International Journal of Biological Macromolecules 115 (2018) 266–272

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: http://www.elsevier.com/locate/ijbiomac

Influences of modified bacterial cellulose nanofibers (BCNs) on structural, thermophysical, optical, and barrier properties of poly ethylene-co-vinyl acetate (EVA) nanocomposite

Shila Shirdel Ghadikolaei [a], Abdollah Omrani [a,*], Morteza Ehsani [b]

[a] Faculty of Chemistry, University of Mazandaran, P. O. BOX 453, Babolsar, Iran
[b] Iran Polymer and Petrochemical Institute, P. O. Box 14965-115, Tehran, Iran

ARTICLE INFO

Article history:
Received 17 December 2017
Received in revised form 4 April 2018
Accepted 13 April 2018
Available online 14 April 2018

Keywords:
Ethylene-vinyl acetate copolymer (EVA)
Bacterial cellulose nanofiber (BCN)
Solution casting
Thermal properties
Surface treatments

ABSTRACT

The BCNs were chemically modified using acetic anhydride with the aim of improving its dispersion and interfacial adhesion. Acetylation of BCNs was confirmed by FT-IR spectroscopy. Morphology studies using TEM and SEM revealed that a reasonable dispersion of the modified BCNs in the EVA matrix was accomplished. The DSC data displayed a little shift in the T_g to higher temperatures with the incorporation of both modified and unmodified BCNs. Increased thermal stability of the nanocomposites consisting acetylated BCNs was confirmed by TGA technique. DMA measurements highlighted that the storage modulus increased and the damping properties decreased for the nanocomposites with regard to the neat EVA.

1. Introduction

In the line of current ecological policies, many attentions have been dedicated to the expansion of bio-nanocomposites with low environmental impacts for numerous industries like electronic, medicine, construction, automotive and packaging. Therefore, considerable research attempts have been assigned to utilize natural fibers in composites for reinforcing thermoplastic matrices as an alternative to primitive mineral fillers [1]. Compared with synthetic fillers, these reinforcements present better renewability, abundance, low density, biodegradability, low cost, and mechanical properties [2,3]. Among natural fillers, nanocellulosic fibers have attracted a great deal of interest as they offer a number of benefits when compared with mineral fillers. These advantages are high surface area, nanoscale dimensions, mechanical strength, as well as the fact that they have unique morphology, hydrophilicity, flexibility, low density, biodegradability and low cost [4–9]. Though the nanocellulosic fibers have numerous potentials as declared above, the main challenge while using them in composite materials as reinforcement is to achieve homogeneous dispersion of polar nanocellulosic fibers in non-polar polymer matrix. This goal is hard to accomplish because of hydrophilic nature of cellulose surface and the subsequent low interfacial compatibility with hydrophobic polymer matrix [10]. Indeed, uniform dispersion of nanofibers in the polymer matrix is a main prerequisite for attaining good mechanical properties of the final nanocomposite materials [11]. The hydrophilic character of cellulosic fibers is attributed to the OH groups that are situated on its surface. Therefore, in order to diminish the hydrophilicity of cellulose and to enhance its dispersion in the hydrophobic polymer matrix, surface modification of cellulose is one of the proposed strategies [12,13]. Among the different ways for chemical modification of cellulose, the acetylation reaction is a promising method. Acetylation is a chemical reaction at which the less hydrophilic acetyl groups are replaced to hydroxyl groups of cellulose [14–16]. However, plants are the main source of cellulose and numerous bacteria can provide cellulose as an alternative producer [17,18]. Bacterial cellulose nanofiber (BCN) was formed by aerobic bacteria from the fermentation of sugar. Compared to the plant sources of cellulose, BCN has received much attention owing to its unique physiochemical properties such as high mechanical strength, pure fiber network structure, high water holding capacity, and high crystallinity [19,20]. Accordingly, it has been used as biomaterial for food ingredient, electrical instrument and medical devices. Poly (ethylene-co-vinyl acetate) is a copolymer of vinyl acetate and ethylene that is generally known as EVA copolymer. It should be noticed that among several copolymer of ethylene, the EVA copolymer has the highest market. The presence of vinyl-acetate in the chain of poly ethylene changes its melting property and crystallinity [21]. EVA has received the widespread applications due to its transparency, significant elastomeric properties and simplicity of processing. Nevertheless, the characteristics of EVA composites have been rarely investigated. Moreover, the

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* Corresponding author.
E-mail address: omrani@umz.ac.ir (A. Omrani).

https://doi.org/10.1016/j.ijbiomac.2018.04.071
0141-8130/

addition of natural fibers to thermoplastic polymers has a significant effect upon the economics, thermal and mechanical properties of these materials [22,23]. Sonia et al. have produced cellulose microfibers (CMF)/EVA composites for food packaging applications. The effect of CMF content on the biodegradation behavior and thermal properties of EVA composites were examined. The results showed that biodegradability and thermal stability of the EVA composite linearly increased with CMF content [24,25]. The blends of PP/EVA with wood powder (WP) have studied by Dikobe and Luyt. The consequences demonstrated that the crystallization behavior of EVA was affected by the presence of WP [26]. The improved thermal and mechanical properties of celluloses whisker loaded EVA composites evaluated by Silviya et al. The EVA/cellulose films revealed superior thermal stability when compared with the neat EVA [27]. The mechanical characteristics of EVA and cellulose acetate (CA) containing natural fibers were also surveyed by Mydul et al. They found that the tensile strength of EVA based composites is reduced by increasing the fiber concentration [28]. The crystallization kinetics of EVA/BCNs nanocomposites was successfully described in our recently published article [29].

As the acetylation treatment is anticipated to improve the compatibility between the polar reinforcement and non-polar polymer matrix, the main goal of this study was to use the partial acetylated bacterial cellulose nanofibers as reinforcing agents in the EVA matrix. With this goal, the EVA nanocomposites were prepared through solution casting. The surface modification of BCN was confirmed by Fourier transform infrared spectroscopy (FT-IR). Also, morphology, thermal stability, visible light transparency, and dynamic mechanical properties of the both acetylated and non-acetylated nanocomposites were addressed in this work.

2. Experimental

2.1. Materials

EVA copolymer with vinyl acetate content of 18% was purchased from Honam Petrochemical Co. (South Korea) with melt flow index (MFI) of 2.5 g/10 min and melting point of 84 °C. Bacterial cellulose nanofibers (BCNs) gel 2.5 wt% (consisting nanofibers with average diameter of 40 nm and purity of 99%) was obtained from Nano Novin Polymer Co. (Sari, Iran). Sulfuric acid (95–97%), acetic acid (100%), acetic anhydride (95%), and tetrahydrofuran (THF) with the purity of >99% were obtained from Merck, Germany. Methanol and acetone were acquired from Sigma-Aldrich Co, Germany. All reagents and solvents were of analytical grade and used without further purification.

2.2. Chemical modification of the BCNs

The surface of bacterial cellulose nanofibers was acetylated according to the procedure proposed by Jonoobi et al. [30]. Prior to the acetylation, BCNs were activated using a mixture of acetic acid (25%) and sulfuric acid (3%) with a ratio of 1:1 by volume and stirred for 30 min at 70 °C. Subsequently, the activated BCNs were collected by centrifugation and decanting. The extracted BCNs were added to a reaction flask containing 20 mL of acetic acid and 5 mL of acetic anhydride. After that, the reaction was allowed to proceed with stirring under reflux at 100 °C for 4 h. In order to eliminate unreacted acetic anhydride and acetic acid by products, the treated fibers were washed with methanol and acetone (in ratio of 1:2 by volume). Then, the solvent was exchanged from methanol and acetone to THF by centrifugation (three times) to obtain homogeneity dispersions of BCNs in THF. It was noticed that the solvent exchange scheme could be very useful technique to improve the better dispersion of polar BCNs in non-polar solvent. The chemical reaction of acetic anhydride with BCNs occurring during the acetylation process was shown in Scheme 1.

2.3. Preparation of EVA nanocomposites filled with BCNs

The pure EVA and EVA/BCNs nanocomposites have been fabricated according to the following procedure. In summary, 1.5 g of EVA was dissolved in 20 mL of THF through heating at 60 °C for 4 h while being stirred strongly. The vaporization of solvent was hindered via a reflux condenser. The mixture was poured into a glass mold and dried at ambient temperature for 24 h. The resultant films of EVA were removed from the mold surface and stored in a desiccator prior to the measurements. In order to prepare EVA nanocomposite films, specified values of the acetylated and non-acetylated BCNs were suspended in THF for 4 h while stirring by a magnetic stirrer. To obtain more homogenized suspension, an ultra turrax T-25 homogenizer with a S25 N-25F probe was used for 15 min. Then, the suspended BCNs and acetylated BCNs were introduced to the previously prepared EVA solution and the mixtures were kept at 60 °C under reflux for 30 min while being stirred. The dispersions were finally poured in a glass mold and allowed the solvent to be evaporated at ambient temperature for 24 h. Two kinds of the nanocomposite films consisting BCNs and acetylated BCNs at 3 and 5 wt % with a thickness of 1 mm were fabricated.

2.4. Characterization techniques

2.4.1. FT-IR spectra

Fourier transform infrared (FT-IR) spectroscopy was performed using a Bruker, model: Tensor 27 instrument. The samples for FT-IR tests were mixed with appropriate amount of KBr. FT-IR analysis was performed in transmittance mode with a resolution of 4 cm^{-1} within the range of 400–4000 cm^{-1}.

2.4.2. Scanning electron microscopy analysis (SEM)

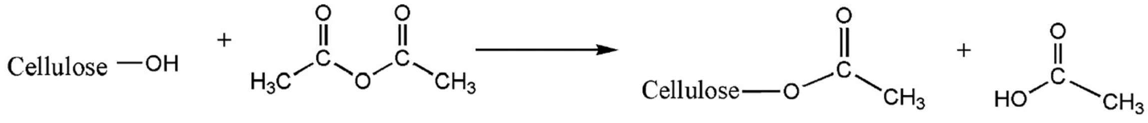
The morphology of fractured surfaces of the pure EVA and its nanocomposites were elucidated by field emission scanning electron microscopy (FE-SEM), Mira 3-XMU model. The fracture surface was acquired by splitting bulk samples and then quenched in liquid nitrogen. To avoid charging, the fracture surfaces of the specimens were sputtered with gold before the observations. The coating time was 2 min and the current prior was 15 mA.

2.4.3. Transmission electron microscopy (TEM)

Distribution of BCNs in the EVA matrix was assessed via transmission electron microscopy using a TEM instrument model Zeiss-EM10C that operated with an accelerating voltage of 80 kV. Specimens were prepared by the ultramicrotomy (UM) technique for the TEM observations.

2.4.4. Differential scanning calorimetry analysis (DSC)

DSC analysis was performed on a Netzsch DSC 200F3 differential scanning calorimeter under nitrogen atmosphere with a flow rate of 50 mL min^{-1}. Around 13 mg of samples were placed in aluminum DSC pans and heated from −30 to 150 °C at 10 °C min^{-1}. The crystalinity percentage was also calculated from the total enthalpy



Scheme 1. Depiction of the acetylation of BCNs using acetic anhydride.