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Development of electrically conductive nano bamboo charcoal/ultra-high molecular weight polyethylene composites with a segregated network

Suiyi Li [a, b], Xiaoyan Li [a], Chuchu Chen [a], Haiying Wang [a], Qiaoyun Deng [a], Meng Gong [b], Dagang Li [a, *]

[a] College of Materials Science and Engineering, Nanjing Forestry University, Nanjing, Jiangsu, 210037, China
[b] Faculty of Forestry and Environmental Management, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada

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ABSTRACT

Electrically conductive nano bamboo charcoal (NBC)/ultra-high molecular weight polyethylene (UHMWPE) composites with a segregated structure were prepared by the high-speed mechanical mixing and hot-pressing method. Instead of uniform dispersion in polymer matrix, NBC distributed along specific paths and formed a segregated conductive network, which resulted in a low electrical percolation threshold (2.0 vol%) of the composites. The composite with 7 vol% NBC possessed a conductivity of 1.1×10^{-2} S/cm, which is adequate for many electrical applications. With the incorporation of NBC, the tensile strength of the segregated composites first increased by 10% with 3 wt% NBC content as compared with neat UHMWPE and then decreased with increasing filler content. Moreover, the thermal stability of NBC/UHMWPE composites was also improved as the loading of NBC increased.

1. Introduction

Recently, electrically conductive polymer composites (CPCs) have worldwide attracted attention due to their uses in a variety of applications, such as antistatic materials, electromagnetic interference shielding, electrode materials and sensor devices [1–3]. These composites are relatively cheap, lightweight, flexible, easy to process and have a wide range of electrical conductivity.

Carbon-based fillers such as carbon black [4], graphene [5–7] and carbon nanotubes [8,9] have been used to increase conductivity. However, as the energy and environment problems become more and more serious, the use of renewable resource as substitute is of great interest. Bamboo charcoal, a chief product of bamboo pyrolysis, is an abundant, environmentally friendly, cheap, and renewable bioresource on earth. As the carbonization temperature is beyond 700 °C, bamboo charcoal will become a conductive material [10]. It also possesses many advantages, such as supplier of negative ions, emitting far infrared rays, humidity regulator, oxidization prevention, and high thermal stability [11–13]. Thus, bamboo charcoal can be used as substitute of non-renewable fillers for melt processing.

Several traditional methods, such as melt compounding [14] and solution blending [15], have been reported to prepare CPCs. However, CPCs fabricated by the conventional melt-mixing method generally need a large amount of conductive fillers to form the conductive network, resulting in high percolation threshold, poor mechanical properties, and high cost. Therefore, in order to achieve a higher conductivity at low conductive filler content, the CPCs with a segregated structure have been developed [16–19]. Turner et al. [20] first proposed the 'segregated conductive network concept' for nickel particle/HDPE composites in 1971. Instead of uniformly distributed in polymer matrix, the conductive fillers were distributed only at the interfaces of polymer granules and formed a segregated conductive network, which resulted in a low electrical percolation threshold and higher electrical conductivity of the composites. Zhao et al. [21] prepared graphene/polymer composites with a segregated network by using the in situ reduction of graphene oxide (GO), which could efficiently improve the electrical conductivity of the composites. Pang et al. [22] used ethanol solvent-assisted dispersion and hot compression method to prepare graphene/UHMWPE composites with a segregated structure

* Corresponding author.
E-mail address: njfuldg@163.com (D. Li).

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and achieved a very low percolation threshold. In comparison to the fabrication process used for solution mixing method, the high-speed mechanical mixing method for preparing nanofiller/polymer composites is a simple and efficient technique [23,24]. However, there are limited studies on development of conductive polymer composites with a segregated network manufactured via the high-speed mechanical mixing method.

This study was aimed at using a high-speed mechanical mixing method and hot-pressing process to prepare NBC/UHMWPE composites with a segregated network to ensure a lower electrical percolation threshold and higher electrical conductivity. The morphologies, tensile properties, thermal stability and X-ray diffraction of NBC/UHMWPE composites were also investigated.

2. Experimental

2.1. Materials

NBC powders used in this study were purchased from Shanghai Hainuo Co., Ltd. UHMWPE powders (Mitsui L5000), which were purchased from Mitsui Co., Ltd., had a molecular weight of $(3-6)\times 10^6$ g/mol, a density of 0.94 g/cm^3 and a volume resistivity of 10^{17} Ω cm.

2.2. Preparation of NBC/UHMWPE composites

NBC powders and UHMWPE powders were first dried in an oven at 105 °C for 24 h prior to processing. Then NBC powders were further carbonized in a tubular furnace (OTF-1200X, HEFEI KEJING, China) under the following conditions: the temperature rise rate was 5 °C/min; the carbonization temperature was 1000 °C; maximum temperature was maintained for 1 h; and the flow rate of argon was 300 ml/min. The density of NBC was 1.29 g/cm^3, which was determined by pycnometer test method.

Then, 4 g dried UHMWPE powders were placed in a high shear mixer (food blender) and stirred for 30 s at a rotation speed of 24,000 rpm to produce static electricity. Next, desired amount of NBC were added into the high shear mixer and stirred for 60 s at a rotation speed of 24000 rpm to produce NBC-coated UHMWPE powders. Finally, the mixed powders were compression molded into films of 0.4 mm in thickness at 200 °C under 8 MPa for 15 min.

2.3. Characterization

The elemental compositions of NBC were measured by CHNS/O analyzer (Vario EL, Perkin Elmer, USA). Approximately 2 mg of dried sample was used for each measurement. Ash content was determined by heating a sample at 750 °C for 6 h under air atmosphere according to ASTM D1762-84 [25] and was calculated as the percentage remaining. The percentage of oxygen content was calculated in terms of the difference between the sample and the sum of C, H, N, S and ash.

The mean particle sizes and distributions of NBC and UHMWPE were measured using Malvern zetasizer nano (Malvern Instruments, UK) and Laser particle size analyzer (Jinan Winner Instrument Co., Ltd., China), respectively.

Olympus BX51 polarizing optical microscope (POM) (Olympus Co., Japan) was employed to observe the morphologies of the NBC/UHMWPE composite samples, which were cut into 20-μm-thick films using a microtome.

The morphologies of NBC particles, NBC-coated UHMWPE powders and fracture surfaces of NBC/UHMWPE composite samples were observed by a field emission scanning electron microscope (HITACHI S-4800, HITACHI, Japan) operating at 5 kV. All the samples were sputtered with gold to avoid electrical charging during examination.

XRD patterns of UHMWPE and NBC/UHMWPE films were obtained by a Rigaku X-ray diffractometer (Ultima IV, Rigaku Corp., Tokyo) using CuKα radiation (40 kV and 30 mA) over a range of 5–30°, with a step interval of 0.02°.

The electrical conductivities of the samples prepared were obtained using two different setups. The volume conductivities of NBC/UHMWPE composites higher than 10^{-5} S/cm were measured using a four-point probes resistivity measurement (RTS-8, 4 Points Tech, China). Volume electrical conductivities below 10^{-5} S/cm were measured using a PC68 digital high resistance meter (Shanghai Precision Scientific Instrument Co., Ltd., China) according to GB/T1410-2006 [26].

Tensile tests were carried out at a speed of 10 mm/min, with a universal testing machine (CMT4202, SANS, China), according to ASTM D 638–14 [27]. Dumbbell-shaped coupon specimens were cut from molded sheets previously conditioned for 24 h at room temperature. At least five specimens of each composition were tested, and the average values were reported with standard deviation.

The thermal degradation behaviors of NBC, UHMWPE and NBC/UHMWPE composites were investigated using Pyris 1 thermogravimetric analyzer (Perkin-Elmer Cetus Instruments, Norwalk, CT). The samples were heated from 30 to 700 °C under nitrogen gas atmosphere at a heating rate of 20 °C/min.

3. Results and discussion

3.1. Chemical compositions of NBC

The chemical compositions of NBC at two carbonization temperatures are presented in Table 1. Bamboo charcoal is composed of a mixture of carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and small quantities of ash. The carbon content of charcoal is a function of many factors such as pyrolysis temperature, residence time, moisture content of the biomass, and composition of the biomass [28]. It can be seen from Table 1 that the carbon content of NBC carbonized under 1000 °C (NBC1000) was 84.88 wt%, which was slightly higher than that of NBC (83.91 wt%), making it act as an ideal filler to reinforce plastic compounds. However the carbon content of NBC is lower than that of the carbon black (above 95 wt %) [29]. NBC1000 also possessed a relatively high content of ash with increasing carbonization temperature, which was in agreement to the finding by Usman et al. [30].

3.2. Morphology and microstructure

The preparation of NBC/UHMWPE composites with segregated networks is illustrated in Fig. 1. First, UHMWPE powders were stirred in a high shear mixer and the strong friction produced electrostatic phenomenon, making UHMWPE carry negative charges [23]. After adding NBC particles and high-speed mechanical mixing, the color of the powders became dark, indicating that the UHMWPE powders were covered with a layer of NBC (Fig. 1c). This is because the electrostatic interaction occurred between UHMWPE and NBC. When UHMWPE with negative charges got

Table 1
Chemical compositions of NBC particles.

Content (wt%)	C	H	N	S	O[a]	Ash
NBC	83.91	0.80	0.49	0.02	9.25	5.53
NBC1000	84.88	0.54	0.46	0.02	6.88	7.22

[a] O (%) = 100-(C + H + N + S + Ash).