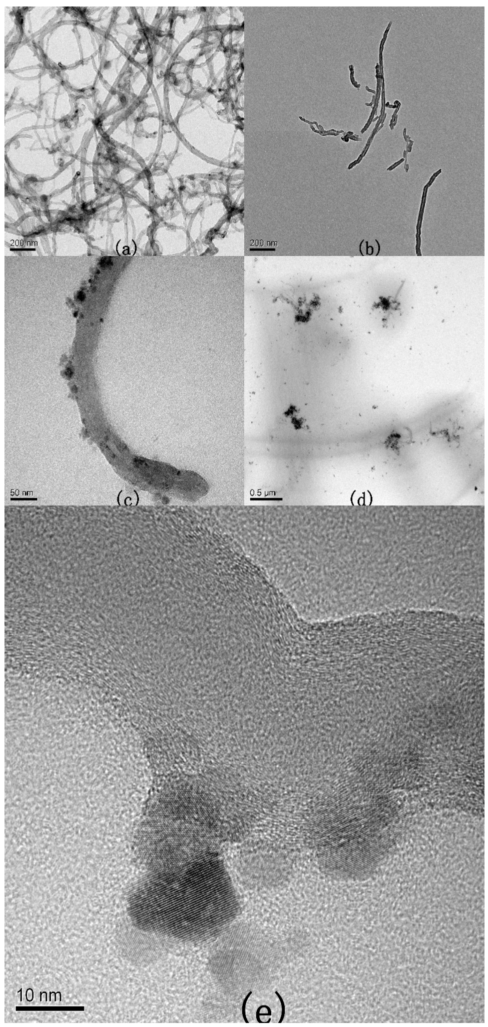

Figure. 5 TEM pictures of (a) pristine MWCNT, (b) carboxylic MWCNT, (c),(d) and (e) liquid-like MWCNT derivative

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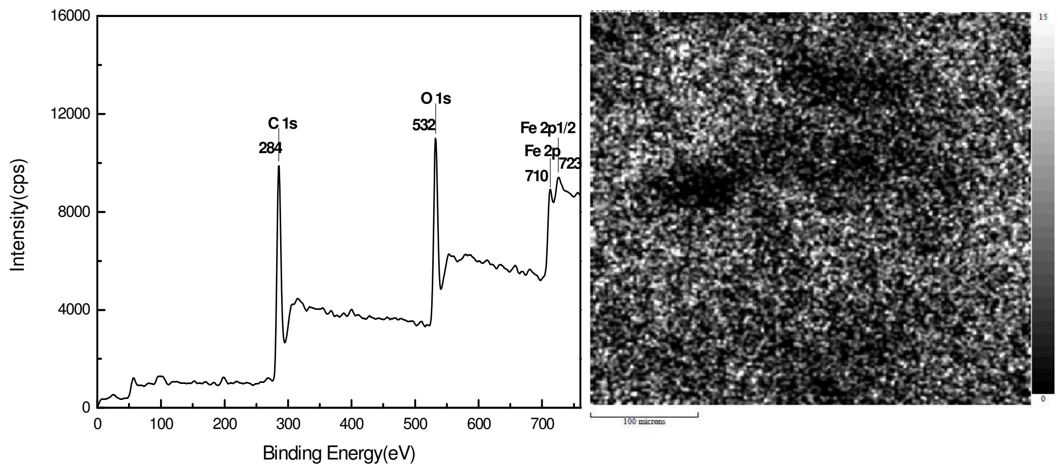
Figure.6



（a） （b）

Figure. 6 (a)XPS curve of MWCNT/Fe_3O_4 (b)XPS imaging for Fe

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Figure 7

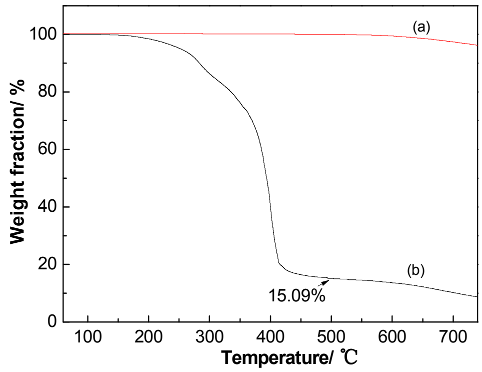

Figure.7 The TGA curves of (a) pristine MWCNT, and (b) liquid-like MWCNT derivative.

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Figure 8

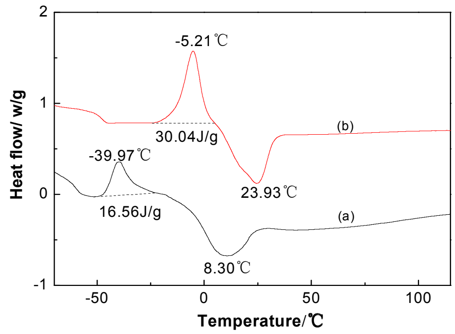

Figure.8 DSC curves of (a) the liquid-like MWCNT derivative; (b) PEGS.

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Figure 9

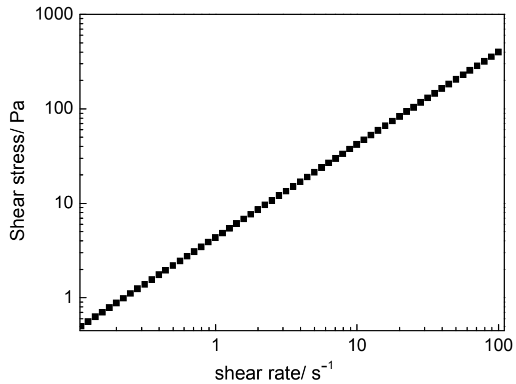

Figure.9 Shear stress vs shear rate of the liquid-like MWCNT derivative at 25°C

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Figure 10

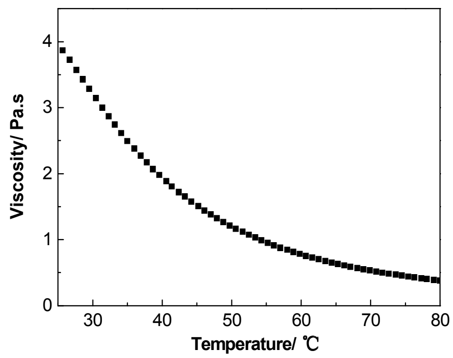

Figure.10 Viscosity of liquid-like MWCNT derivative vs temperature at $10s^{-1}$.

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Figure 11

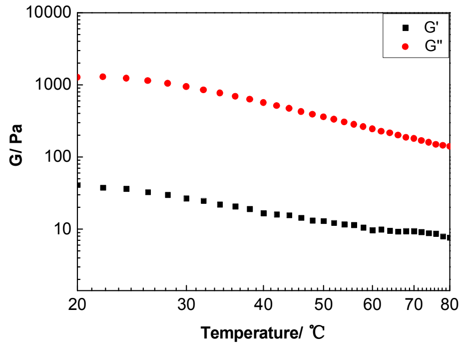

Figure.11 The modulus of the liquid-like MWCNT derivative vs temperature at $50s^{-1}$.

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Figure 12

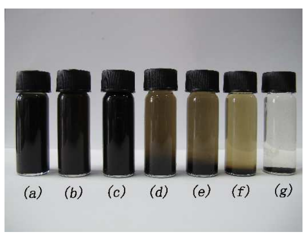

Figure.12 Solubility of liquid-like MWCNT derivative in (a)water, (b) acetone, (c) dichloroethane, (d) methanol, (e) tetrahydrofuran, (f) methylbenzene and (g) aether after 1day

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Figure 13

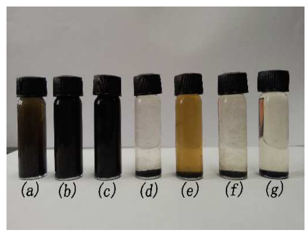

Figure.13 Solubility of liquid-like MWCNT derivative in (a)water, (b) acetone, (c) dichloroethane, (d) methanol, (e) tetrahydrofuran, (f) methylbenzene and (g) aether after 10days

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Figure 14

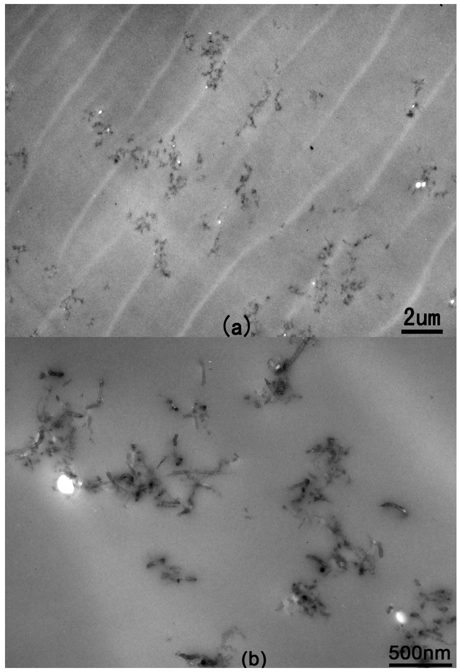

Figure.14 TEM pictures of the liquid-like MWCNT derivative/epoxy nanocomposite

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Figure 15

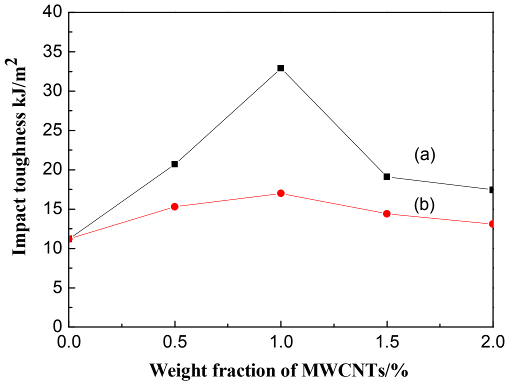

Figure.15 Impact toughness of (a) liquid-like MWCNT derivative/epoxy nanocomposites, (b) MWCNT/epoxy nanocomposites

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Figure 16

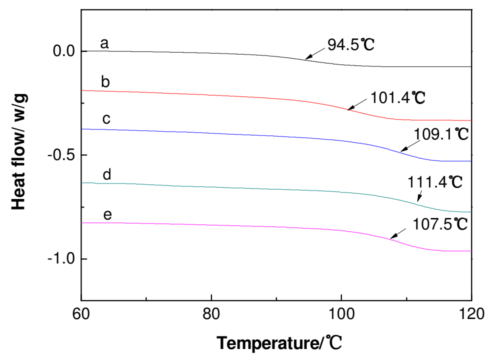

Figure.16 The DSC curves of liquid-like MWCNT derivative/epoxy nanocomposites with MWCNT derivative loading of (a) 0%. (b) 0.5%, (c) 1%, (d) 1.5%, (e) 2%.

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Figure 17

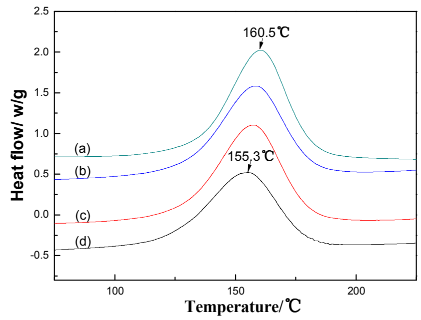

Figure.17 DSC curves of the nanocomposite curing process. MWCNT derivative loading (a) 0%. (b) 0.5%, (c) 1%, (d) 1.5%

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Figure 18

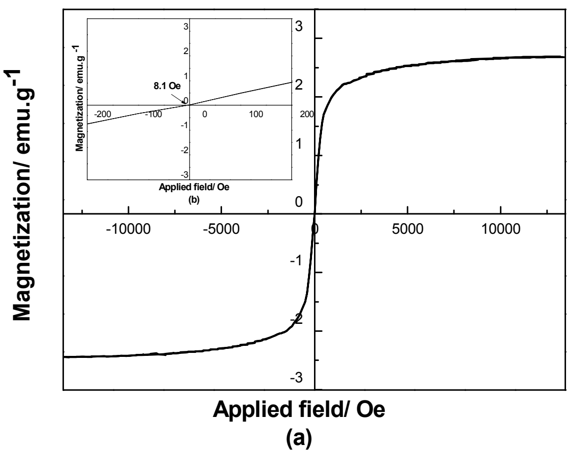

Figure.18 The hysteresis cycle of the MWCNT derivative

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Figure 19

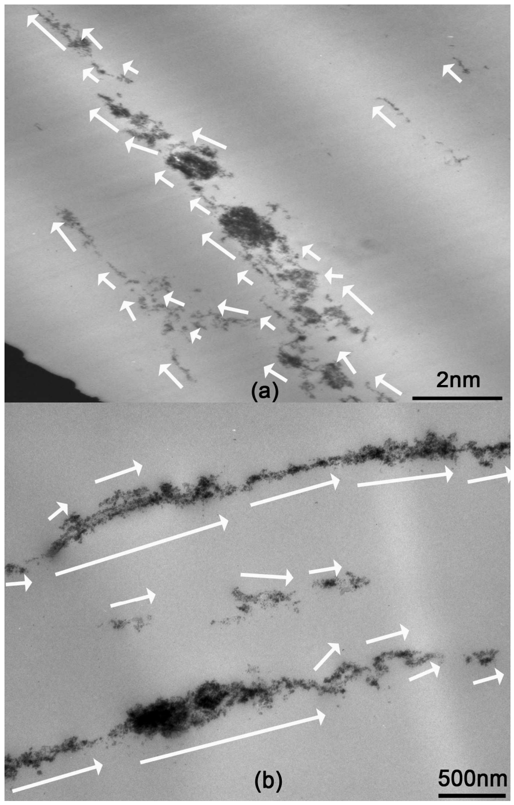

Figure.19 The alignment of the MWCNT derivative in epoxy matrix

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PAPER

Functional liquid-like multiwalled carbon nanotube derivative in the absent of solvent and it's application in nanocomposites

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Abstract: Multiwall carbon nanotube (MWCNT) derivative with liquid-like behaviour at room temperature was prepared by attach Fe_3O_4 on the surface of MWCNT and employing tertiary amine terminated organosilanes as a corona and sulfonic-acid as a canopy. The MWCNT derivative is a Newtonian fluid at low shear rate. It has relative low viscosity at room temperature(3.87pa.s at 25.7°C). It shows good solubility in organic solvents such as ethanol, acetone and dichloroethane. Transmission electron microscope (TEM) images confirmed the good dispersion of MWCNT derivative in solvent and epoxy matrix. The MWCNT derivative is a super-paramagnetism material with specific magnetization of 2.68emu/g. According to TEM picture, the derivative can be aligned in epoxy matrix under magnetic field. The MWCNT derivative can improve the impact toughness of pure epoxy by 194% and glass transition temperature (T_g) by 16.9°C. The MWCNT derivative has many novel properties and can be used in nanocomposites.

Introduction

One of the major challenges for the application of multiwall carbon nanotube (MWCNT) is to disperse MWCNTs uniformly in solvent and polymer matrix.[1-7] Therefore, a versatile way was developed to keep nanoparticles isolated and uniformly dispersed in solvent and polymer matrix.[8] By grafting short oligomer onto the surface of the MWCNT, we can get liquid-like MWCNT derivative in the absent of solvent, which can be dispersed well in solvent and polymer matrix.[9-10]

There are several works reported in the field of liquid-like MWCNT derivative. Chuanxi Xiong prepared PEG-functionalized CNTs (PEG-CNTs) with higher functional density and smaller aspect ratio[11]. They found that the novel controllable rheology liquid-like MWCNT derivative could be achieved by controlling the oxidation time of carbon nanotubes. Notably, they also prepared 500-nm-long functional carbon nanotubes, which displayed liquid-like behaviour in the solvent-free system.[12] Robert prepared a MWCNT derivative by radical-based reaction.[13] In addition, liquid-like MWCNT derivative could also be obtained through hydrogen bonds and steric effect with pluronic copolymer.[14] The material was in waxy solid state at room temperature, which melted and behaved liquid at 45 °C. There are also many liquid-like derivatives, which based on different materials like fullerenes and ZnO as a core.[15-18] Rodriguez[19] reported SiO_2 nanoparticle derivative based on 18 nm diameter silica nanoparticles as the core, sulfonic acid terminated corona and tertiary amines as the canopy. The viscosity of the fluid can be controlled by varying the volume fraction of the core, the canopy geometry and molecular weight. Michinobu[20] prepared a solvent-free room temperature liquid-like fullerenes by attaching single substituent of 1,3,5-tris(alkyloxy)benzene unit to C_{60} or C_{70} under the Prato conditions. By attaching branched low-viscosity aliphatic chains to the anthracene core, Sukumaran Santhosh Babu[21] reported nonvolatile, blue-emitting and highly stable liquid-like anthracenes at room temperature, which acceptor dyes can be doped to tune the luminescence color. However, liquid-like MWCNT/Fe_3O_4 derivative was not attempted before. In this paper, we prepared a liquid-like derivative by attaching organosilanes SID3392 and sulfonic-acid PEGS onto the surface of MWCNT//Fe_3O_4 (prepared by chemical co-precipitation).

Many scientists have explored the application of MWCNT in polymeric nanocomposite.[22-23] There are two common ways to disperse solid MWCNT uniformly in polymer matrix. The first one is to use solution processing technique. MWCNTs were dispersed in ethanol with epoxy monomer and curing agent by sonication and mechanically. After evaporation of the volatile solvent, the mixture was poured into molds and cured. [24] The second method is melt mixing. Jin[25] have blended MWCNTs and PMMA in a laboratory mixing molder at a speed of 120rpm (200°C). The mixed samples were then compressed under pressure at 210°C using a hydraulic press to yield composite films. But both techniques have shortcoming. The melt compounding processing often yields poorly dispersion of MWCNTs since the viscosity of the MWCNT and polymer mixture is very high.[26] Solution processing technique, with expensive organic solvent and complex post-treatment, induces defects and hampers the mechanical property of composites.[27]

Therefore, a new way to prepare MWCNT/polymer

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nanocomposite were developed. Li[28] used liquid-like MWCNT derivative to prepare liquid-like MWCNT/PA11 nanocomposites. The fracture elongation of the liquid-like MWCNT/PA11 nanocomposites maintained the range of 140-260%. The tensile modulus of nanocomposite had increased by about 22% when the loading of liquid-like MWCNT was 0.8wt%. Yang[29] reported that liquid-like MWCNT derivative improved the tensile property of the epoxy. When liquid-like MWCNT derivative content was 0.5wt%, the Young's modulus, tensile strength, failure strain and toughness of epoxy nanocomposites were increased by 28.4%, 22.9%, 24.1% and 66.1%, respectively. But none of these papers ever discussed heat resistance of the nanocomposites and effect of the MWCNT derivative on curing process of the epoxy.

Several works have been reported in the field of alignment of MWCNT in polymer. Camponeschi's research showed that pristine MWCNT aligned in epoxy matrix under a magnetic field of 17T, the properties of the resulting composites are superior to those that were not exposed to a magnetic field.[30] Iron oxide decorated CNT can also be aligned under mangetic field of 0.4 T.[31] According to Abdalla's research[32], pristine MWCNTs were partially aligned in epoxy under a magnetic field of 9.4 T. The modulus parallel to the alignment direction, as measured by dynamic mechanical analysis, showed significant anisotropy, with 72% increase over the neat resin, and 24% increase perpendicular to the alignment direction. Sharma[33] aligned SWCNT and MWCNT in PC matrix by applying an external magnetic field of 1200 Gauss. Magnetically aligned CNT/PC nanocomposites had better gas permeability than the random oriented CNT/PC nanocomposites. H_2 was found to be more selective than N_2 and CO_2. Although there are many works reported about alignment of solid MWCNT in polymer matrix, alignment of liquid-like MWCNT derivative was not attempted before.

In this paper, we have prepared liquid-like MWCNT derivative utilizing MWCNT/Fe_3O_4 as a core. The liquid-like MWCNT/Fe_3O_4 derivative was aligned in epoxy to prepare nanocomposites. The toughness, glass transition temperature and curing process were studied. The findings reported here can provide fundamental data about the structure control of MWCNT-based derivative, and their output properties determined by structure can also be tuned according to the property-structure relationship.

Experimental Section

1. Materials and preparation

The MWCNTs(diameter 20–30 nm, length 5-15 um) used in this study were synthesized by chemical vapor deposition (CVD) and provided by Chengdu organic chemicals Co., Ltd. $FeCl_3\cdot6H_2O$(wt%>99.0%) and $FeCl_2\cdot4H_2O$(wt%>99.7%) were obtained from Tianjing Organics. N,N-Didecyl-N-Methyl-N-(3-Trimethoxysilylpropyl)Ammonium Chloride（SID3392） was from Gelest. Inc. Poly(ethylene glycol)4-nonylphenyl 3-sulfopropyl ether and potassium salt(PEGS) were purchased from Aldrich. Methyl tetrahydrophthalic anhydride(METHPA) was from GuangZhou Weibo Chemistry Co. Ltd. 2,4,6-tri(dimethylaminomethyl) phenol (DMP-30) was bought from Aladdin Chemistry Co. Ltd. Epoxy resin (CYD-128) and curing agent 593 were from Yueyang Petrochemical Co. Ltd. Other analytical grade chemicals were H_2SO_4, HNO_3, $NH_3\cdot H_2O$, ethanol, methanol, acetone, methylbenzene, tetrahydrofuran, dichloroethane and aether.

To begin with, MWCNTs were modified with H_2SO_4/HNO_3 (volume ratio 3:1) for three hours at 70 °C. The products were washed with the deionized water in order to remove residual acid and dried at 70 °C for 24h. $FeCl_2\cdot4H_2O$ and $FeCl_3\cdot6H_2O$ with a molecule ratio of 1:1.75 were dissolved completely in de-ionized water. Subsequently, acid MWCNTs were added to the suspension, stirred, and sonicated for 2 h at 30 °C. Ammonia (5%) was dropped slowly into the solution and reacted for 30 min. MWCNT/Fe_3O_4 hybrids were deposited at the bottom of beaker under magnetic field. MWCNT/Fe_3O_4 hybrids were rinsed with de-ionized water until pH=7, dried at 60 °C, and grinded to powder.

Then MWCNT/Fe_3O_4 hybrids (0.5g) were mixed with 20mL deionized water through the ultrasound dispersion for 30mins. . Ammonia (5%) were added into the mixture until the pH was 10. After that, SID3392 methanol solution(3mL, weight fraction 40-42%) were added into the mixture dropwise. The black precipitate, which was formed immediately, was aged for 24h at room temperature by shaking it intermittently. Then, the solvents were discarded and solid was rinsed three times with water and ethanol. The solid was dispersed in tetramethylene oxide and upper layer solution was collected and dried at 50 °C.

At last, the product(1.2g) was dispersed in 100 mL deionized water and PEGS ethanol solution(15g, weight fraction 20%) was added into the solution. The reaction proceeded under mechanical stirring at 40 °C for 24h and dried at 50 °C. The product was disolved in acetone and centrifugated at 1000 rpm for 10 min. Solids on the surface of the tube were discarded. Finally, the supernatant liquid was collected, concentrated and dried at 50 °C.

Then liquid-like derivative were aligned in the epoxy matrix. The liquid-like derivative were dispersed in epoxy resin with sonication for 30 min at 60 °C. The curing agent 593 was added into the mixture and stirred slowly. The mixture were placed under vacuum at 36°C to get rid of bubbles. After that, the mixture was immediately poured into a mold, and a 3T magnetic field was applied for 24 h. The liquid-like MWCNT derivative was added into the epoxy resin at 65°C and sonicated for 30min. 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 90min, followed by 100 °C for 30min, 110 °C for 30min, 120 °C for 30min and 140 °C for 90min.

Finally, the liquid-like MWCNT derivative/epoxy nanocomposites were prepared. The impact toughness and T_g of the liquid-like MWCNT derivative/epoxy nanocomposites were tested.

2. Characterization

The surface groups on the MWCNT derivative were investigated by Fourier transform-infrared spectrometer (FTIR) (Mode: WQF-310) using KBr pellets. The product was characterized by X-ray diffraction (XRD, Rigaku, model D/max-2500 system). Transmission electron microscope (TEM) images of MWCNT, MWCNT/Fe_3O_4 and MWCNT derivative were obtained at an accelerating voltage of 100 kV with the JEM-2100 instrument after a few drops of sample/ethanol solution were

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placed on a copper grid and dried. X-ray Photoelectron Spectroscopy（XPS）curve and imaging were obtained with the Kratos Axis Ultra DLD instrument after a few MWCNT/Fe_3O_4 nanoparticles were placed on a conductive blanket. The wide scan ranged from 0eV to 760eV. Differential scanning calorimetry (DSC) traces of MWCNT derivative and nanocomposite 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 by using TGAQ50 TA instrument. Rheological properties were studied by the rheometer of TA instrument (AR-2000). The cone-plate geometry with a cone diameter of 40 mm and a cone angle of 2° was used. A steady flow test was carried out at the temperature of 25 °C. Then a temperature ramp test was carried out at 100 s^{-1}. After that, frequency sweep test was carried out at 20 °C and constant strain of 5%. Finally, the temperature sweep test was carried out at the frequency of 50 s^{-1} and constant strain of 5%. Magnetic study was performed by a vibrating sample magnetometer (VSM, Riken Denshi, BHV-525). Impact toughness of the nanocomposites with different weight fraction of MWCNT derivative was tested on the universal testing machine (CMT-5105). The test followed standard GB/T 2567-2008.

Results and Discussion

1. Characterization of liquid-like MWCNT derivative

The liquid-like MWCNT derivative was synthesized through four reaction steps (Figure.1). The product exhibits liquid-like behaviour in the absent of solvent (Figure.2).

The groups on surface of these hybrids were studied by FTIR spectra (Figure.3). For the FTIR spectra of carboxylic MWCNT (Figure.3(b)), the absorption peak at 3310 cm^{-1} is for hydrogen bonding of hydroxyl (-OH). The one at 1654 cm^{-1} relates to the formation of hydrogen bonding between the carbonyl of carboxyl and the hydroxyl of another carboxyl. The absorption peak of C-O bond is at 1392 cm^{-1}. These absorption peaks indicate that the carboxyl groups (-COOH) and hydroxyl groups (–OH) have been successfully decorated onto the surface of the MWCNT. For FTIR curve of MWCNT/Fe_3O_4 (Figure.3(c)), the absorption peak of Fe-O bond vibration at 570cm^{-1} confirmed that Fe_3O_4 has been attached onto the surface of MWCNT. As for the liquid-like MWCNT derivative (Figure. 3(d)), there are absorption peak of Si-OH at 950 cm^{-1}[34] and absorption peak of Si-C at 840 cm^{-1}[35]. These absorption peaks indicate that SID3392 has been attached onto the surface of the MWCNT/Fe_3O_4. Meanwhile, the absorption peak at 1112 cm^{-1} is assigned to the asymmetric stretching vibration of -CH_2-O-CH_2, suggesting that PEGS has also been decorated. 1728 cm^{-1} assigned to the C=O stretching vibrations of the -COOH groups, Several absorption bands in the region of 1500－1200 cm^{-1} assigned to the O-H deformations of the C-OH groups, stretching vibrations. The absorption peaks at 720 and 1969 cm^{-1} represent $SO_3^-$and R_3NH^+, respectively. [36] Because of the intensity of these polar groups are relatively strong, the Fe-O characteristic peak at 570cm^{-1} was covered up by other strong peaks in Figure.3(d).

The XRD curves of MWCNT and MWCNT/Fe_3O_4 were shown in Figure.4. According to the MWCNT standard card (41-1487) and the Fe_3O_4 standard card (19-0629), it can be indicated that for MWCNT (Figure.4(a)), the diffraction peaks at 2θ=26.04º, 43.8º are assigned to (002), (100) planes of MWCNT. These two diffraction peaks are attributed to the graphitic structure of MWCNT.[37] For MWCNT/Fe_3O_4, the (220), (331), (222), (511), (440) planes of Fe_3O_4 were observed at 2θ= 30.06º, 35.36º, 43.14º, 57.2º, 62.72º, respectively. The characteristic peaks of MWCNT still exist in Figure.4(b), indicating that the graphitic structure of MWCNT isn't destroyed after MWCNTs are coated with Fe_3O_4 nanoparticles.

The TEM images of the liquid-like MWCNT derivative were shown in Figure.5. Compared with the pristine MWCNTs (Figure.5(a)), the carboxylic MWCNTs (Figure.5(b)) are shorter, suggesting that the carboxylation procedure can incise the MWCNTs effectively. It can be observed that in the liquid-like MWCNT derivative, the Fe_3O_4 nanoparticles are attached onto the MWCNT effectively (Figure.5(c) and Figure.5(e)). The size of the Fe_3O_4 nanoparticles ranges from 8 to 12 nm.

The XPS curve of MWCNT/Fe_3O_4 was shown in Figure.6(a), there were different atoms, including the C1s photoelectron at 284eV, the O1s photoelectron at 532eV, the Fe2p photoelectron at 710eV and the Fe2p1/2 photoelectron at 723eV, respectively. The XPS imaging for Fe was shown in Figure.6(b). The small spot areas were Fe, which distributed in the hybrid system. It can be seen that the MWCNT were encrusted with Fe_3O_4 nanoparticles.

TGA curves of the liquid-like MWCNT derivative (Figure.7(b)) showed 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. Decomposition of MWCNT starts from 580°C (Figure.8(a)). The content of inorganic component (MWCNT and Fe_3O_4) in liquid-like MWCNT derivative is about 15.09 wt%.

There are many –CH_2CH_2O- (EO) units in PEGS. PEGS can crystallize at low temperature. DSC trace (Figure.8(b)) of the PEGS shows a large exotherm at -5.21°C and a endotherm at 23.93 °C, corresponding to crystallization and melting of PEGS, respectively. As for the liquid-like MWCNT derivative, the crystallizing temperature decreases to -39.97°C and the crystalization heat is 16.56 J/g. It means that crystallinity percentage decreases from 100% of PEGS to 55.1% of liquid-like MWCNT derivative. The possible reason is that MWCNTs confines the crystal of EO unit. Therefore, crystalline structure of MWCNT derivative is damaged and melting temperature of MWCNT derivative decreases. Rodriguez[38] and Warren[39] reported the similar conclusion.

2. Rheological property of liquid-like MWCNT derivative

Steady flow test result (Figure.9) showed that the MWCNT derivative exhibited Newtonian behaviour. It agreed with the work of Chen and Prasher, which reported Newtonian behaviour for EG/TiO_2[40] and propylene glycol/Al_2O_3[41] nanoparticle-based fluids.

The viscosity of the liquid-like MWCNT derivative decreased dramatically with the temperature increasing (Figure.10). To be exactly, the viscosity decreases from 3.87pa.s (25.7°C) to 0.37pa.s (80°C). This feature makes it possible for

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future application of the liquid-like MWCNT derivative in fabricating MWCNT/polymer nanocomposites. When the temperature is 60.7°C, the viscosity of the liquid-like MWCNT derivative is 0.75pa.s. The viscosity is so low that the liquid-like MWCNT derivative can disperse homogeneously in polymer matrix. As a result, the processability of the nanocompositess is improved remarkably.

Storage modulus (G') denotes the elastic behavior of materials, which is the driving force for molecule deformation. Loss modulus (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.11 showed that he liquid-like MWCNT derivative shared the same characteristic with liquid material since G'' was always higher than G' over the temperature range from 20°C to 80°C.

By grafting organic materials onto the surface of the MWCNT/Fe_3O_4, the solubility characteristic of the MWCNT derivative was changed. Figure.12 and Figure.13 shows the solubility of liquid-like MWCNT derivative in solvent after stewing for 24h and 10 days. The concentration of the solution is 10mg/mL. MWCNTs are nearly insoluble in all organic solvent. However, the liquid-like MWCNTs derivative is soluble in good solvent of PEGS, such as acetone (Figure.13(b)) and dichloroethane (Figure.13(c)). The two solutions are quite stable. No Large-scale agglomeration was observed after 10 days. The derivative is slightly soluble in water (Figure.13(a)). Large-scale agglomeration was observed after 5 days. Unfortunately, the derivative is still insoluble in aether (Figure.12(g)), even in short term. Large-scale agglomeration was observed after 10 minutes. This is probably because aether is non-solvent for surfactant we used.

4. Dispersion of liquid-like MWCNT derivative in solvent and polymer matrix

One of the crucial challenge for nanoparticle research was to improve the dispersion of nanoparticle in solvent and polymer matrix. From Figure.5 (d), the MWCNT derivative disperse homogeniously in ethanol. The weight fraction of MWCNT derivative in the MWCNT derivative/ethanol solution is 1%. Besides, TEM pictures of MWCNT derivative/epoxy nanocomposite (Figure.14) shows that the MWCNT derivative disperse homogeniously in epoxy matrix. The weight fraction of the liquid-like MWCNT derivative is 1% and the curing agent is METHPA.

It is highly possible that the better dispersion of the liquid-like MWCNT derivative in epoxy is due to the long and flexible organic surfactant shell. The canopy of liquid-like MWCNT derivative, which was made up by PEGS, consists of many EO units. These EO units can improve compatibility of liquid-like MWCNT derivative in ethanol and epoxy matrix. Besides, the long and flexible organic surfactant shell can bridge MWCNTs and makes it harder for MWCNTs to entangle.

5. Property of MWCNT derivative/epoxy nanocomposites

Since the MWCNT derivative can disperse well in the epoxy matrix, the mechanical and thermal property of MWCNT derivative/epoxy nanocomposites may improved significantly. Therefore, impact toughness and T_g of MWCNT derivative/epoxy nanocomposites were investigated. According to Figure.15, when the content of the MWCNT derivative is 1wt%, the liquid-like MWCNT derivative can improve the impact toughness of epoxy by 194% . For comparision, adding solid MWCNT can only improve the impact toughness of epoxy by 51.7%. The liquid-like MWCNT derivative has an organic shell consist of long flexible chain, which can act as plasticiser and improve compatibility of nanoparticles and matrix[42-43]. 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. Besides, the dispersion of nanometer-sized particles in the polymer matrix has a significant impact on the mechanical properties of nanocomposites[44]. Therefore, better dispersion of MWCNTs in epoxy is one of the reasons why impact toughness of epoxy resin improved.

According to Figure 16, the liquid-like MWCNT can improve the T_g of the epoxy by 16.9°C. The result is quite impressive since traditional ways to improve toughness of polymer (like adding plasticizer) can often deteriorate the thermal property of polymer.[45] But the MWCNT derivative can improve the impact toughness and T_g simultaneously. The possible reason is that nanoparticles may react with epoxy matrix and act as chemical crosslinking points. The hydroxyl and carboxyl groups on the surface of MWCNT and Fe_3O_4 nanoparticles can react with epoxy matrix. Therefore, chemical crosslinking was formed and crosslink density was increased. As a result, the T_g of epoxy was improved.[46]

Figure.17 shows the DSC curve of curing process of nanocomposite. The curing temperature of the liquid-like MWCNT derivative/epoxy nanocomposite decreases slowly as the liquid-like MWCNT derivative loading increases. This is because there are a lot of hydroxyl groups in the derivative. Hydroxyl group can accelerate curing process of epoxy. In this way, the liquid-like MWCNT derivative can act as accelerant and decrease the curing temperature of the nanocomposite.

6. Magnetic property of liquid-like MWCNT derivative

According to Figure.18, the MWCNT derivative is a typical super-paramagnetism material. The specific magnetization of the MWCNT derivative is 2.68 $emu.g^{-1}$. It means that the MWCNT derivative can act as a special ferrofluid with PEGS as a carrier. The surfactant SID3392 is attached onto the surface of the MWCNT derivative through covalent bond. There are electrostatic interaction between PEGS(Carrier) and SID3392 （surfactant）. The MWCNT derivative is quite stable, no large scale agglomeration is observed after stewing for 3 month.

7. Alignment of liquid-like MWCNT derivative in solvent and polymer matrix

Since the MWCNT derivative is a magnetic material, it may be aligned in a bulk composite under a magnetic field. Figure.19 shows alignment of MWCNT derivative in epoxy matrix. In this picture, each MWCNT derivative is marked by a white arrow. The shape, diameter and length of each MWCNT derivatives are

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different. But all MWCNT derivative aligned in a similar direction and some MWCNT derivative connected end-to-end. The matrix is epoxy and curing agent is 593. In the MWCNT derivative, MWCNT formed a magnetic rod since Fe_3O_4 nanoparticles were attached onto the surface of MWCNT. Therefore, the MWCNT derivative can be easily aligned to the magnetic field direction. Due to their magnetic susceptibility, the north and south poles of the MWCNT derivative stack near linear, which result the end-to-end connectivity.

Conclusions

MWCNT derivative with liquid-like behaviour at room temperature were prepared by employing MWCNT/Fe_3O_4 as a core, tertiary amine terminated organosilanes as a corona and sulfonic-acid as a canopy. The derivative was soluble in organic solvent and dispersed homogeniously in solvent and polymer matrix. Besides, the derivative can improve impact toughness and heat resistance of epoxy simutaneously. What's more, the MWCNT derivative can aligned in epoxy matrix under magnetic field. These advantages make it possible for us to develop a green and efficient route to fabricate high performance nanocomposite by using liquid-like nanoparticle derivative. The super-paramagnetism nature of the MWCNT derivative may provide us a new way to manufacturing ferrofluid. Our future study will focus on application of liquid-like nanoparticle derivative in other promising field like nanocatalysis and exploring the fluidity mechanism of the liquid-like nanoparticle derivative.

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The liquid-like MWCNT//Fe_3O_4 derivative can be aligned in epoxy matrix and improved the properties of epoxy resin.

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