Original Article

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Poly(methyl methacrylate)/bacterial cellulose nanofiber nanocomposites prepared by solution casting method and its reinforcement study

Mojdeh Mirshafiei[1], Hossein Asiani[2*],

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[1]Department of Biotechnology, School of chemical Engineering, College of Engineering, University of Tehran, Tehran, Iran

[2]Department of chemical engineering, college of engineering, Tarbiat Modares University, Tehran, Iran

Abstract

Bacterial cellulose nanofibers as biobased reinforcement with biodegradability, renewability and good physical properties for the lightweight construction design of polymer composite materials with high performance are often explored. The current work addresses the fabrication of a series types of poly(methyl methacrylate) (PMMA) composites consisting of three different concentrations of bacterial cellulose nanofiber (BCNF) networks (1, 2, and 3 Wt.%) by solution casting method. The prepared PMMA/BCNF was characterized with scanning electron microscopy and thermogravimetric analysis (TGA). It was evident that the PMMA/BCNF nanocomposite film (1 Wt.%) has a flat and smooth surface and the BCNF filler is scattered on the PMMA surface matrix but barely detected in the PMMA/BCNF composite film due to the compatibility between the PMMA matrix and BCNF filler. TGA analysis demonstrates that plots shifted to higher temperatures with the increase of BCNF concentration in PMMA matrix. The wettability and mechanical properties of obtained composite films were studied and compared to neat PMMA. The results show that the PMMA/BCNF nanocomposite film (1 Wt.%) has the best hydrophilicity and mechanical properties such as tensile strength, tensile strain, and Young's modulus. This work is intended to spur all researchers to more research and development for enhanced potential application of PMMA nanocomposites that are reinforced with BCNF in a wide application fields such as photocatalysis-wastewater treatment, packaging, flexible screens, optically transparent films.

Keywords: Poly(methyl methacrylate), Bacterial Cellulose Nanofiber, Nanocomposite, Wettability, Mechanical properties

1. Introduction

Polymer composites as heterogeneous materials are prepared from the combination of two or more different materials with distinct chemical or physical characteristics such as glass fiber, carbon black, talc, and carbon fibers as reinforcement fillers [1-3]. Recently, in contrast to the conventional polymer composite, nanocomposites are most advantageous because of the attractive properties of nanofillers such as high surface area and excellent monodispersity in polymer matrix and can play important roles in polymer blends [4-6]. For construction/preparation design and application of nanocomposites, the usage of nanofillers that are low cost, abundance, good physical properties, biodegradability, renewability and safety is one of the most important topics [7,8]. From the viewpoint of energy and environmental issues, nanofillers such as bacterial cellulose nanofiber (BCNF) with high mechanical properties are potentially applicable as a reinforcement filler to produce a polymer nanocomposite with ideal performance because BCNF can form a well-defined nanofiber network in the gel or polymer [9-12].

In recent decades, poly(methyl methacrylate) (PMMA), as transparent polymer and representative thermoplastic with glassy viscoelastic behavior has gained attention due to their excellent optical clarity, good processability and high mechanical–dynamical properties and can be used for several applications such as contact lenses, and optical devices [13-16].

It is evident that the engineering applications of the PMMA matrix can be enhanced and a variety research has been conducted via effective reinforcement with nanosized and microsized fibers owing to obtain a nanocomposite with sufficient mechanical strength, impact resistance and biodegradability.

In this work, a series of poly(methyl methacrylate) (PMMA) with BCNF PMMA/BCNF were prepared by a colloid based on the solution casting method. First, a oil-in-water microemulsion system as a soft template composed of methyl methacrylate as oil phase, polyvinyl alcohol (PVA) as surfactant and template, acrylic acid as co-surfactant and water as polar phase was used to prepare PMMA nanoparticles. Then a dispersion system of BCNF in chloroform based on BCNF solid content were prepared and PMMA nanoparticles was added and

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Corresponding Authors: Hossein Asiani
h.asiani6807@gmail.com

left overnight at 40 °C to evaporate the chloroform and several nanocomposite films were prepared and compared with pure PMMA. The prepared nanocomposite was characterized with scanning electron microscopy (SEM) and Thermogravimetric analysis (TGA). After that, the mechanical properties and wettability of the obtained nanocomposites were studied and compared with neat PMMA.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, 99%) monomer as oil phase without further purification, acrylic acid (AAc, 99%) were used as cosurfacatnt, Poly(vinyl alcohol) (PVOH, PVA, or PVAl) as a water-soluble synthetic polymer, Ammonium persulfate (APS), and chloroform (>99.0%), were purchased from Merck. Cellulose nanofiber (99.9%, diameter: 0.004 nm) was purchased from nanoshel.

2.2. PMMA nanoparticles preparation in oil-in water colloid template

A solution of PVA surfactant in water with a concentration of 0.1 M was prepared. The MMA oil-in-water microemulsion system was prepared by adding 2 Wt.% MMA oil phase. The system was mixed for 20 min by stirring and a cloudy colloidal solution was obtained. By titration with acrylic acid, as co-surfactant, the clear phase oil-in-water microemulsion was resulted at room temperature. Then ammonium persulfate (APS) as an initiator (0.6 wt.% based on the weight of MMA) was added to the microemulsion system with rigorous stirring. The system was kept at 60 °C for 8 h under static conditions for monomer polymerization to obtain a cloudy nanocolloid, indicating the PMMA formation. The resulting PMMA nanocolloid was centrifuged and the white and fine PMMA powder was dried at room temperature for 24 h.

2.3. PMMA/BCNF nanocomposite preparation by solution casting method

First, in three beackers a dispersion of BCNF in chloroform (for 1, 2, and 3 wt. %) was prepared. Next, 1 g of PMMA were added to three beackers, separately. The mixture was stirred for 1 h at room temperature to solve PMMA. The mixture was then poured into a Petri dish and left overnight at 40 °C to evaporate the chloroform. The samples were denoted as PMMA/BCNF (1, 2, and 3 Wt.%). A pure PMMA (without BCNF filler) as a control sample was prepared based on the mentioned above procedure.

2.4. Characterization

The morphology of the PMMA/BCNF nanocomposite (1 Wt.%) film was observed with a scanning electron microscopy (SEM) instrument (Philips XL30) using an Au coating to increase the sample's surface conductivity. Thermogravimetric analysis (TGA) using (PL-1500) is a characterization method that measures the mass of all samples over a wide temperature range at N_2 atmosphere (10 °C/min). TGA is commonly used to characterize thermal stability of a material.

2.5. Wettability measurement

To determine the contact angle, immediately after preparing the pure polymer film and nanocomposites, first each film was placed on a plane that was aligned with the horizon. Then, a drop of distilled water was dripped on each film by a syringe, and a transverse view was taken by a Nikon 100-D digital camera (Japan, Tokyo, Nikon Corp.) fixed on a tripod with a macro lens with a certain standard distance from the samples. Photographs were taken. During the shooting, the camera and the samples were completely aligned with the horizon. This work was repeated for 3 film and control samples separately. Then the photos were coded and scanned, and using Photoshop software, the contact angle of each drop in the surface was measured [17-19].

2.6. The mechanical properties study

The mechanical properties of all sample nanocomposite films were investigated and compared to pure PMMA based on the following the JIS K6251-8 standard using a universal testing machine (EZ Graph, Shimadzu, Kyoto, Japan). Each sample was cut into dumbbell shapes for at least five tests [20].

3. Results and discussion

3.1. SEM image

Fig. 1 shows the SEM image of PMMA/BCNF nanocomposite film (1 Wt.%). As shown in Fig. 1, the PMMA/BCNF nanocomposite film exhibits a flat and smooth surface and the BCNF filler is scattered on the PMMA surface but barely observed in the PMMA/BCNF nanocomposite film that confirming the compatibility between the PMMA matrix and BCNF filler. Thus, the agglomeration of BCNF at this BCNF concentration of 1 wt.% has been avoided.

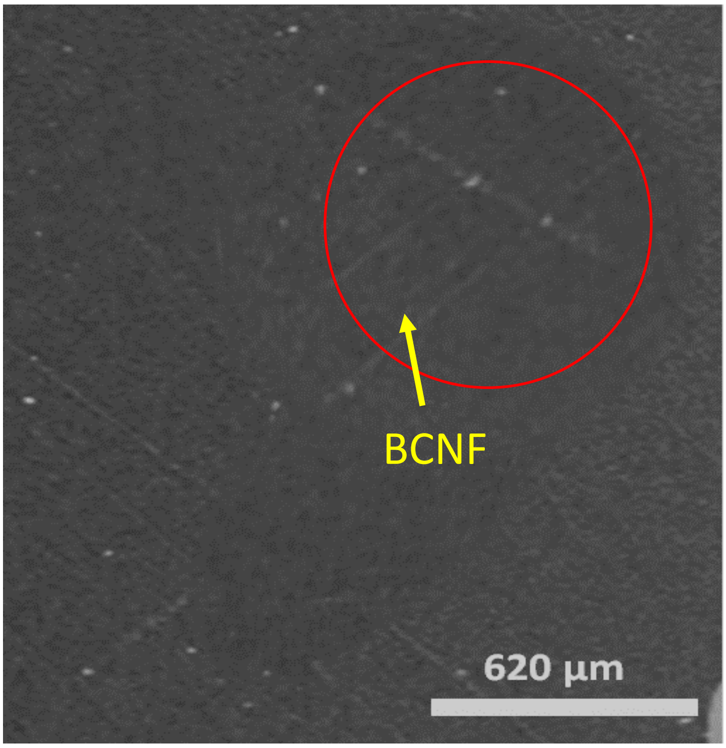

Fig. 1. The SEM image of PMMA/BCNF nanocomposite film (1 Wt.%) prepared by solution casting method

3.2. Thermal Property

Fig. 2 shows TGA plots of mass remaining versus temperature for all sample nanocomposites with different BCNF contents and the neat PMMA control sample. Fig. 2 demonstrates that plots shifted to higher temperatures with the increase of BCNF concentration in the PMMA matrix. Fig. 2. shows the temperature and thermal stability at 12.0% mass loss increased with the increase of BCNF content compared to PMMA.

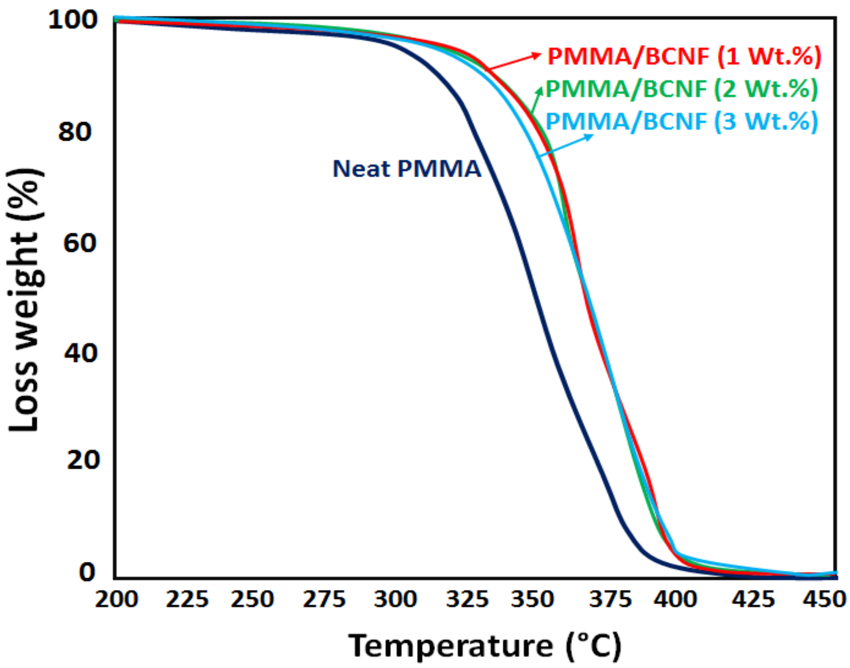

Fig. 2. TGA curves of all nanocomposite samples with different BCNF contents and neat PMMA

3.3. The effect of BCNF loading on the wettability of nanocomposite

As summarized in Table 2, the neat PMMA prepared by microemulsion systems shows an average water contact angle of 84.0°, whereas the PMMA/BCNF nanocomposite (1% Wt. BCNF in the PMMA matrix) film is 80.1°. It was demonstrated that PMMA/BCNF (1%) nanocomposite has a lower water contact angle compared to pure PMMA and PMMA/BCNF nanocomposite (2 and 3% Wt. BCNF in PMMA matrix) 83.5 and 83.1, respectively. This observation is attributed to the monodispersity of hydrophilic BCNF in polymer matrix at low loading of BCNF and the hydrophilicity of PMMA/BCNF nanocomposite films reduced by introducing a high amount of BCNF fillers due to agglomeration on nanofillers and incompatibility of PMMA and BCNF.

3.4. The effect of BCNF loading on the mechanical properties of nanocomposite

The mechanical property values of all samples are presented in Table 1. As can be seen from Table 1, the neat PMMA film exhibits a tensile strength of 31.5 MPa, and the PMMA/BCNF nanocomposite (1% Wt. BCNF in PMMA matrix) film shows an increase in tensile strength (38.2 MPa) owing to the compatibility of PMMA and BCNF, confirming the homogeneity of the BCNF in the PMMA matrix. In contrast, at high loading of BCNF does not cause any increase in tensile strength and values of 32.5 and 32.6 MPa were measured for PMMA/BCNF nanocomposite (2 and 3% Wt. BCNF in PMMA matrix), respectively because of not compatibility between the components. It is interesting to note that the tensile strain and Young's modulus (GPa), are increased for PMMA/BCNF nanocomposite (1% Wt. BCNF in PMMA matrix) compared to pure PMMA and PMMA/BCNF nanocomposite (2 and 3% Wt. BCNF in PMMA matrix). This is because the higher concentration of BCNF leads to inhomogeneity of the filler with the PMMA matrix.

Table. 1. The mechanical property values of the all samples

Sample	Tensile strain (MPa)	Tensile strength (MPa)	Young's modulus (GPa)
Pure PMMA	31.5	2.9	0.97
PMMA/BCNF (1 Wt.%)	38.2	3.6	1.45
PMMA/BCNF (2 Wt.%)	32.6	3.1	1.33
PMMA/BCNF (3 Wt.%)	32.5	3.0	1.33

4. Conclusion

In this work, we prepared a series types of poly(methyl methacrylate) (PMMA) composites consisting three different concentrations of bacterial cellulose nanofiber (BCNF) networks (1, 2, and 3 Wt.%) as biobased reinforcement by solution casting method. The result of scanning electron microscopy evident that the PMMA/BCNF nanocomposite film (1 Wt.%) has a flat and smooth surface and the BCNF filler is scattered on the PMMA surface matrix but barely detected in the PMMA/BCNF composite film due to the compatibility between the PMMA matrix and BCNF filler. TGA plots of mass remaining versus temperature demonstrate an increase of thermal stability for all sample nanocomposites with different BCNF contents compared to the neat PMMA control sample. The wettability and mechanical properties of obtained composite films were studied and compared to neat PMMA. The results show that the PMMA/BCNF nanocomposite film (1 Wt. %) has the best hydrophilicity and mechanical properties such as tensile strength, tensile strain, and Young's modulus.

Conflicts of Interest

The author declares no conflict of interest.

Author information

*Corresponding Author: Hosseini Asiani
h.asiani6807@gmail.com

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