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Material Properties

Dependence of mechanical and electrical properties of silver nanocubes impregnated bacterial cellulose-silk fibroin-polyvinyl alcohol films on light exposure

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ABSTRACT

Flexible and transparent substrate materials were fabricated by using bacterial cellulose (BC), silk fibroin protein (SF) and/or polyvinyl alcohol (PVA). The BC-SF and BC-SF-PVA films obtained were further modified by impregnation with silver nanocubes (AgNC). The influences of the silver nanocubes and white light illumination on the electric and viscoelastic properties of the films were investigated. Complex conductivity measurements showed that the films with PVA component are more sensitive to light exposure and there is an increase in conductance when the sample is illuminated. The films that contained silver nanocubes showed higher values of specific susceptance than their unmodified counterparts. DMA analyses revealed that the storage shear moduli of the films increase with addition of silver nanocubes. It was also found that the relaxation transition observed at elevated temperatures in the BC-SF-PVA-AgNC films is highly sensitive to the light exposure. Above the glass transition of PVA, both storage- and loss-shear moduli change dramatically if the sample is illuminated during the measurements with respect to the case when it was kept in the dark.

1. Introduction

In recent years, there has been strong interest in development of new transparent materials with good flexibility and dimensional stability. A large number of materials are presently being tested due to their possible application in flexible display technology [1,2]. Taking into account these current trends, we decided to study the flexible hybrid films comprised of bacterial cellulose (BC), silk fibroin (SF) protein and polyvinyl alcohol (PVA). The materials were chosen due to their environmental friendliness and biodegradability. Bacterial cellulose is an extracellular product made by the *Acetobacter* species. With respect to its plant counterparts, BC exhibits favourable properties such as higher molecular weight, porosity, mechanical strength, water retention capability and cellulose crystallinity (60–90%) [3]. Also, it is fully biocompatible and free of hemicellulose, lignin and pectin. Yano et al. [4] claimed that the BC nanofibres might be beneficial component of composite electronic display due the low coefficient of thermal expansion. It was also shown that BC nanofibres with cross section of $10 \times 50\,nm^2$ are almost free from light scattering, and that the composite films exhibit high transparency at fibre contents as high as 70%. Here, silk fibroin protein and PVA were blended with BC in order to improve the mechanical properties of the substrates. Silk fibroin protein is a natural polymer obtained from the cocoon of *Bombyx mori* silkworms [5,6]. It consists of repetitive amino acid sequences, including serine, glycine and alanine [7]. Optically transparent and flexible silk fibroin thin films have been proven to be suitable for the optical and sensor applications as well as for bio-integrated electronics [5,6,8]. Polyvinyl alcohol (PVA) is a hydrophilic and biodegradable polymer, which has good mechanical properties, good charge storage capacity and excellent film forming ability [9]. It is odourless, nontoxic material, resistant to the permeation of oils and organic solvents.

The present paper is focused on the viscoelastic and electrical properties of BC-SF and BC-SF-PVA films modified with silver nanocubes. These materials are suggested as novel types of flexible organic light emitting diode (FOLED) substrates. The successful application of these films depends on their behaviour under a variety of external stimuli. Here, we investigated whether the viscoelastic and electrical properties were influenced by illumination of the samples. In the BC-SF-PVA films with incorporated Ag-nanocubes, it was observed that the DMA spectrum at elevated temperature changed when the sample was exposed to light. We believe that the observed fundamental effect should be communicated as a separate study. The opto-electrical properties of the films as FOLED substrates will be reported in a forthcoming paper.

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2. Materials and methods

2.1. Materials

2.1.1. Basic materials

Nata de coco was kindly supplied by Thongaumphai's production, Thailand. Cocoons of silkworm *Bombyx Mori* were obtained from Chul Thai Silk Co., Ltd., Thailand. Sodium hydroxide (NaOH), sodium carbonate (Na_2Co_3), 37% hydrochloric acid fuming solution (HCl), polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA), potassium bromide (KBr), ethylene glycol (EG), copper (II) chloride ($CuCl_2$), silver nitrate ($AgNO_3$) and methanol (CH_3OH) were purchased from Sigma-Aldrich Co., Hungary. All chemicals were used as received without further purification.

2.1.2. Purification of Nata de coco and preparation of dried microfibrillated bacterial cellulose films

The procedure for the purification of *Nata de coco* and preparation of dried BC films is explained elsewhere [10]. Briefly, *Nata de coco* was cut and boiled in water until pH reached ~7. Then, it was treated in 0.1 M NaOH solution at 80 °C to eliminate non-cellulosic materials. During this step, the initially yellow suspension became a transparent gel. After that, the gel was boiled in distilled water several times until the pH became neutral. The gel was blended by a blender and subsequently dried in an oven to get microfibrillated BC films. They were further used for preparation of nanocrystalline BC.

2.1.3. Preparation of nanocrystalline bacterial cellulose films

The dried microfibrillated BC films were placed in a desiccator with 37% HCl fuming solution and left overnight [10]. During this step, degradation of cellulose occurred and nanocrystalline cellulose was formed.

2.1.4. Degumming of silk cocoons and preparation of nano-silk fibroin films

The purification of silk cocoons was carried by boiling in 0.02 M Na_2CO_3 followed by washing several times in water at 50 °C. The degummed SF was put in an oven to dry. The dried degummed SF was left overnight in the desiccator with 37% HCl vapor in order to obtain nano-silk fibroin [10].

2.1.5. Preparation of polyvinyl alcohol solution

In order to prepare 5%wt. PVA solution, 2.5 g PVA powder was dissolved in 50 ml water. Then, the solution was heated and stirred at 95 °C for 2 h until a clear solution was obtained.

2.1.6. Synthesis of silver nanocubes (AgNCs)

Silver nanocubes were prepared according to the method reported in Ref. [11]. A mixture of 0.668 g of PVP, 0.01 g of KBr, and 20 ml of EG was heated to 170 °C and kept at constant temperature with continuous stirring. After that, 0.05 g $CuCl_2$ was added. The mixing continued for another 3 min and then 0.22 g of $AgNO_3$ was titrated for 10 min into the flask. The flask was heated for 2 h to ensure that the growth of Ag nanocubes was completed. After that, the solution was left to cool down and centrifuged at 2000 rpm for 30 min to separate the cubes that remained in the supernatant. Then, the supernatant was centrifuged twice at 6000 rpm for 30 min to precipitate the cubes. The supernatant with EG, PVP and other impurities was discarded and the sediment of AgNCs was dispersed in 5 ml of methanol.

2.1.7. Fabrication of bacterial cellulose nanocomposite films

Two types of bacterial cellulose composite films were prepared. The first, BC-SF film, was obtained by using silk fibroin only and the second, BC-SF-PVA film, by using mixture of silk fibroin and polyvinyl alcohol. Microfibrillated and nanocrystalline BC was mixed with silk fibroin in 80 ml of distilled water. The dispersion was treated ultrasonically at 20 kHz until it homogenized. Then, PVA solution was added and the mixture was stirred overnight. To prepare BC-SF and BC-SF-PVA films, the corresponding mixtures were poured onto petri dishes and left to dry in oven at 40 °C for three days. Silver nanocube (AgNC) impregnated films were prepared by mixing the solutions (prior to drying) with 0.076 ml of AgNCs suspension. The thicknesses of BC-SF films and the BC-SF-PVA films were ~30 μm, and ~80 μm, respectively.

2.2. Methods

2.2.1. Field emission-scanning electron microscopy (FE-SEM)

FE-SEM micrographs were obtained using a Hitachi SU 8230 instrument at acceleration voltages of 5 and 10 kV. The samples were coated with gold.

2.2.2. Complex conductivity

Complex conductivity measurements were performed on an Agilent 4284 A at various frequencies (7, 22, 70 and 200 kHz) using the parallel mode capacitance (*C*p) model. In that model, the AC conductivity (admittance) can be presented as $Y = G + iB$ (*G*-conductance and *B*-susceptance). The samples were placed in a homemade cell and they were in no contact with the electrodes (the photograph of the cell is given in Supporting information, Figure S1). They were further investigated in the dark and under the white light illumination at relative humidity of ~40%. A white LED lamp ($P = 2\,mW\,cm^{-2}$ and $\lambda \geq 405$ nm) was used to illuminate the samples. The measurements were carried in three steps comprising the periods when the sample is in the dark (the 1st and the 3rd steps) and the periods when the sample is illuminated (the 2nd step). The total duration of the single measurement was 105 s and the sample was illuminated for 20 s after approximately 45 s. Due to the specific geometry of the cell and non-contact measurements, effective voltage (U_{eff}) was used to calculate conductance and susceptance (this is also explained in Supporting information). It should be emphasized that the illumination did not significantly affect the temperature of the sample, since the lamp exhibited negligible level of radiation in the infrared part of the spectrum. After the illumination for 20 s, the maximum increase in temperature was less than 0.1 °C.

2.2.3. Dynamic mechanical analysis

DMA analyses of the composite films were performed in shear mode on a METRAVIB DMA50 machine. The measurements were carried at a frequency of 1 Hz in the dark and under the illumination with white light. The temperature range was −100 to 200 °C, and the heating rate was $3\,°C{\cdot}min^{-1}$. Prior to both types of measurement, the films were stored in the dark for 12 h.

3. Results and discussion

It was mentioned in the introduction that the intent was to use BC composite films as possible flexible OLED substrates. This is not the topic of the present paper but in order to show the proof of concept, the images of the BC-SF-PVA films with deposited optically active layers are included in the Supporting information (Figure S2). Here, focus will be on the electrical and dynamic mechanical properties of these films.

3.1. Surface morphology

FE-SEM images of dried BC-SF-PVA-AgNCs film are shown in Fig. 1. A typical network structure attributed to BC and SF can be observed (Fig. 1a). The surface structure of the BC-SF is characterized by a 3-D fibrous ultrafine network of well-arranged nanofibrils, stabilized by hydrogen bonds in PVA matrix. The nanoscopic view of the film surface did not reveal any bacterial skeletons and/or other impurities. Fig. 1b shows isolated silver nanocubes with identical side lengths.