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Covalently grafted carbon nanotube on bacterial cellulose composite for flexible touch screen application

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ABSTRACT

Carbon nanotube was successfully grafted on hydroxyl group of bacterial cellulose molecule by conventional synthetic method. The purpose of incorporated carbon nanotube on bacterial cellulose was to enhance the polarization effect on its composite. The appearant peak from Fourier transform infrared at 1730 and 1350 cm^{-1} exhibited that chemically modified bacterial cellulose by insertion of carbon nanotube was observed. Scanning electron microscope revealed that the structure of composite was designed as 3 stacks of grafted carbon on bacterial cellulose encapsulated on both sides by resin. In addition, significant enhancement on dielectric properties can be remarkably observed, suggesting bacterial cellulose composite exhibited superiority on polarization effect and it may initially be developed as electroactive macterials.

1. Introduction

Due to the growing environmental awareness and concerns over reliable availability of petrochemicals in the future, the polymer industry and academia have been pressed to design and produce polymers and composites based on renewable natural resources. In the past decades, the push towards flexible electronic device based on “Green composite materials” has been evident. Achievement of this new promising concept can easily lead to flexible displays and optoelectronics, as well as more novel ideas such as smart textiles, photovoltaic cells, and building lighting. Among the flexible electronic displays, organic light emitting diode (OLED) [1] is a versatile platform system that has attracted worldwide attention. OLED has been traditionally fabricated on rigid glass sheet substrates. Although flexible polymer substrates have been expected as potential alternatives in replacing the glass substrate, the use of conventional polymer substrates has been limited by their coefficient of thermal expansion (CTE). Okahisa [2] and Choi et al. [3] suggested that the CTE of the substrate should be restricted to 20 ppm/K at most, as the thermal expansion of the substrate can lead to the destruction of functional materials of the OLED circuit during the temperature fluctuation in OLED assembly and mounting processes. To overcome the CTE limitation of the flexible polymer substrate, our previous works have focused on the exploitation of the composite of nano-sized cellulose and polymeric matrices [4]. Bacterial cellulose, which is a nano-sized extracellular product of the bacteria strain *Acetobacter xylinum*, has the CTE of as low as 0.1 ppm/K. The incorporation of bacterial cellulose into polymeric matrix can be expected to yield a composite film with much decreased CTE to be less than 20 ppm/K. In addition, bacterial cellulose has the typical thickness and width of 10 and 50 nm. Its nano-entity will allow the fabrication of optically transparent OLED substrate as any element with size smaller than one-tenth of visible light wavelength is free of visible light-scattering. Moreover, up to the present time, in order to prolong the service lifetime of electronic device, this bacterial cellulose composite was further developed for water vapor transmission barrier [5] and surface smoothness [6], respectively.

Recently, on the other hand, small amount of carbon nanotube (CNT) incorporated on cellulose composite has been pioneered to re-discover as a smart material that can be utilized for sensors and actuators, so-called electro-active paper (EAPap). It commonly offered numerous advantages including lightweight, dryness, large deformation as well as minimal on power consumption. Due to this achievement on electro-active properties on cellulose modified by carbon-based material, not only elastic modulus and mechanical properties can be improved, but also, it can open to the wide vision on the development of successfully transparent and flexible cellulose composite with additional feature of touch screen characteristic. However, as the structure of cellulose was strongly evident as

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nano-fibril network. The important idea is to insert carbon nanotube in the air gap among cellulose chain and it may covalently be grafted at OH position in cellulose structure for not only electroactive but also mechanical properties if this cellulose will be further developed in industrial commercialization. Therefore, in this research work, we wish to extend our study on bacterial cellulose composite. Small amount of carbon nanotube was preliminary investigated by covalently grafted on bacterial cellulose composite for electro-mechanical properties purpose [7,8]. The actuator properties were evaluated by investigating on preliminary experiment on piezoelectric properties. This bacterial cellulose will exhibit excellent properties on "Touch Screen" feature in the near future.

2. Materials, instruments and methods

Materials: Bacterial cellulose was extracted from commercially available Nata de coco (Uno Foods product), an indigenous Filipino-originated dessert of which the main component was reported as bacterial cellulose. The characterization of transparent and flexible feature of bacterial cellulose from Nata de coco were carried out in our previous article [9]; and its characteristics matched those of bacterial cellulose extracted from the culture of *A. xylinum*. Polyurethane based resin was purchased from Ferguson Chemical Innovation, Brampton, ON, Canada. The specific gravity and density of resin are 1.120 and 9.35 lbs./gal., respectively. Irgacure 184 and Irgacure 819 as curing catalyst were supported from BASF, The Chemical Company, Florham Park, NJ, USA. Both resin and curing catalyst must be always stored in dark room in order to preferably avoid light sensitive problem. Carbon nanotube ($>95\%$ of carbon nanotube content) was purchased from Chengdu Organic Chemicals Company, Chinese Academy of Sciences, People Republic of China. The average diameter and length are less than 10 nm and 30 μm, respectively. Prior to use, carbon nanotube was dispersed in deionized water in order to prevent any agglomeration concern.

Instruments—Field emission scanning electron microscope (*FE-SEM*): The morphological properties of bacterial cellulose and its nanocomposite can be investigated by field emission scanning electron microscope (Hitachi, S-4800). It operated at acceleration voltage of 2 kV. Prior to investigation, the sample was stored in desiccators for humidity prevention. Then, each sample was subsequently placed on the carbon tape and follow by sputtered with gold particles before analysis.

Fourier transform infrared (*FTIR*): FTIR was performed on a Thermo Nicolet, NEXUS 670. The absorption peak was recorded over 4000–400 cm^{-1} wavenumbers region at a resolution of 8 cm^{-1} with 1024 scans using a deuterated triglycine sulfate (DTGS) detector.

Raman spectroscopy: The Raman spectra were excited by a Spectra-Physics model 127 He–Ne laser producing highly polarized light at 633 nm and collected at a nominal resolution of 2 cm^{-1}. The scattering peak was recorded over 1000 and 2000 cm^{-1}.

LRC meter: The dielectric constant and dielectric loss were measured by a precision LCR meter (Agilent E4980A) at room temperature and various frequencies ranging from 100 Hz–1 MHz. Prior to measurement, the sample was coated by silver paint as electrode on both sides.

Methods—Extraction and purification of bacterial cellulose: Bacterial cellulose was extracted from Nata de coco. The Nata de coco gel was first rinsed with distilled water and blended using a laboratory blender. The bacterial cellulose suspension was then treated in 0.1 M NaOH at 80 °C for 20 min to remove any remaining microorganisms, medium component and soluble polysaccharide. The purified bacterial cellulose was then thoroughly washed with distilled water until neutral pH. After extraction procedure, bacterial cellulose was kept under 4 °C in order to prevent any fermentation and prolong the lifetime of bacterial cellulose product.

Additional information on bacterial cellulose extraction and purification was explained this academic thesis [9].

Fabrication of carbon nanotube (CNT) reinforced bacterial cellulose, composite preparation: Prior to composite preparation, in order to disperse bacterial cellulose particle, the suspension was freeze-dried and consequently re-dispersed in DMF at 115 °C for 1 h, then, it was cooled down to 60 °C. In parallel, carbon nanotube (3 mg) as received was functionalized with carboxyl and hydroxyl groups by dimethylacetamide (10 ml) and lithium chloride (0.1 mg) treatment, after that it was continuously filtered and washed with deionized water until the pH reached to 7. The functionalized carbon nanotube was dispersed by sonication technique for 30 min.

In order to covalently grafted carbon nanotube on cellulose chain, functionalized carbon nanotube (3 mg) was poured with respect to that of cellulose (200 mg). The reaction was continuously performed for 30 min until it homogenize. After that, it was chemically esterified in microwave for 5 min.

To fabricate the composite, the bacterial cellulose sheet was first prepared from carbon nanotube grafted on bacterial cellulose and suspension. The water was removed from the suspension through filtration with a Buchner funnel fitted with Polyterafluoroethylene membrane filter (0.1 μm mesh, 90 mm diameter), which was connected to a Buchner flask and a vacuum pump. The volume of the carbon nanotube grafted bacterial cellulose suspension was adjusted to achieve a cellulose disc with the dried weight of 0.25 g. The filtration was continued until the wet sheet of cellulose was formed. The wet sheet was then dried between two Polyterafluoroethylene membranes under the applied pressure of 58 psi, following the paper hand sheet formation standard SCAN C 26:76. The dried cellulose sheet was then impregnated with PU resin and cured under UV at 25 mW/cm^2 for 3 min. As a reference, the neat PU based resin sheet was also fabricated in similar manner. All samples had the thickness of 0.3 mm. All experiments involving the resin were conducted in dark room as the resin was sensitive to light. The fiber content of the nanocomposite was 10–50 wt%.

3. Results and discussion

Carbon nanotube (CNT) grafted on bacterial cellulose preparation and characterizations: Bacterial cellulose was successfully exacted from Nata de Coco product. SEM investigation were used to study the size of bacterial cellulose. It can be seen that bacterial cellulose nanofibrils were about 50–100 nm in width and numerous micrometers long. The orientation of exacted bacterial cellulose exhibited three dimensional network structure, with air interstices in between. This is probably due to the fact that along bacterial cellulose molecular structure, there is hydroxyl group and it resulted in repulsive force acting among bacterial cellulose fibrils, disrupting the cohesion force among bacterial cellulose chain. This morphological properties of extracted bacterial cellulose from Nata de Coco product was consistent with our previous experiment [9].

Carbon nanotube (CNT) was well dispersed in deionized water and its particle size was roughly estimated as of 30–40 nm. The data was strongly associated with company's technical data sheet.

In order to investigate the covalently grafted carbon nanotube on bacterial cellulose by using sodium hypophosphite as reaction catalyst. Fig. 1 exhibits the FTIR spectra of chemically modifed bacterial cellulose structure. The carbonyl transmission peak at 1700 cm^{-1} and C–N stretching peak at 1350 cm^{-1} of chemically modified bacterial cellulose can be remarkably observed. The area below these peaks was able to explain that the amount of C═O