Polymer 50 (2009) 2953–2957

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

The synthesis of functionalized carbon nanotubes by hyperbranched poly-(amine-ester) with liquid-like behavior at room temperature

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ARTICLE INFO

Article history:
Received 5 December 2008
Received in revised form
6 April 2009
Accepted 22 April 2009
Available online 3 May 2009

Keywords:
Carbon nanotubes
Liquid-like behavior
Solvent-free nanofluids

ABSTRACT

The solvent-free multi-walled carbon nanotubes (MWNTs) nanofluids are obtained through acid–base reaction and hydrogen bond roles with hyperbranched poly(amine-ester) (HPAE). MWNTs content is 16.8 wt%. The functionalized MWNTs exhibit liquid-like behavior in absence of solvent at room temperature. Correspondingly, the dense surface coverage is one modifying molecule per 30 carbon atoms on the surface of MWNTs. The functionalized MWNTs are soluble in good solvent of HPAE, but insoluble in non-solvent of HPAE. Their dispersibility, high thermal stability and ability to flow at room temperature make them attractive as lubricants, plasticizers and film-forming precursors.

1. Introduction

Carbon nanotubes (CNTs) have a unique combination of the outstanding chemical, mechanical, electrical properties and so on [1,2], which have been the focus of scientific research. Much progress has been made in a variety of fields for application since the discovery of carbon nanotubes in 1991 [3], such as high-performance composites, biological and chemical sensors, magnetic recording, nanoelectronic devices, tips for scanning probe microscopy and flat panel displays [4–7]. However, it is known that the CNTs are not compatible with all solvents because of their chemical inertness. Besides, it is also difficult to obtain a homogenous dispersion in composite matrix [8]. In recent years, a large amount of research work is focused on the surface functionalization of CNTs in order to increase their solubility and dispersion in the organic solvents and composite matrix. In general, those conventional functionalized methods make nanoparticles behave solid-like behavior in absence of solvent and do not undergo a microscopic solid-to-liquid transition at temperature below 150 °C.

Recently, it had been reported that functionalized nanoparticles exhibited liquid-like behavior in absence of solvent. The solvent-free nanoparticle fluids, which called solvent-free nanofluids, were synthesized by attaching a corona of flexible chains onto an inorganic oxide core such as SiO_2, γ-Fe_2O_3, TiO_2, or ZnO. The nanofluids alway contained at least 15 wt% inorganic content [9,10]. Since the thermal conductivity of nanoparticles is higher than that of liquids, the nanoparticles exhibiting liquid-like behavior possessed higher thermal conductivity [11]. Because of their small size, they can act as a lubricant in contact with a solid surface and thus minimize fabrication [12]. In addition, those are proposed as alternative coolants for several thermal-management applications, such as transportation, microelectro mechanical systems (MEMS) and refrigeration systems [13].

The functionalized multi-walled carbon nanotubes (MWNTs) with liquid-like behavior were synthesized by attaching a canopy of an epoxy-terminated silicone chains onto the nanotubes [14]. The waxy solid contained 85 wt% MWNTs and exhibited fluid behavior at ambient conditions. When MWNTs were modified with polyethylene glycol (PEG) chains, they could melt reversibly at 35 °C and yielded a homogeneous viscous fluid [15]. Similarly, Michinobu et al. also prepared alkyl-derivatized fullerenes that could flow at room temperature [16].

CNTs were also grafted with some kinds of hyperbranched polymer including hyperbranched poly(ether-ketone) [17], hyperbranched polyester [18,19], fluorinated dendrimer-type block copolymers [20] and so on. But those functionalized CNTs exhibited solid-like behavior in absence of solvent or a suspending medium and did not undergo any macroscopic solid-to-liquid transition. In this case, solvent-free MWNTs nanofluids were prepared via hyperbranched poly(amine-ester) and exhibited liquid-like

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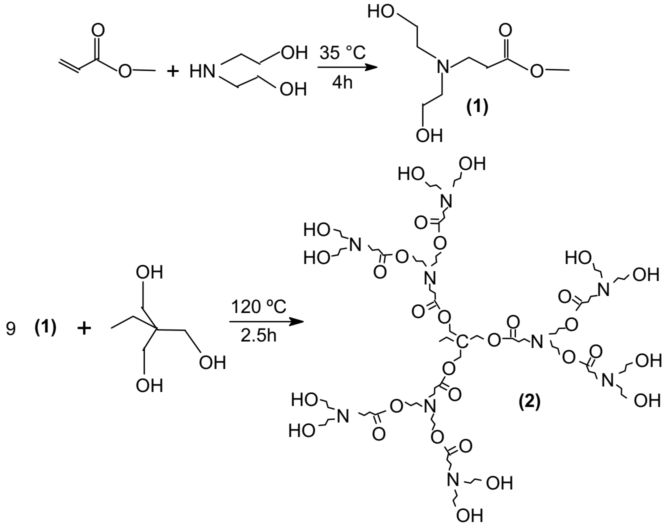
doi:10.1016/j.polymer.2009.04.042



Scheme 1. The synthetic route of HPAE.

behavior at room temperature. The amount of MWNTs was 16.8 wt%.

2. Experimental section

2.1. Material

The MWNTs were synthesized by chemical vapor deposition (CVD) and was obtained from Timesnano, Inc., Chengdu. The average diameter of the nanotubes was 20–30 nm with several micrometers in length. And the pure MWNTs content was more than 95 wt%. Analytical grade organic solvents were used: trimethanol propane, diethanolamine, p-toluene sulfonic acid, methy acrylate, methanol, acetone, HNO_3 (67%), H_2SO_4 (98%), which were purchased from Xi′an Chemistry Reagent Company.

2.2. The synthesis of hyperbranched poly(amine-ester)

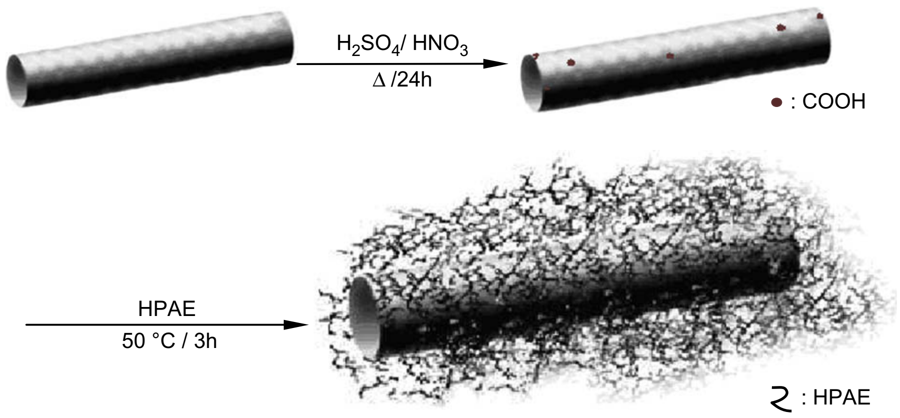
Hyperbranched poly(amine-ester) (HPAE) had trimethylolpropane as a core and N,N-diethylol-3-amine methylpropionate as the AB_2 branched monomer. It was synthesized by a pseudo-one-step process. The N,N-diethylol-3-amine methylpropionate (**1**) synthesized via Michael addition of methyl acrylate and diethanolamine in methanol solvent, followed by removing solvent through vacuum distillation, obtained faint yellow oily liquid (**1**). In another reaction, 0.1 mol trimethylolpropane, 0.3 mol (**1**) and 0.5 wt% catalyst of p-toluene sulfonic acid were stirred at 120 °C for 2.5 h. The residual un-reacted monomers were removed by vacuum distillation. HPAE was yellow oily liquid and yield was 94%. FTIR analysis: 1750 cm^{-1} (ester C=O), 1050 cm^{-1} (C–N stretch), strong band at 3390 cm^{-1} (–OH), 2860–2950 cm^{-1} (C–H sat.); elemental analysis: C (51.28%), N (7.94%), and H (7.31%), theoretical value: C (52.11%), N (8.37%), and H (8.05%) (the values were calculated according to molecule of HPAE). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.1 ($C\mathbf{H}_3CH_2$–), 4.4 (–$OCOC\mathbf{H}_2CH_2$–), 4.1–4.3 ($R'R_2CC\mathbf{H}_2$–OCO–), 3.6–3.8 (–$OCOCH_2C\mathbf{H}_2NR''_2$), 3.4–3.6 (–$N(CH_2C\mathbf{H}_2OH)_2$), 3.3 (–$N(C\mathbf{H}_2CH_2OH)_2$), 2.4–3.1 (m, $CH_3C\mathbf{H}_2CR_3$), 4.8 (–$CH_2CH_2O\mathbf{H}$). The products required no further purification before ligated onto the MWNTs surface. The synthesis route was shown in Scheme 1.

2.3. The acidification process of MWNTs

The MWNTs 1.0 g was first treated with refluxing of the 3:1 mixture of concentrated sulfuric and nitric acid (200 mL) for 24 h. This mixture was then sonicated for 2 h at ambient temperature in an ultrasonic bath to introduce carboxylic acid groups on the MWNTs surface. Upon completion, the mixture was diluted five times by distilled water and then filtered through a 0.22 μm pore size polycarbonate filter paper; the filter residue was then washed with distilled water until no residual acid was present (pH > 5). The sample was then dried in a vacuum oven at 80 °C for 4 h. The sample was marked as $MWNT_{COOH}$.

2.4. The synthesis of solvent-free MWNTs nanofluids

Surface functionalization $MWNT_{COOH}$ with the HPAE was carried out. After HPAE (5 g) mixed with distilled water (50 g) in a beaker, $MWNT_{COOH}$ (0.5 g) was put into the beaker. Mixtures were dispersed with the high-speed dispersion homogeneous machine for 15 min. Then the suspension were poured into a 3-necked flask and reacted for 3 h at 50 ± 5 °C. The products were rinsed with deionized water, followed by centrifugation at 8000 rpm for 30 min, resulting in a homogeneously black solution and the supernatant liquid was collected, concentrated, and dried at 70 °C. In order to remove excess un-reacted HPAE, material was carefully rinsed with deionized water and acetone several times. Finally, the product was dried at 60 °C for two days. The product was marked as $MWNT_{HPAE}$. The synthesis route was shown in Scheme 2.



Scheme 2. Synthetic route of solvent-free MWNTs nanofluids.

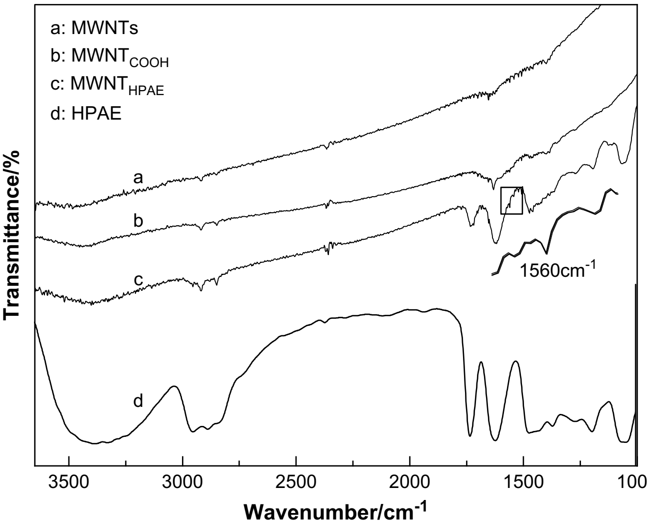


Fig. 1. FTIR spectra of a) MWNTs, b) $MWNT_{COOH}$, c) $MWNT_{HPAE}$ and d) HPAE.

2.5. Measurements

The surface groups on the MWNTs were investigated by Fourier transform-infrared (FTIR) spectrometer (WQF-310) with KBr pellet method. Differential scanning calorimetry (DSC) traces were collected using a Q1000 TA instrument at a heating rate of 10 °C min^{-1}. Thermogravimeric analysis (TGA) measurements were taken under N_2 with 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 modulus G' and G'' were measured at a constant temperature in the angle frequency range 0.1–1000 rad s^{-1}. The strain amplitude γ_0 was 20%. All measurements were performed at small enough strains so that the deformations were in the linear-viscoelastic stage.

3. Results and discussion

The modification, showed in Scheme 2, was based on a two-step process. The end of carboxylic MWNTs was opened and created polar hydrophilic groups (–COOH, C=O, –OH) on the surface. These groups enhanced the activity of the MWNTs and were necessary to further reaction. Then ternary amine of HPAE was protonated with the carboxylic groups via an acid–base reaction, which leaded to form the ionic attachment on the surface of MWNTs [15,21]. The HPAE could also be introduced onto the surface of MWNTs via hydrogen bonding between the –OH, C=O groups and the ternary amine groups. At last, the interaction between MWNTs and HPAE induced to form homogeneous hybrid systems.

Fig. 1 showed the FTIR results of the MWNTs obtained at different processing steps. For the MWNTs (Fig. 1a), the weaker peak at 3375 cm^{-1} was attributed to the presence of hydroxyl groups (–OH) on the surface of the MWNTs, which were resulted from either ambient atmospheric moisture bound to the MWNTs or oxidation during purification of the raw material [22]. Compared to the MWNTs, $MWNT_{COOH}$ exhibited quite different spectra. The stretching vibration of the –COOH groups was observed at 1581 cm^{-1}, and the band at 3375 cm^{-1} was attributed to the –OH stretching vibrations (Fig. 1b). All these observations confirmed that the surface of the MWNTs had been functionalized or activated by the strong acid. In this process, free oxygen atoms released by strong acids reacted with unstable carbon atoms of the surface MWNTs, this reaction introduced –COOH and –OH groups. Those groups are necessary to further reaction because of their activity.

In the FTIR results of the $MWNT_{HPAE}$ (Fig. 1c), the band at 3375 cm^{-1} became broader and stronger due to the HPAE containing large amount of –OH. The new bands at 2918 cm^{-1} and 2849 cm^{-1} associated with the stretching of the methylene groups from the HPAE molecules appeared. The new additional peak at 1560 cm^{-1} was attributed to the ionic bond, which indicated that HPAE was grafted on the $MWNT_{HPAE}$ surface by the formation of carboxylate groups after protonation of the tertiary amine. In our previous experiment, the original MWNTs that were not active by strong acid directly treated with HPAE, which was solid and did not undergo a microscopic solid-to-liquid transition at temperature below 150 °C. There were also similar FTIR traces between MWNTs and treated directly MWNTs by HPAE (see Supplementary data). These indicated that HPAE was grafted covalently onto the surface of $MWNT_{COOH}$, which made functionalized MWNTs exhibit liquid behavior and good dispersion.

Fig. 2 showed the typical TEM images of the MWNTs. TEM images of the MWNTs revealed the presence of hollow tubes with 25 nm in mean diameter. From the TEM image of $MWNT_{HPAE}$, we could find that the wall became rough and the mean diameter was

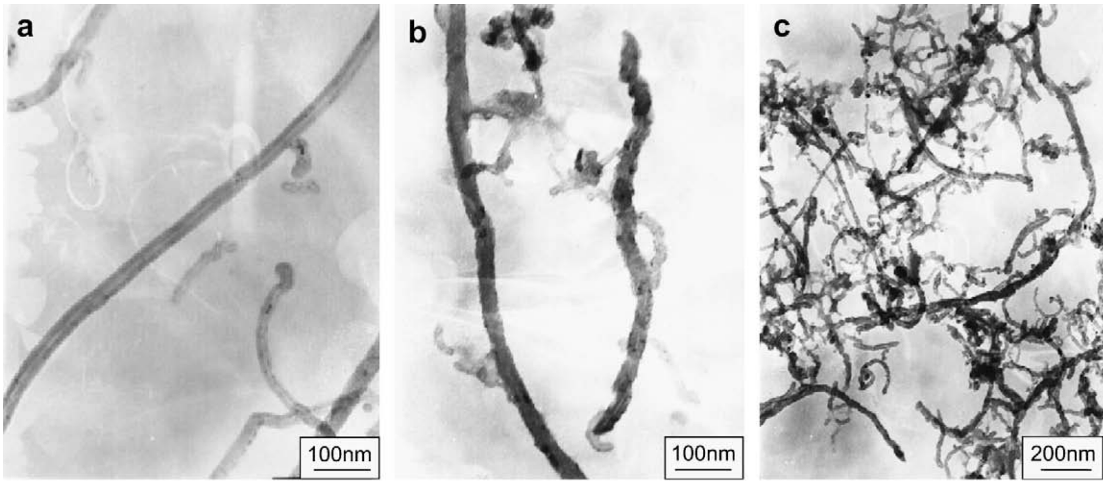


Fig. 2. TEM images of a) MWNTs, b) and c) $MWNT_{HPAE}$ with different enlarged ratio.

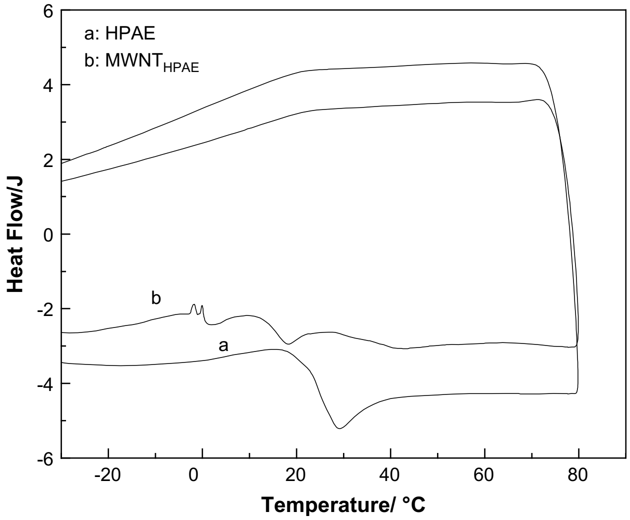


Fig. 3. DSC curves of a) HPAE and b) MWNT$_{HPAE}$.

30 nm. Those values indicated that MWNTs core was effectively functionalized with a soft organic shell through the acid reaction and hydrogen bonding role, HPAE provided enough "solvent" for the dispersion of MWNTs. The modified system formed single component colloids that were distinguished from conventional colloidal suspension, which was a two-component system.

The DSC samples were subjected to a cycles of heating from −20 °C to 80 °C and then cooling to −20 °C with ramping rate of 10 °C min^{-1} (Fig. 3). In the heating scans of samples, there was glass temperature (T_g) at 24.3 °C for the HPAE. But the T_g decreased to 14.5 °C and it appeared new peak at about 0 °C for MWNT$_{HPAE}$. For the pseudo-one-step AB$_x$ polymerization as conversion tended towards 100%, the molecular weight distribution tended towards width and infinity [23,24], So in our experiment, we obtained the hyperbranched poly(amine-ester) blend. For HPAE, there was one peak of T_g at 24.3 °C. For MWNT$_{HPAE}$ DSC curve, there were two peaks of T_g at 14.5 °C and 0 °C. The HPAE was composed with different molecular weight, but similar molecular. In the DSC curve, the peaks of different molecular T_g were overlapped for HPAE. When MWNTs were modified with HPAE, MWNTs could affect the T_g of HPAE and make it move to the lower temperature. We consider that the MWNTs act as nucleating agents and induce molecular motion of HPAE at lower temperature. The T_g gap of different molecular weight became broad. So there were two different peaks at DSC curve of MWNTs derivative. In the cooling scans of samples, they exhibited the similar behavior.

The weight content of HPAE influences the properties of MWNT$_{HPAE}$ nanofluids. So the thermogravimeric analysis (TGA) was carried out to confirm the thermal stability (Fig. 4). It could be seen that the weight loss of pristine MWNTs at 650 °C was negligible. The decomposition temperature of MWNT$_{HPAE}$ nanofluids was more than 200 °C, which was similar to the HPAE. The MWNTs content was about 16.8 wt% and HPAE content was 83.2 wt%. It indicated that the MWNTs derivative was almost solvent-free. There was a little decomposition (<5%) temperature less than 200 °C, which arose from residual water molecule. Due to the low content, this didn't influence the phase state of sample. Correspondingly, the dense surface coverage was calculated according to the following formula.

$$n = \frac{W_C}{m_C} \Big/ \frac{W_{polymer}}{m_{polymer}} \tag{1}$$

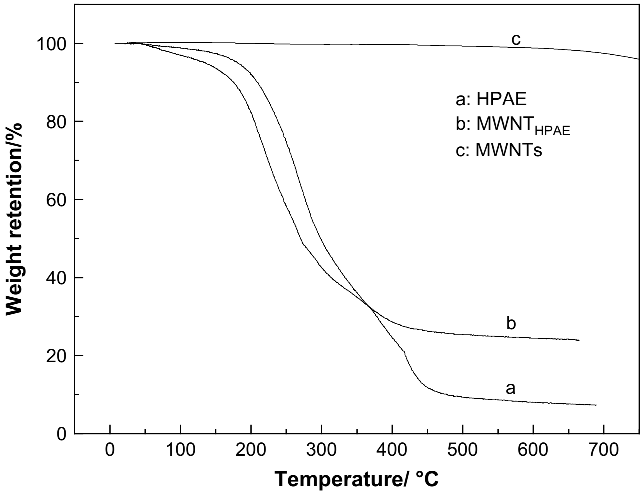


Fig. 4. TGA traces of the MWNTs derivative under nitrogen atmosphere.

Where n is the number of carbon atom per organic molecule. W_C and $W_{polymer}$ are weight of the carbon and organic polymer in sample, respectively. m_C and $m_{polymer}$ are the molecular weight of carbon and the second generation HPAE of organic polymer in sample. The dense surface coverage is one HPAE molecule per 30 carbon atoms of the MWNTs. Georgakilas et al. [25] reported that other modified method leaded to a dense surface coverage of one modifying molecule per 100–200 carbon atoms. However, Dyke and Tour [26] developed another modification method, which exhibited a denser surface coverage of one modifying molecule per 10 carbon atoms.

Usually, a dynamic spectrum can be used to understand the structures and properties of material. It is well known that storage modulus G' and loss modulus G'' of Rheometrics Mechanical Spectcometry exhibit the relationship between the molecular motion and rheological behavior of the material [27]. The corresponding rheological behavior of sample was carried out at 25 °C (Fig. 5). It showed that dynamical storage modulus G' and loss modulus G'' increased with the angular frequency increasing. G' embodies the elastic behavior of materials, which is the drive force of molecule deformation. And G'' is consumption energy of viscous deformation for materials [28,29]. For the MWNT$_{HPAE}$ nanofluids, the G'' was much higher than the G'. Liquid material has permanent deformation with flowing and exhibits viscous behavior, G'' of liquid material is higher than the G' [30]. In addition, the curves of

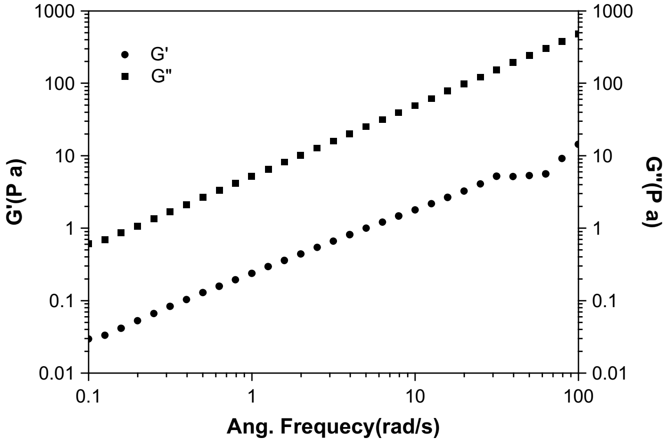


Fig. 5. Rheological behavior of the solvent-free MWNTs nanofluids at 25 °C.

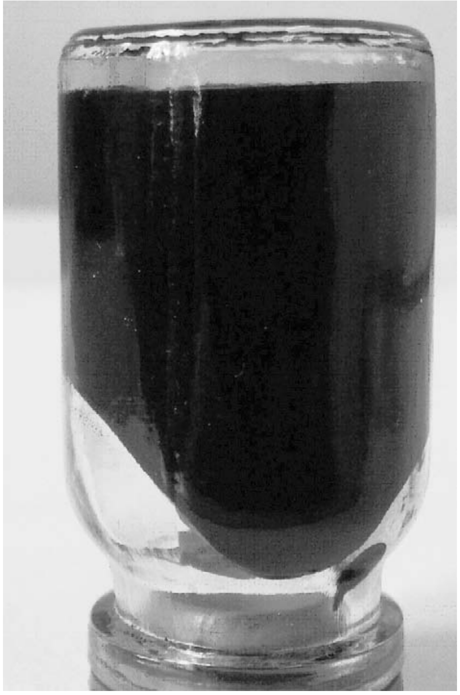


Fig. 6. Digital photo of solvent-free MWNTs nanofluids.

sample expressed the law of $G'(\omega) \propto \omega$ and $G''(\omega) \propto \omega$. The values of G' and G'' are totally smaller, suggesting a Newtonian fluid-like with lower viscous and elastic properties. The rheological property is influenced by the volume fraction and flocculation of solid particle [31]. Generally, the flow resistance of $\mathrm{MWNT_{HPAE}}$ increased with the concentration of MWNTs increasing. The $\mathrm{MWNT_{HPAE}}$ derivative was a viscous liquid (Fig. 6). The organic shell of HPAE acted like a lubricant among the core MWNTs and accelerated mobility.

Finally, it was found that the different functionalized methods obviously affected the solubility characteristics of the resulting materials. As showed in Fig. 7, $\mathrm{MWNT_{HPAE}}$ were soluble in good solvents of HPAE, such as water, chloroform and acetone; while insoluble in ether, which is non-solvent for HPAE. The solutions could be stable for weeks without macroscopic precipitation. In contrast, when MWNTs directly treated by HPAE, they exhibited insolubility in those solvents such as ether and benzene, regardless of their compatibility with HPAE.

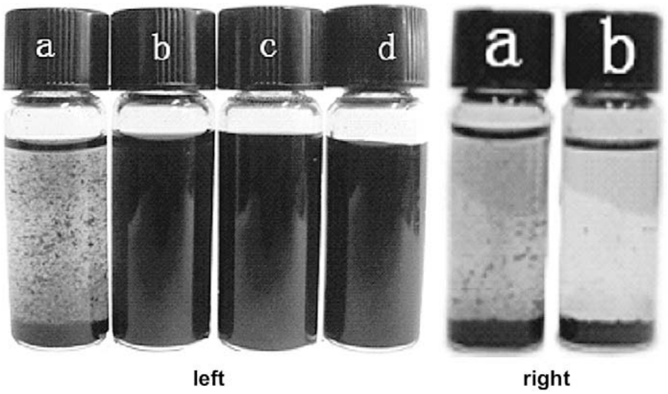


Fig. 7. Solubility of $\mathrm{MWNT_{HPAE}}$ (left) in ether, chloroform, water and acetone, respectively (from left to right). The MWNTs directly treated by HPAE (right) in benzene and ether (from left to right). All samples were prepared by gentle sonication for 30 min and then kept for weeks before photographing. For comparison, the concentrations of all samples were fixed to be 0.5 mg/mL.

4. Conclusions

Solvent-free MWNTs nanofluids were prepared by HPAE. The dense surface coverage was one HPAE molecule per 30 carbon atoms of the MWNTs. It was a viscous liquid at room temperature and could flow in absence of solvent. Solvent-free MWNTs nanofluids are Newtonian fluid-like with lower viscous and elastic properties and they were soluble in good solvent of HPAE, but insoluble in non-solvent of HPAE. The method will develop a new family of modified nanoparticles that exhibit potential application in lubricants, plasticizers, or film-forming precursors and so on.

Acknowledgements

We greatly acknowledge the fund supported by NPU Foundation for Fundamental Research (NPU-FFR-w018105), the Doctorate Foundation of Northwestern Polytechnical University (CX200816) and Shaanxi Natural Science Funds 2007(2007E108).

Supplementary data

The FTIR spectra of a) MWNTs, b) MWNTs directly treated by HPAE. This material is available free of charge via the Internet at http://ees.elsevier.com. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2009.04.042.

References

[1] Coleman JN, Khan U, Blau WJ, Gun'ko YK. Carbon 2006;44:1624–52.
[2] Baughman RH, Zakhidov AA, de Heer WA. Science 2002;297:787–92.
[3] Iijima S. Nature 1991;345:56–8.
[4] Singh KV, Pandey RR, Wang X, Lake R, Ozkan CS, Wang K, et al. Carbon 2006;44:1730–9.
[5] Esplandiu MJ, Bittner VG, Giapis KP, Collier CP. Nano Lett 2004;4:1873–9.
[6] Banerjee S, Kahn MGC, Wong SS. Chem Eur J 2003;9:1898–908.
[7] McCarthy B, Coleman JN, Czerw R, Dalton AB, Panhuis M, Maiti A, et al. J Phys Chem B 2002;106:2210–6.
[8] Chen CS, Chen XH, Xu LS, Yang Z, Li WH. Carbon 2005;43:1660–6.
[9] Bourlinos AB, Herrera RA, Chalkias N, Jiang DD, Zhang Q, Archer LA, et al. Adv Mater 2005;17:234–7.
[10] Bourlinos AB, Chowdhury SR, Herrera RA, Jiang DD, Zhang Q, Archer LA, et al. Adv Funct Mater 2005;15:1285–90.
[11] Xue L, Keblinski P, Phillpot SR, Choi SUS, Eastman JA. Int J Heat Mass Transfer 2004;47:4277–84.
[12] Hu ZS, Dong JX. Wear 1998;216:92–6.
[13] Bi SS, Shi L, Yong HL, Wang RX. J Refrig 2006;27:1–4.
[14] Bourlinos AB, Georgakilas V, Boukos N, Dallas P, Trapalis C, Giannelis EP. Carbon 2007;45:1583–5.
[15] Bourlinos AB, Georgakilas V, Tzitzios V, Boukos N, Herrera R, Giannelis EP. Small 2006;2(10):1188–91.
[16] Michinobu T, Nakanishi T, Hill JP, Funahashi M, Ariga K. J Am Chem Soc 2006;128:10384–5.
[17] Choi JY, Han SW, Huh WS, Tan LS, Baek JB. Polymer 2007;48:4034–40.
[18] Zhou W, Lv SC, Shi WF. Eur Polym J 2008;44:587–602.
[19] Zhou W, Xu JW, Shi WF. Thin Solid Films 2008;516:4076–82.
[20] Yoshioka H, Suzuki M, Mugisawa M, Naitoh N, Sawada H. J Colloid Interface Sci 2007;308:4–10.
[21] Huang WJ, Fernando S, Allard LF, Sun YP. Nano Lett 2003;3:565–8.
[22] Ramanathan T, Fisher FT, Ruoff RS, Brinson LC. Chem Mater 2005;17:1290–5.
[23] Flory PJ. J Am Chem Soc 1952;74:2718–24.
[24] Mo ZL, Niu GP, Li HJ, Liu YZ, Chen H. Polym Bull 2006;10:48–51.
[25] Georgakilas V, Kordatos K, Prato M, Guldi DM, Holzinger M, Hirsch A. J Am Chem Soc 2002;124(5):760–1.
[26] Dyke CA, Tour JM. Nano Lett 2003;3:1215–8.
[27] Xu PX, editor. Polymer rheology and their application, vol. 1. Beijing: Chemical Industry press; 2003. p. 3–10.
[28] Yin JH, Nie JY, Yang JS, Hua BJ. Acta Mater Comp Sin 1992;9:103–9.
[29] Guo XT, Zhao YM, Ning P, Li LK. China Plastics Industry 2006;34:35–8.
[30] Wu QH, Wu JG, editors. Polymer materials rheology, vol. 1. Beijing: Higher Education Press; 1994. p. 2–8.
[31] Chen HS, Yang W, He YR, Ding YL, Zhang LL, Tan CQ, et al. Powder Technol 2008;183:63–72.