Theses of the PhD dissertation

Bacterial cellulose-Silk fibroin-Polyvinyl alcohol-Silver nanocubes for flexible and transparent organic light-emitting diode display

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Sopron

2018

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INTRODUCTION

In recent years, the development of flexible display has been taken place a flat panel for using in electronic devices, i.e. smartwatch, smartphone, and television panel. Nowadays organic light-emitting diode (OLED) technology is used mostly in phones. It is strongly becoming more prevalent, with over 400 million AMOLED screens manufactured in 2017 and continues growing in the market. Presently, the smartphones are launching the new models to replace the obsolete devices every year, raise electronic wastes (e-waste) after a few short years of the consumers use. The out-of-date electronic wastes are rapidly filling the landfill sites of the globe. As such, the concerning for handling of e-waste issue is also an interesting topic. In this work, biodegradable materials were used for solving this e-waste problem. Generally, the producers use glass or plastic for fabricating display application. There are also polymer blends as one of the most capable methods to have new material with required properties. Therefore, bacterial cellulose (BC), silk fibroin protein (SF), and polyvinyl alcohol polymer (PVA) were studied in this research. The BC structure has abundant surface of hydroxyl groups that describing it as hydrophilic, biodegradable, and chemical-modifying capacity. Silk fibroin protein has discovered for various applications such as tissue engineering or other biomedical applications because of its high tensile strength, biocompatibility, biodegradability, and non-cytotoxicity. PVA has the advantages of good film forming properties and high resistance to water, oil, grease, and solvent makes it adaptable for various applications. It is known as a biodegradable material, biocompatible, nontoxic, noncarcinogenic and extensively used in paper sizing, fiber coating, adhesives, emulsion polymerization, and medical field. Silver can produce the highest electrical conductivity, transparent conductive electrodes for optoelectronics, and the lowest optical losses of all metals. In this manner, silver nanocube (AgNC) was used and can be covered onto flexible substrates by cost-effective and scalable roll-to-roll fabrication.

1. Aim of the research

- Objective I: Preparation of flexible and transparent substrate for OLED display

Bacterial cellulose, silk fibroin protein, polyvinyl alcohol, silver nanocubes were used to prepare the thin films for OLED substrate. To the best of our knowledge, this is the first invention of the flexible displays by using these materials mix together. BC and SF fibrils were first hydrolyzed by fuming acid to obtain the nano-size fibrils. Then, ten samples were prepared; BC-PVA (S1), SF-PVA (S2), PVA (S3), BC-PVA-AgNC (S4), SF-PVA-AgNC (S5), PVA-AgNC (S6), BC-SF-PVA-AgNC (S7), BC-SF (S8), BC-SF-AgNC (S9), BC-SF-PVA (S10). In case of AgNC, it was synthesized and used as a conductive material.

- Objective II: Investigation of physical, mechanical, thermal, and electrical properties of ten samples

First, the visually transparent of each film were compared by photographs. Then, the properties of ten films were studied by using UV-Vis spectroscopy, XRD, FESEM, ATR-FTIR, DSC, TGA, Tensile tester, DMA, and Complex conductivity analysis. The effect of

PVA, AgNC, and acid hydrolysis were also examined. Some of those films were performed on the influence of light and investigate the mechanical and conductivity properties.

- Objective III: Comparison the characteristics of these samples according to the standard requirement of flexible electronic display

Not only the basic properties need to studies, but the requirements of these substrates also important to consider. Recently, the flexible electronic substrate has the standard regulations. Therefore, our films need to be compared with glass, plastic, or other polymer composite films. Finally, our ten substrates were chosen for the preferential to further fabricate the OLED display for smartphone.

2. Materials and Methods

- **Purification of Nata de coco and preparation of dried microfibrillated and nanocrystalline bacterial cellulose films**

Raw Nata de coco was first cut and boiled in water until reached pH~7. Then, it was purified in 0.1 M NaOH solution at 80°C to eliminate non-cellulosic materials. This process changed the color from yellow to pale gel. Then, the gel was boiled in distilled water several times until the pH become neutral. The gel was blended by a blender and dried in an oven to get dried microfibrillated BC films. These films were further used for preparing nanocrystalline BC films. The dried microfibrillated BC films were placed in a desiccator which contained 37% HCl fuming solution inside. The degradation of cellulose occurred and the nanocrystalline cellulose was achieved during this step. Then, it was dried in an oven to calculate the remaining weight of BC after hydrolysis.

- **Degumming of silk cocoons and preparation of nano-silk fibroin films**

The cocoons were boiled in 0.02 M Na_2CO_3 and washed in water for several times at 50°C. Then, the degummed SF was put into an oven to dry. According to hydrolysis reaction, the dried degummed SF was placed into desiccator with 37% HCl vapor inside to obtain nano-silk fibroin. The nanosilk was then dried in an oven for calculating the weight after hydrolysis.

- **Preparation of polyvinyl alcohol solution**

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

- **Synthesis of silver nanocubes (AgNC)**

A mixture of 0.668 g of PVP, 0.010 g of KBr, and 20 ml of EG was heated and kept temperature constant in a flask at 170°C with continuous stirring. Subsequently, 0.050 g $CuCl_2$ was added to the flask. The combined solution was allowed to mix for 3 minutes. Then, 0.220 g of $AgNO_3$ powder was titrated for 10 minutes into the flask. To ensure the

growth to be completed, the flask was heated for 2 hours. After the solution was cooled down, it was centrifuged at 2000 rpm for 30 minutes to separate the cubes which remained in the supernatant. The supernatant was then centrifuged twice to precipitate the cubes at 6000 rpm for 30 minutes. After the supernatant which contain EG, PVP, and other impurities was discarded, the sediment of AgNC was stored in 5 ml of methanol.

- **Fabrication of dried films by evaporation drying technique**

Table 1. **Component of each sample**

Sample code	Microfibrillated BC dried film (mg)	Nanofibrillated BC dried film (mg)	Nanosilk (mg)	5% wt PVA solution (mL)	AgNC (mL)
S1	20	60	-	1	-
S2	-	-	26.7	1	-
S3	-	-	-	1	-
S4	20	60	-	1	0.07
S5	-	-	26.7	1	0.07
S6	-	-	-	1	0.07
S7	20	60	26.7	1	0.07
S8	20	60	26.7	-	-
S9	20	60	26.7	-	0.07
S10	20	60	26.7	1	-

The samples were poured onto trays (diameter 7 cm). The trays were put in an oven at 40°C for 3 days until the dried films were obtained.

Characterization

The ten different types of samples were characterized by using eight types of measurements discussed below. Not all samples were used in every test.

- **Ultraviolet-visible (UV-VIS) spectroscopy**

Ultraviolet-visible (UV-Vis) spectra were investigated on WPA lightwave S2000 UV/VIS spectrophotometer for recording the light transmittance of the samples over the visible wavelength of 400-800 nm. A base line was recorded and calibrated using air. Measurement was conducted in triplicates.

- **X-Ray Diffraction Analysis (XRD)**

X-ray diffraction measurement of nanosilk was performed on the Angle dispersive XRD beamline (BL-12) of Indus-2 synchrotron source, RRCAT (India), using an image plate area detector (MAR345dif). The X-ray wave length (1.1 Å) used for the present study was accurately calibrated by doing X-ray diffraction on LaB6 NIST standard.

- **Morphological analysis of the nanocomposite films by FE-SEM microscopy**

The morphologies of seven types of nanocomposite films (S1, S2, S3, S4, S5, S6, and S7) were carried out by using a field emission scanning electron microscope (SU8230) at an accelerating voltage of 5 and 10 kV. The samples were cut in the size of 5×5 mm in the rectangular shape and carbon was painted at the edge of the surface. The films were coated with a thin layer of Au for 45 sec prior to analysis.

- **ATR-FTIR spectroscopy**

ATR-FTIR data collection was conducted on a Jasco FT/IR6300 equipped with an ATR PRO 470-H spectrometer. All spectra were measured using air as a background. A total of 25 cumulative scans were taken per sample with a resolution of 4 cm^{-1}, in the absorbance mode, in the frequency range of 4000-400 cm^{-1}. The testing was done at room temperature, in triplicates.

- **Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry (DSC) measurements for the S1, S2, S3, S4, S5, S6, and S7 samples were carried out using Mettler Toledo DSC 3+ instrument under nitrogen purge (50 mL/min). The heating and cooling rates were 10°C/min. They were sealed in a standard aluminum pan (40 μL). In this measurement a heat-cool-heat system was used and the second heating scan thermogram applied for thermal analysis. First, the sample was heated from 0 to 220°C to erase thermal history. Then, it was cooled down to 0°C before re-heating it to 220°C.

- **Thermogravimetric Analysis (TGA)**

The thermogravimetric analyses were carried out using Mettler Toledo TGA/DSC 3+. The S1 to S7 samples were cut and placed into an experimental sample pans with a sensitive microbalance. A furnace was provided with nitrogen atmosphere at the rate of 50 mL/min, in the temperature range from 25 to 500°C. The heating rate was 10°C/min.

- **Tensile test of sample films**

Tensile tests were performed on the INSTRON 3345 Tensile Tester. A length and a width of the strips of BC and SF containing nanocomposite films was 45 mm and of 15 mm, respectively. The applied cross-head speed was 5 mm/min on all five specimens of each samples (S7, S8, S9, S10).

- **Dynamic mechanical analysis (DMA)**

DMA measurement of BC nanocomposite films (S7, S8, S9, and S10) was performed in shear mode on a METRAVIB DMA50 machine with a DYNATEST 6.9 software. Specimens were prepared to dimensions of approximately 2×10×0.034 mm. Temperature scans were run from -100 to 200°C at a heating rate of 3°C/min with a frequency of 1 Hz. All samples were carried out under the white light illumination and measured the value of storage modulus (E′)

and loss tangent (tan δ). In case of S7, the light effect was investigated; therefore, it was stored in the dark for more than 12 hours and measured without any light.

- **Complex conductivity (Conductance) measurements**

Four types of samples (S7, S8, S9, and S10) were used for measuring the conductivity at 2.4 kHz in the homemade cell and there were no contact with the electrodes. Humidity was around 40±2%. For each sample, time dependent measurements in the dark and under illumination were also performed.

3. Results and Discussions

- **Optical property**

All films exhibited different levels of transparency but visually seemed homogenous with no bubbles, could be simply removed from the plate and were flexible. The greatest clearity was shown by films of pure PVA and PVA-AgNC (S3 and S6). Also, it confirmed by the results of the optical transmittance in the visible region (380-780 nm) of the electromagnetic spectrum which showed the notable transmission (transmittance between 78 and 80%). In contrast, the films containing BC (S1, S4, S7, S8, S9, and S10) displayed decreased of the transparency.

- **Surface of dried films**

S7 presents a 3-D fibrous ultrafine network structure. The BC nanofibrils diameters were found the average less than 100 nm and many pores were filled with silk fibroin and PVA matrix with the diameter size in the range of 30 to 182 nm. S2 shows separate phases between silk fibroin fibrils and PVA polymer in contrast with BC-SF-PVA-AgNC film. It is implying that PVA can well-penetrated to the BC-SF fibrils than SF-PVA blend film. In the case of pure PVA film, the surface is smooth and homogeneous because of its excellent film-forming properties. The width of AgNC was found between 180-200 nm and the length was shown from 160 to 200 nm. It was found that AgNC was well distribution and no aggregation in the other components except SF-PVA film.

- **Structure of the samples**

The obtained spectra from ATR-FTIR analysis in the region of 4000-400 cm^{-1} exhibited the structure of BC, SF, PVA, and AgNC films. All types of samples, the spectra were corresponded to the main characteristics of bacterial cellulose and some peaks of silk fibroin protein. It was observed that the intermolecular H-bonds between OH groups of BC cellulose and NH in the amide groups of SF was formed, in contrast with a decrease in intramolecular H-bonds of cellulose. This present work also shows the characteristic of β-sheet of silk fibroin structure. Therefore, this strong intensity of the β-sheet peaks proves the presence of the crystalline of silk fibroin protein. In addition, the characteristics of random coil conformation and α-helix (silk I) absorption peaks are disappeared after blended cellulose with silk fibroin. The β-sheet conformation was the result of the formation of intermolecular hydrogen bonds between cellulose and silk fibroin protein. When the AgNC was blended

(BC-SF-AgNC and BC-SF-PVA-AgNC), no new peaks were noticed other than common characteristics peaks of BC and SF nanofibrils.

- **Thermal properties**

Thermal properties of the samples which are the important characteristics of OLED display were investigated by DSC and TGA techniques. All of the samples present thermal stability up to 140°C before melting and 180°C before degradation. Interestingly, BC-SF-PVA-AgNC sample was unrecognized the glass transition peak. This fact suggests the highly crosslinked structure of the substances.

- **Mechanical, elastical, and viscoelastical properties**

Tension was applied to a sample while measuring the applied force and the elongation. In case of S8, the ratio of BC/SF blending film is 70:30 gives the opportunity of producing strong intermolecular interactions of hydrogen bonding. It encouraged β-sheet conformation of silk fibroin formation and the changes in silk fibroin structure, and increases the ability to react elastically to an applied force. Meanwhile, when AgNC were added to BC composite film, more tensile load was required to break the film.

Dynamic mechanical analysis revealed that the silver nanocubes in the BC-SF and BC-SF-PVA films have different effect on the film properties. It can be observed that after incorporation of AgNCs to BC-SF film, storage modulus (E′) significantly increases and the shape of both E′- and E″-curves also changes. The E″ value of the S9 sample at ∼75 $^{\circ}$C is almost two times higher than that of the unmodified BC-SF sample. The T_g of S8 and S9 films are around 75 $^{\circ}$C with an additional transition that appears at ∼125 $^{\circ}$C originated from SF. The E″ spectrum of S9 sample displays the presence of an additional peak at low temperature (−50 $^{\circ}$C). This is referred to the amplification of some local conformation rearrangements of silver nanocubes; probably they affect the motions of the amorphous parts in cellulose fibres, which exhibit a broad relaxation transition in that temperature range. The relaxation transition at – 50 $^{\circ}$C is also more pronounced in the S7 film. The dependence of the storage shear moduli of S10 and S7 films on temperature is similar to that of the pure PVA polymer from −50 $^{\circ}$C until the Tg of PVA (∼75 $^{\circ}$C). The glass transition of S7 sample is slightly shifted to higher temperature due to reduced mobility of PVA chains in the presence of AgNC. On the other hand, the another relaxation process displays at higher temperature above the glass transition, storage curves of both samples show additional fall, which is not present in the curves of pure PVA. This indeed was observed in the loss moduli spectra of S7 and S10 samples. The additional process is probably related to SF. The observed shift of the position of the relaxation peak towards lower temperature in the presence of nanostructured silver particles might be the result of the altered interaction of BC and SF. The AgNC obviously affect the motion of all three components in the film.

The storage (E′) and loss (E″) shear moduli curves of S7 film recorded in the dark and under illumination with white light were studied. E′ is increasing in the range from 90 to 125 $^{\circ}$C implying the photons somehow cause the rearrangement of the constituents of the film. This is followed by increased losses in the material i.e. the highest temperature E″-peak of the

illuminated sample present much higher intensity than that of the same sample recorded in the dark. Also, this peak is positioned at lower temperature (~125 °C) when the light is on than when the light is off (~140 °C). It should be mentioned that dielectric cubes could assemble under the influence of light. A rise in dipole moments is obviously amplified in the presence of AgNC. These effects might not be significant below the glass transition temperature. However, above the glass transition, the mobility of the matrix chains is much higher and the photo-illumination effects may contribute to the shear forces induced by external periodic loading. For this reason, there is a strong influence of light on the position and intensity of the high-temperature relaxation transition in S7 sample.

- **Complex conductivity (Conductance)**

To study the conductivity properties of the substrate, AgNCs were incorporated into the films. The electrical conductivity of the samples was measured. It can be seen that PVA containing films (S7-S10) are more sensitive to illumination, ie: the specific conductance of these samples increases with application of light. This is more pronounced if silver nanocubes are present (S7). The conductance of S8, S9 films is less sensitive to photo-induced effects. Obviously, photo-generation of the electrons does not depend solely of the presence of more conductive silver nanocubes. It should be emphasized that observed changes are small but they directly correspond to the possible effects of light.

4. Conclusion of thesis

Fabrication of flexible, thin, transparent, and self-standing substrate for OLED display by using natural materials: bacterial cellulose, silk fibroin, and polyvinyl alcohol together with silver nanocubes via normal casting evaporation drying technique was successful owing to high thermal stability, mechanical strength, and electrical conductivity properties.

5. List of publications related to the dissertation

- Worakan Hosakun, Yanin Hosakun, Duško Dudić, Vladimir Djoković, and Levente Csóka. “Dependence of mechanical and electrical properties of silver nanocubes impregnated bacterial cellulose-silk fibroin-polyvinyl alcohol films on light exposure” Polymer Testing Journal, vol. 71, 110-114, 2018.

- Worakan Hosakun, Levente Csóka. “Study of bacterial cellulose composite films by dynamic mechanical analysis” (submitted).

- Worakan Hosakun, Yanin Hosakun, Duško Dudić, Vladimir Djoković, and Levente Csóka. “Thermal and electrical properties of transparent and flexible films based on bacterial cellulose-silk fibroin-polyvinyl alcohol impregnated with silver nanocubes for flexible electronic display” 6th International Scientific Conference on Advances in Mechanical Engineering (ISCAME). Meeting place and date: Faculty of Engineering, University of Debrecen, Hungary, 2018.10.11-2018.10.12.

- Worakan Hosakun. “Study of bacterial cellulose composite films by dynamic mechanical analysis” PhD Complex Exam Presentation at University of Sopron, 2018.

- Worakan Hosakun, Levente Csóka. “Properties of bacterial cellulose nanocomposite films with and without silver nanowires for electronic display” 7th Interdisciplinary Doctoral Conference 2018. Meeting place and date: University of Pécs, Hungary, 2018.05.17-2018.05.19.

- Worakan Hosakun, Levente Csóka. “Study of bacterial cellulose composite films with and without silver nanowires by dynamic mechanical analysis” 5th EPNOE International Polysaccharide Conference 2017. Meeting place and date: University of Applied Sciences Jena, Germany, 2017.08.20-2018.08.24.

- Worakan Hosakun, Levente Csóka. “Study of bacterial cellulose nanocomposite films by dynamic mechanical analysis” COST Action FP1205: Innovative Applications of Cellulose Fibers Regenerate Wood: Cellulosic material properties and industrial potential - Final meeting in COST FP1205. Meeting place and date: KTH Royal Institute of Technology, Stockholm, Sweden, 2017.03.07-2017.03.09.

- Worakan Hosakun, Levente Csóka. “Fabrication of bacterial cellulose and bacterial cellulose/silk fibroin embedded in silver nanowires for flexible electronic displays” PhD Conference at University of Sopron, 2017.