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Effect of poly(sodium 4-styrenesulfonate) modified carbon black on the dispersion and properties of waterborne polyurethane nanocomposites

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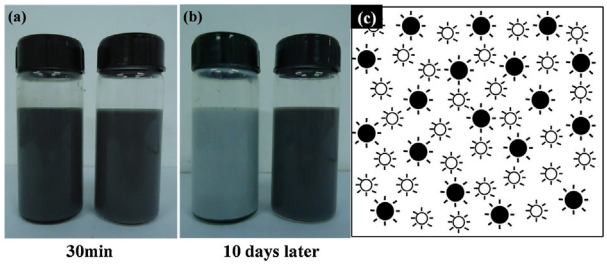
HIGHLIGHTS

- Highly hydrophilic CB nanoparticles were prepared by one-step in situ ball milling.
- The resulting PCB exhibited the smallest particle in water at the pH of 5.
- The PCB dispersed homogeneously in WPU emulsion though electrostatic repulsion.
- The properties of WPU/PCB hybrid films were enhanced with the addition of PCB.

GRAPHICAL ABSTRACT

The PCB exhibits an extraordinary stability than the pristine CB in WPU emulsion. The negatively charged PCB particles could homogeneously disperse in the anionic WPU emulsion through electrostatic repulsion and yield an excellent stability. The properties of the WPU/PCB hybrid films were improved with the addition of PCB.



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ABSTRACT

In this work, the poly(sodium 4-styrenesulfonate) modified highly hydrophilic carbon black (PCB) have been successfully prepared by one-step in situ ball milling method. The resulting PCB exhibited an excellent dispersion in water with an encapsulation of 14.9 wt%. The results of laser particle analyzer showed that the PCB exhibited the smallest particle size of 127 nm at the pH of 5 in water. The PCB was firstly used to prepare blend films with waterborne polyurethane (WPU) emulsion and the effect of PCB content on the structure and properties of the resultant films were discussed. The excellent dispersibility of PCB in WPU emulsion through electrostatic repulsion was observed, which played an important role in improving the homogeneous structure of blend films. Compared with the neat WPU films, the tensile strength of the WPU/PCB hybrid films increased from 39.8 to 54.2 MPa and the break elongation decreased from 1200 to 827%.

1. Introduction

Organic/inorganic composites have been widely studied for both research and application interests [1–4]. Carbon black (CB) is one of the most important inorganic materials because of its numerous merits such as excellent chemical stability, heat resistance, electrical conductivity, darkness, and safe features. So it has been widely used as reinforcing agent in rubber industry, as filler in polymeric matrixes, as an electrode for supercapacitors and pigment in modern print technologies [5–9]. However, due to its extremely large surface-area/particle-size ratio, CB particles tend to strongly agglomerate in nanocomposites, hence reducing the

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mechanical strength of the nanocomposite materials [10,11]. Many efforts have been taken to overcome this problem and enhance the filler dispersibility and its interaction with the matrix, among which the most economical and environmental approach is to enhance the hydrophilicity of CB to overcome the agglomerate in aqueous medium [10,12].

Polyurethane is an important class of polymer materials for a variety of applications in coatings, structural foams, and composites, due to its excellent abrasion resistance, toughness, low temperature flexibility, chemical and corrosion resistance, and a wide range of mechanical strength [4,13,14]. However, a mass of organic solvents should be used both in the polyurethane synthesis and application, which is harmful to environment and people's health. Recently, waterborne polyurethane (WPU) has gained attention among technology developers because they evolve only water instead of volatile organic compounds when drying. And the environmental friendly trend demands a "green" strategy for preparing the WPU-based nanocomposites in aqueous solution [15–19]. Therefore, WPU-based nanocomposites have become one of the major research and development fields because of its environmental friendliness.

In the previous study, many researchers have published their research regarding inorganic/organic composites systems and new type of CB based materials. Jin et al. prepared the stress sensitive photoluminescence elastomers by introducing ZnO tetrapod [20]. Qian et al. prepared the organic/inorganic flame retardants containing phosphorus, nitrogen and silicon in epoxy resins matrix as a novel intumescent flame retardant system [21]. Bavio et al. prepared the electrochemical capacitor electrode material by using polyaniline and polyaniline-carbon black nanostructures [22]. Zhang et al. studied the influence of kaolinite/carbon black hybridization on combustion and thermal decomposition behaviors of NR composites [23]. Therefore almost all of the methods mentioned above required harsh conditions such as high-demand temperature, accurate time and precise reactant ratio control, leading to the hazardous, laborious and time consuming preparation process.

In this study, we prepared the poly(sodium 4-styrenesulfonate) (PSS) modified highly hydrophilic carbon black (PCB) by using an environmental-friendly and simple method. And then the PCB can be used to prepare the PCB/WPU hybrid films through simple mechanical blending. The effect of PCB amount on the structure and properties of the resultant blend films were discussed. An environmental-friendly method for preparing the PCB/WPU hybrid films without using any organic solvents are provided in this paper.

2. Experimental

2.1. Materials

CB (Mogul-L), obtained from Cabot Corp., was dried under vacuum at 105 °C for 24 h before using. PSS was purchased from Nanjing Searchbio Tech Co. Ltd., with the molecular weight of 200 000. WPU (Polyester urethane) emulsion was supplied by Bayer Corp., with the solids content of 40 wt% and particle size about 0.1 μm, The pH of PCB suspension was adjusted with 10 M NaOH or 10 M HCl followed by dispersion period.

2.2. Preparation of the PCB suspension

The preparation of PCB suspension can be described as follows. Firstly, the grinding balls with good proportion were filled into the grinding bowl, which took up at least one-third of its volume to reduce the wear between grinding balls and bowl. Then 5.0 g CB and 5.0 g PSS were put into the grinding bowl. To ensure that the samples were effectively grounded, 200 ml deionized water was filled but not past three quarters of the bowl volume. The closed grinding bowl was then placed into the planetary ball mill and secured using the "safe lock". The counter weight was adjusted based on the weight of the bowl and sample to reduce the vibration of the milling operation [24], the mixture was ball milled for 24 h. Finally, the modified CB was separated from aqueous solution by ultra-centrifuge (SORVALL RC6+ Centrifuge, American) at 20 000 rpm for 30 min. The PCB suspension with known concentration was prepared by ultrasonically dissolved in deionized water.

2.3. Preparation of WPU/PCB hybrid films

The PCB/WPU hybrid films were prepared by simply mixing the PCB suspension with the WPU emulsion with suitable pH and treated with ultrasonic for 20 min. Then put the mixture into the vacuum oven under the pressure of 0.1 MPa for 3 h to eliminate the bubbles in the emulsion. Finally, the hybrid films were prepared by simple casting the mixture into the mould and dried at 40 °C for at least 12 h. The solid content was kept at 10 wt% during the preparation process. The WPU/PCB hybrid films containing different amount of PCB were named as PU, PU1, PU2.5, PU5, PU7.5 and PU10, respectively.

2.4. Characterizations

The surface morphologies of the PCB particles were observed by Transmission Electron Microscope (TEM) (JEM-2010, Hitachi, Japan). The PCB was ultrasonically dispersed in deionized water, and then a drop of the solution was deposited on a copper screen for TEM characterization. Thermogravimetric analysis (TGA) (STA449 F3 Jupiter, NETZSCH, German) was used to estimate the content of PSS coated onto the surface of CB and the thermal stability of WPU/PCB hybrid films. Each sample weighing about 10 mg was heated from room temperature to 700 °C at a rate of 10 °C/min in nitrogen atmosphere. The particle size distribution and Zeta Potential of the PCB at different pH was measured by a laser particle analyzer (Zetasize Nano-ZEN3600, Malvern, Great Britain). The PCB sample was dispersed in deionized water with ultrasonic for 5 min, and then the dispersion (0.005 wt% CB) was laid up in the laser particle analyzer. The cross-section morphology of the hybrid films were carried out by scanning electron microscope (SEM, JEOL JSM-6360 LV, 15 kV). Dynamic mechanical analysis (DMA) of composites was made with a Rheogel-E4000 (UBM Co., Japan) using a temperature ramp of 3 °C/min, with the frequency of 11 Hz. An X-ray diffractometer (XRD) (RIGAKU, D/MAX 2550 VB/PC) was also used to investigate the PCB, PU0, PU1, PU2.5, PU5, PU7.5 and PU10 samples. Tensile strength test was carried out on a tensile tester (Shenzhen, New Sansi Co. Ltd., China) at room temperature with a speed of 300 mm/min. All measurements have an average of five runs. The dumbbell type specimen was 30 mm length at two ends, 0.2 mm thickness and 6 mm wide at the neck.

3. Results and discussions

The PCB and untreated CB suspensions are compared to investigate its stability in deionized water by natural sedimentation. It can be seen from Fig. 1(b) that the pristine CB precipitated to the bottom completely after 15 days, while the PCB nanoparticles showed an excellent hydrophilicity and yielded a stable colloidal dispersion in water. As shown in Fig. 1(b) and (c), the PCB nanoparticles formed a homogeneous dispersion in water and kept stable for at least fifteen days before any noticeable flocculation, and even when the bottle was inversed, there was no precipitates staying on the bottom. The results indicate that the CB encapsulated by PSS having excellent stability in water.