Journal of Materials Science & Technology ■■ (2015) ■■–■■

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

ZnS/Bacterial Cellulose/Epoxy Resin (ZnS/BC/E56) Nanocomposites with Good Transparency and Flexibility

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ARTICLE INFO

Article history:
Received 27 April 2015
Received in revised form
5 August 2015
Accepted 13 August 2015
Available online

Key words:
ZnS
Bacterial cellulose
Epoxy resin
Nanocomposites
Properties

ZnS/bacterial cellulose/epoxy resin (ZnS/BC/E56) nanocomposites with good transparency and flexibility were prepared and characterized. When the precursor Zn^{2+} concentrations were not more than 1 wt%, the size of the introduced ZnS nanoparticles was smaller than 50 nm and the distribution was homogeneous within the composites. Under the condition, outstanding transmittance more than 70% in the visible light was obtained. By incorporation of ZnS nanoparticles with excellent thermo-optic stability to the composites, the thermo-optic coefficient was obviously increased from -361×10^{-6} to $-310\times10^{-6}K^{-1}$. The good flexibility, optical and mechanical properties endow the nanocomposites potential applications in the flexible optoelectronic materials.

1. Introduction

Multifunctional composite material is growing rapidly driven by advancement in optoelectronics information technology. And continuous "roll-to-roll" processing using flexible substrates is taking place of the conventional "batch" processing on glass substrates[1] which can deposit the functional material on flexible substrate, resulting in relatively easy and inexpensive processing suitable for future technologies such as optical devices, actuators, electronic papers. It is very important to select the flexible substrate with good properties to satisfy the application.

Bacterial cellulose (BC), obtained through fermentation mainly by the *acetobacter xylinum*, has an ultrafine nano sized three-dimensional (3D) fibrous network comprised of the ribbon-shaped nanofibers with diameters of 30–100 nm[2,3]. Its nanofibers are smaller than one-tenth of visible light wavelength, which means that the light-scattering arising from the mismatch of refractive index could be negligible owing to the nanosize effect when BC was composited with other polymers[4]. So far, using BC as the reinforcement to optically transparent polymer matrix has aroused more and more research interests due to its unique properties[4–7]. It has been reported that incorporation of BC into transparent optical resin could maintain high transparency with less than 8% loss of light transmittance, even at fiber contents as high as 70 wt%[5,6]. Moreover, the toughness is another advantage even at fiber contents as low as 5 wt%. It can be foldable for 180° without fracture[4–7]. Since BC is comprised of bundles of cellulose microfibril which are aggregates of semicrystalline extended cellulose, the rigid nanofiber network of BC can totally constrain the polymer matrix while maintaining the flexibility and ductility of the polymer matrix[4]. In our previous report[8], BC was introduced to bisphenol A epoxy resin (E56) and prepared BC/E56 composites which have obviously reduced coefficient of planar thermal expansion (CTE) from $83.8\times10^{-6}K^{-1}$ (epoxy resin) to $40.6\times10^{-6}K^{-1}$ at low fiber content (2.6 wt%). The high transparency was observed to be insensitive to the temperature change from room temperature to 90 °C despite the decrease in the refractive index of epoxy resin was 0.01 due to the nano effect of BC. The BC nanofibers reinforced polymer composites have been expected as promising potential alternatives to replace the conventional polymer substrate in the application of flexible electronic materials.

ZnS nanomaterials are known as semiconductors with a direct wide band-gap energy, high refractive index, high transparency in visible spectrum. These materials have attracted enormous research interests in recent years due to their unique optical and photochemical properties[9,10]. Thus, it is of great importance to introduce ZnS nanoparticles into polymer matrix and this kind of composite materials have been considered as promising candidates in application fields such as optical, electronic and optoelectronic

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http://dx.doi.org/10.1016/j.jmst.2015.08.014

Please cite this article in press as: Fangyi Guan, Shiyan Chen, Jingjing Yao, Weili Zheng, Huaping Wang, ZnS/Bacterial Cellulose/Epoxy Resin (ZnS/BC/E56) Nanocomposites with Good Transparency and Flexibility, Journal of Materials Science & Technology (2015), doi: 10.1016/j.jmst.2015.08.014

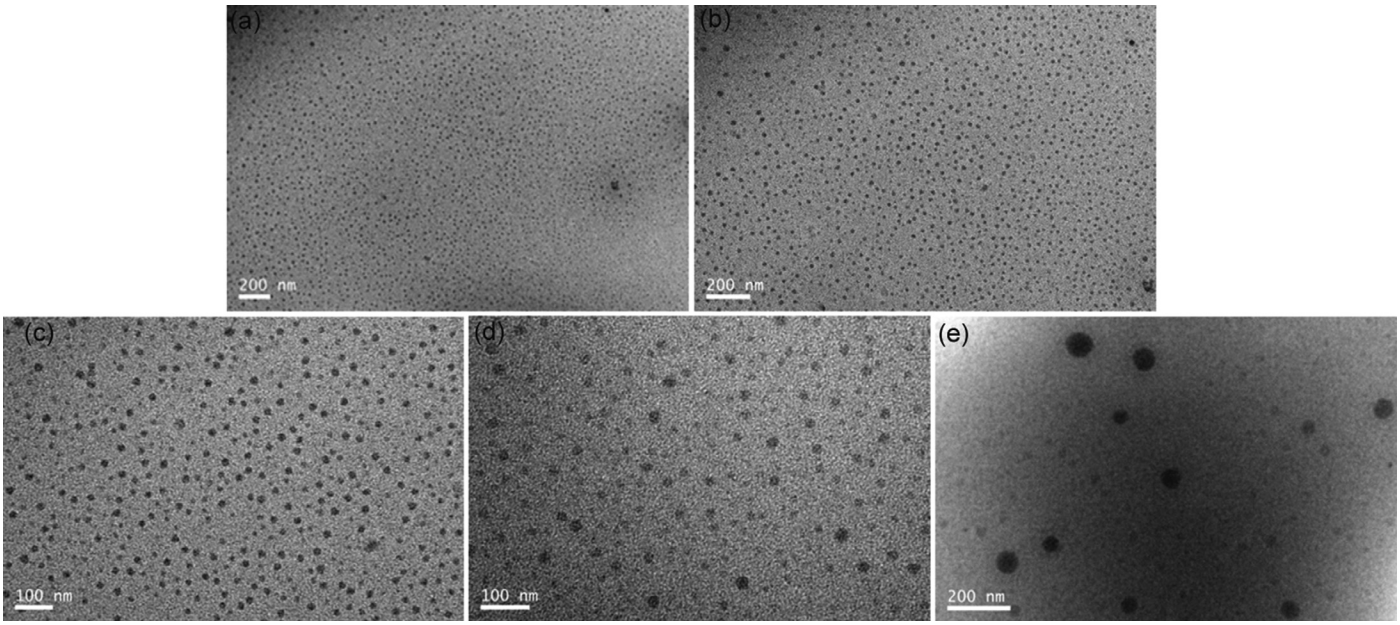

Fig. 1. TEM images of ZnS/BC/E56 membranes with different precursor Zn^{2+} concentrations: (a) 0.1 wt%, (b) 0.5 wt%, (c) 1 wt%, (d) 2.5 wt%, (e) 5 wt%.

devices. Therefore, the immobilization of the nano ZnS into a flexible organic matrix through the hybridization polymer matrix has been investigated during the last decades for potential application in security paper with optical signatures[11–15].

In this work, ZnS/BC composite membranes were first prepared and then introduced to E56 to prepare ZnS/BC/E56 nanocomposites. The transparency, thermo-optic stability and mechanical properties were characterized. We offered a good method to prepare multifunctional composite materials.

2. Experimental

2.1. Materials

Bisphenol A epoxy resin (E56) was purchased from Shanghai Resin Co., Ltd. Six hydrogen methyl anhydride and benzylamine were used as the curing agent and the accelerant, respectively. BC membranes were prepared in our lab. Other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were of analytical grade and were used as received. Distilled water was used in all experiments.

2.2. Characterization

The fiber contents of BC reinforced nanocomposites were determined by the element analysis (EA). The transmittance between 200 and 1000 nm were characterized by UV-Vis spectroscopy (TU-1901 Lambda 950 equipped with a 60 nm diameter integrating sphere). Spectroscopic ellipsometer (Ellip-SR-II) equipped with a flexible heater was used to determine the refractive index at different temperatures. The samples with the size of 10 mm × 4 mm were tested in tensile mode. Tensile strengths of the samples were measured using a WDW 3020 universal testing machine at room temperature with the crosshead speed of 5 mm/min. The freeze-dried samples were cut into 50 mm in length, 20 mm in width and 200 μm in thickness prior to mechanical measurements. Transmission electron microscopy (TEM) images were obtained on a Tecnai G2 spirit Brotwin using an accelerating voltage of 120 kV.

2.3. Preparation of ZnS/BC/E56 nanocomposites

First, ZnS/BC nanocomposites were prepared according to our previous report[16]. Then the obtained nanocomposites with a thickness of 10 mm consisting of about 99.9 wt% water were exchanged with ethanol and then cold compressed to adjust the thickness to control the fiber content while maintaining the same amount of BC. Afterwards, the solvent replaced sheets were impregnated with E56 under a reduced pressure (–0.1 MPa). The ethanol completely evaporated when resin impregnation was under reduced pressure. The E56 impregnated BC membranes were then cured under hot-compress at 140–150 °C for 3 h. The fiber content in the nanocomposites is about 24.8 wt% and the corresponding thickness of the nanocomposites is about 200 μm.

3. Results and Discussion

3.1. Morphology of ZnS/BC/E56 nanocomposites

The morphology of ZnS/BC nanocomposites was characterized using TEM by ultra-thin sections shown in Fig. 1. The ZnS in the composites shows a round nanoparticle and the Zn^{2+} precursor concentrations have significant impact on the size and distribution of ZnS nanoparticles. With increasing precursor Zn^{2+} concentration from 0.1 to 1 wt%, the size of the nanoparticle is smaller (<50 nm) and the distribution is homogeneous within the composites. When the precursor Zn^{2+} concentration increases above 2.5 wt%, a few nanoparticles are observed (Fig. 1(d, e)) and the distribution is heterogeneous. This observation indicates the effect of Zn^{2+} concentration on the ZnS nanoparticle size. Increase of the precursor Zn^{2+} concentration leads to larger nanoparticles, and the larger ZnS nanoparticles are difficult to enter the 3D network of BC for the pore size which is smaller than 100 nm. Thus, they are easily attached to the BC surface. According to the SEM images of ZnS/BC nanocomposites in our previous report[16], the size of ZnS on the surface of BC is more than 100 nm under the condition.

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