



Suspended carbon black fluids reinforcing and toughening of poly(vinyl alcohol) composites

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ARTICLE INFO

Keywords:

Nanofluids
Reinforcement
hydrogen bonds
Nanocomposites

ABSTRACT

A convenient and green approach was utilized to prepare the suspended carbon black fluids (SCBF) using carboxylic CB nanoparticles with diameters of 15 nm as the core and poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) as surface modifier *via* hydrogen bonding interaction. It was found that when the total polymer content (strongly adsorbed layer and weakly adsorbed or free layer) was greater than 60 wt%, the SCBF exhibited liquid-like behavior without solvent. More interestingly, the flow mechanism mainly related to surface polymer content, which greatly differed from ionically or covalently nanofluids systems. Besides, the thermal, dispersibility, electrical conductivity properties and rheological behaviors, as well as microstructure of SCBF were systematically investigated using various methods. Moreover, the SCBF as fillers were used to prepare SCBF/Poly(vinyl alcohol) (PVA) composites for producing the simultaneous reinforcement and plasticization effect due to the unique fluidity of SCBF and interfacial interactions between the PVA molecules and SCBF *via* hydrogen bondings.

1. Introduction

Over the past four decades, carbon black (CB) as a versatile material has been extensively used in many fields such as conductive composites [1], rubber tire [2], water treatment [3], printing ink [4], and harvesting solar-energy and pharmaceutical drug-delivery vectors [5] due to its exceptional advantages such as electrical conductivity [6], reinforcement [7–8], catalyst [9], adsorption [10] and tinting [11]. However, due to the high surface energy of CB particles, the highly irregular shaped CB nanoparticles consisting of nanopores exhibit a strong tendency to agglomerate, which seriously deteriorate the electrical, mechanical, thermal and optical properties of polymer materials. Hence, it is a great challenge for obtaining the stable dispersion of CB nanoparticles in other mediums. In order to solve these problems, a series of physical and chemical approaches mainly including covalent polymer grafting or noncovalently polymer encapsulation [13], surfactant adsorption [14], surface oxidation [15], diazonium chemistry [16], are used to modify the surface property of CB nanoparticles, and further improve CB dispersion in organic or polar

mediums [12].

Nevertheless, surface-modified CB nanoparticles *via* the above-mentioned approaches exhibit solid-like behavior without the existence of solvent or dispersing medium cannot undergo any macroscopic solid-to-liquid transition with temperature variation. Meanwhile, the preparation routes consume a large amount of volatile organic solvents, which is not environmentally friendly. What's more, recently, it has been reported that functionalized CB nanoparticle synthesized by firstly sonification-assisted oxidation, then covalent grafting by a charged polysiloxane quaternary ammonium salt and ion exchange with a poly(ethylene) glycol-functionalized sulfonate salt, exhibits liquid-like behavior in the absence of solvent, named as ionic CB nanofluids. Most importantly, the CB nanofluids as nanofiller has synergistic effect for achieving the homogeneous distribution in polymer matrix and improving the processability of composites [17] because of its monodispersity, zero-vapor-pressure, low viscosity, and high refractive index [18]. The combination of solvent-free nature and fluidity of CB fluids provides an environment-friendly route to prepare the high performance polymer composite. Unfortunately, the low yield and high cost

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of the preparation route of CB nanofluids *via* ion exchange approach are still two main disadvantages. In addition, it is time-consuming to synthesize a large number of samples by many reaction processes. Therefore, it is desirable to develop a facile and green approach with low cost and high efficiency to fabricate a novel CB nanofluid.

In this paper, the nonionic CB nanofluids are fabricated for the first time *via* a facile physical method for strongly adsorbed amphiphilic polymer (PEO-*b*-PPO-*b*-PEO) by hydrogen bonding between nanoparticles and polymer. The obtained CB nanofluids display excellent dispersibility and fluidity without solvent, as well as good thermal stability. Meanwhile, the facile and green approach can be utilized for further improving the stiffness and toughness of CB nanoparticles in the Poly(vinyl alcohol) (PVA)-based nanocomposites due to the higher level of dispersion and fluidity of CB nanoparticles in PVA matrix.

2. Experimental

2.1. Materials

The original CB nanoparticles (average size of 15 nm) were purchased from China Carbon Black Research and Design Institute. The pluronic copolymer, poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (PEO-*b*-PPO-*b*-PEO) pellets ($M_n = 14,600$ g/mol, PEO = 82.5 wt%) from Aldrich. PVA ($M_n = 79,245.92$ g/mol, hydrolysis degree of 98–99%) were purchased from Sigma Aldrich. Other reagents of analytical grades were purchased from Beijing Chemical Factory.

2.2. Carboxylation of CB powder

Firstly, 2 g original CB powder was dissolved in concentrated H_2SO_4/HNO_3 mixture (3:1 in volume ratio) and stirred ultrasonically at 70 °C for 10 h. Then, the black suspension was filtered and washed with deionized water until pH = 7. The obtained black powder was redispersed in deionized water, and then followed by centrifugation at 7000 rpm for 30 min to eliminate untreated CB powder. Finally, the supernatant liquid was filtered and then dried in a vacuum oven at 60 °C for 48 h to obtain carboxylic CB.

2.3. Preparation of CB nanofluids

1 wt% of carboxylic CB suspension was formed through dispersing carboxylic CB in deionized water under ultrasonication. Next, 10 wt% of carboxylic CB suspension was added into 100 ml of 10 wt% PEO-*b*-PPO-*b*-PEO pre-dispersed in water solution, and stirred for 24 h to obtain a homogeneously brown solution. Then the solution dialyzed using a cellulose dialysis membrane/bag (trapped molecular weight > 15,000) by circulating deionized water around the dialysis bag for 7 days to further remove the excess free polymer and other impurities. Finally, the product was dried at 60 °C in a vacuum oven for two days to obtain the black self-suspended CB fluids (named as SCBF). Additionally, in order to further fully remove the free polymer of SCBF, the sample was further purified by centrifugation to ensure that the sample was only composed of the CB particles and bound polymer by hydrogen bonding. 1 g SCBF was once again dispersed in 10 ml deionized water, then transferred into a plastic centrifuge tube. Then the SCBF were centrifuged at 30000 rpm for 25 min. The liquid supernatant was extracted from the tubes, and the residue was dried 60 °C in vacuum oven. Finally, a black gel-like CB (denoted as g-CB) composed of bound polymer and CB nanoparticles were obtained. The preparation route and digital pictures are shown in Fig. 1.

2.4. Fabrication of SCBF/PVA composites

SCBF/PVA and CB/PVA composite films were prepared by dissolving PVA in 100 ml deionized water followed by adding the SCBF or CB

in the solution under ultrasonication for 30 min, then poured into glass dishes and dried at 60 °C in vacuum for 3 days to obtain composite films. The content of SCBF or CB in the SCBF/PVA films is 0 wt%, 1 wt%, 2 wt% and 3 wt%, respectively.

2.5. Characterization

The amount of N, C, H and S elements for original CB and carboxylic CB were measured by Elemental analysis (Thermo Scientific FLASH 2000 CHNS/O). The infrared (IR) spectra of original CB and carboxylic CB, SCBF and g-CB were investigated by Fourier transform-infrared (FTIR) spectrometer (Nicolet iS10, Nicolet instrument corporation) using KBr pellets. Infrared spectra of PVA composites specimens were obtained from attenuated total reflection infrared spectroscopy (ATR-IR) (a Nicolet NEXUS 670). Diameters of carboxylic CB and SCBF were determined using a particle size analyzer (BI-90 plus, Brookhaven Instruments, USA) at 25 °C. Thermogravimetric analysis (TGA) measurements were taken under nitrogen atmosphere flow using a TGAQ50 TA instrument at heating rate of 10 °C/min. Differential scanning calorimetry (DSC) traces were collected using a Q1000 TA instrument at a heating rate of 10 °C/min. Diameters of original CB and SCBF dispersed in water (0.5 wt%) were determined using dynamic light scattering (DLS) at 25 °C with a particle size analyzer (BI-90 plus, Brookhaven Instruments, USA). Transmission electron microscopy (TEM) images were obtained at an accelerating voltage of 100 kV on a JEM 1200EX instrument. A few drops of ethanol dispersion of carboxylic CB and SCBF were placed on a 400-mesh carbon-coated copper grid, and we observed the morphology after ethanol evaporated. The composite films embedded by epoxy resin were microtomed into sections of 100 nm thickness for TEM observation. The surface morphology of composite films was observed by SEM (S4800, Hitachi, Japan) at an acceleration voltage of 5.0 kV. The storage modulus (G') and loss modulus (G'') were measured at fixed angular frequency ω of 6.28 rad s^{-1} and strain amplitude of 1% at the temperature range of 35–100 °C using the Rheometer (AR-G2, TA instrument). The viscosities were measured at a constant frequency 1 s^{-1} in the temperature range of 55–100 °C. The gap distance was kept about 600 μm for all tests with parallel plate of 45 mm in diameter. The electrical conductivity apparatus was used to estimate the conductivity of SCBF dispersed in water. The dispersibility and stability of carboxylic CB and SCBF in water were quantitatively analyzed using an ultraviolet spectrophotometer (UV-vis). Mechanical tests were measured using the universal testing machine (Instron 8871, UK, capacity 25 kN). The X-ray diffraction patterns of pure PVA and PVA composites were performed using Bruker D8 Advance X-ray diffractometer with CuK α radiation. The X-ray powder diffraction pattern was recorded in the 2θ range from 5 °C to 80 °C with scanning speed of 5 °C/min.

3. Result and discussion

3.1. Structural analyses

Generally, a large amount of carboxyl and hydroxyl groups were successfully generated on the original CB nanoparticles surface *via* strong acid oxidation [19]. In order to estimate the surface carboxylic degree of CB nanoparticles, elemental analysis was utilized to quantify the amount of C, O and H elements. The obtained results for original CB and carboxylic CB were summarized in Table 1. The amount of hydrogen (H) element increased from 0.11 wt% to 0.72 wt% while carbon (C) element decreased from 99.74 wt% to 80.50 wt% after surface oxidation treatment. Based on the law of mass conservation, the oxygen (O) element increased from 0.15 wt% to 18.78 wt%. Hence, elemental analysis results confirmed that a large amount of carboxyl and hydroxyl groups were formed on the surface of CB nanoparticles.

Infrared spectroscopy was a highly effective method for probing hydrogen bonding interaction in polymer composites. For revealing the

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