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Preparation and properties of poly(vinyl alcohol)/silica nanocomposites derived from copolymerization of vinyl silica nanoparticles and vinyl acetate

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Abstract

Nanocomposites of poly(vinyl alcohol)/silica nanoparticles (PVA–SNs) were prepared by in-situ radical copolymerization of vinyl silica nanoparticles functionalized by vinyltriethoxysilane (VTEOS) and vinyl acetate with benzoyl peroxide (BPO, i.e., initiator), subsequently saponified via direct-hydrolysis with NaOH solution. The resulting vinyl silica nanoparticles, PVA–SNs were characterized by means of fourier transformation spectroscopy (FTIR), transmission electron microscopy (TEM) and elemental analysis method. Effects of silica nanoparticles on viscosity and alcoholysis of PVA–SNs were studied by an ubbelohode capillary viscometer and back titration method. The morphological structure of PVA–SNs film was investigated by scanning electron microscopy (SEM). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile test were used to determine the thermal and mechanical properties of PVA–SNs films. The results indicated that the content of vinyl group on the surface of the vinyl silica nanoparticles was up to 3.02 mmol/g and vinyl silica nanoparticles had been successfully copolymerized with vinyl acetate. Furthermore, compared to pure PVA, silica nanoparticles bonded with polymer matrix in low concentration affected the viscosity and alcoholysis of the PVA–SNs materials. At the same time, it resulted in the improvement of the thermal and mechanical properties of the PVA–SNs materials due to strong interaction between silica nanoparticles and polymer matrix via covalent bond. Also, it could be found that optical clarity of membrane was changed through UV–Vis absorption spectrum because of introduction of silica nanoparticles.

Keywords: Poly(vinyl alcohol); Silica nanoparticles; Nanocomposites; Thermal and mechanical properties

1. Introduction

Recently, PVA nanocomposites have evoked intensive research interests because these materials have potential applications in biomedical devices, matrices for drug delivery systems, carrier for cells

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immobilization, carrier for signaling molecules, and bioseparation membranes [1–7]. In previous reports, the organic–inorganic hybrids including PVA have prepared by sol–gel [1,8–13], intercalation [14–17], and action with functionalized carbon nanotubes technologies [18,19] to improve the thermal and mechanical properties. Also, Hye Min Jung et al. prepared Poly(vinyl acetate) (PVAc)/Poly(vinyl alcohol) (PVA)/montmorillonite (MMT) clay nanocomposites microspheres with a core/shell structure via a suspension polymerization [20]. Peng et al. recently synthesized a novel PVA/silica nano-composite by employing electrostatic attractive and hydrogen bonding interactions as the driving forces, which had improved thermal, mechanical, and solvent resistant properties and had great potential for biomedical and biochemical applications [21]. In the polymer–inorganic nanocomposites, strong chemical bonds or interactions such as van der Waals force, hydrogen bonding, or electrostatic forces, often exist between the polymer and inorganic components [20]. In order to enhance the properties of nanocomposites, the interfacial actions must be improved between the polymer and inorganic components [22]. So far, the main driving forces were focused on van der Waals force, hydrogen bonding, or electrostatic forces according to previous reports. However, strong chemical bonds between PVA and inorganic components have not been reported. Recently, it was known that appending polymers onto silica nanoparticles was an effective way to obtain organic–inorganic hybrids [23,24]. By this method, silica nanoparticles bonded polymer strongly, which was stable and resulted in significantly improvement of properties of nanocomposites. However, this method has not been reported to prepare nanocomposites including PVA and silica nanoparticles, which was simple but effective.

In this paper, a series of PVA–SNs were prepared by this method. Firstly, silica nanoparticles were functionalized by vinyltriethoxysilane (VTEOS) with ultrasonic vibration in methanol. The resulting vinyl silica nanoparticles were characterized by elemental analysis, FTIR, and TEM to demonstrate vinyl group content on the surface of silica nanoparticles and compatibility of copolymerization system. Then, vinyl acetate mixed with vinyl silica nanoparticles under the help of ultrasonic vibration were initiated with BPO and followed by direct-hydrolysis with NaOH solution. The as-synthesized PVA–SNs materials were also characterized by FTIR spectroscopy and TEM. The results suggested that copolymerization was successfully carried out. The content of silicon, viscosity and alcoholysis of the PVA–SNs materials were determined by colorimetric method, an ubbelohode capillary viscometer and back titration method. The morphological images of the PVA–SNs film was studied by SEM. Effects of silica nanoparticles on the thermal stability, mechanical properties and optical clarity in the form of free-standing composites film were also investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile test and UV–Vis absorption spectra, respectively.

2. Experimental

2.1. Materials

Silica nanoparticles used were obtained from Zhoushan Mingri Nano-materials Co. Ltd., Zhejiang, China. The surface area, particle size and silanol group content were 640 m^2/g, 10 nm and 48%, respectively. It was dried in vacuum at 110 °C for 48 h before use. BPO (99%, Guangzhou Chemical Factory, China) was recrystallized before use. Vinyl acetate (99.5%, Tianjin Chemical Co. Ltd., China) was distilled before use. Methanol and VTEOS were purchased from Tianjin Chemical Co. Ltd. NaOH was applied to prepare the 20% NaOH aqueous solution. Deionized water was supplied by Lanzhou University.

2.2. Measurements

Elemental analysis (EA) of C, H was performed on Elementar vario EL instrument. Bio-RAD FTS-165 infrared spectrometer was used for the IR analysis. A JEM-1200 EX/S transmission electron microscopy (TEM) was applied to observe the images of vinyl silica nanoparticles dissolved in methanol and PVA–SNs dissolved in deionized water. The content of silicon was determined by colorimetric method. An ubbelohode capillary viscometer was used to measure the viscosity of PVA–SNs materials at 30 °C. The alcoholysis degree of the PVA–SNs materials was determined by back titration method. Scanning electron microscopy (SEM) of the free-standing films coated with Au was carried on a TEOL JSM -5600LV instrument. Differential scanning calorimetry (DSC) was performed in a Perkin–Elmer DSC7 at a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was conducted