CHAPTER V

DEVELOPMENT OF TRANSPARENT BACTERIAL CELLULOSE NANOCOMPOSITE AS SUBSTRATE FOR FLEXIBLE ORGANIC LIGHT EMITTING DIODE (OLED) DISPLAY

5.1 Abstract

Nanocomposite film composed of bacterial cellulose (10 – 50 wt%) and polyurethane (PU) based resin was fabricated and utilized as a substrate for flexible organic light emitting diode (OLED) display. The performance of the nanocomposite satisfied the criteria for the substrate of OLED with an additional feature of flexibility. The visible light transmittance of the nanocomposite film was as high as 80 %. Its thermal stability was stable up to 150 °C while its dimensional stability in terms of coefficient of thermal expansion (CTE) was less than 20 ppm/K. After OLED was fabricated on the substrate through thermal evaporation technique, the OLED performed highest current efficiency of 0.085 cd/A and power efficiency of 0.021 lm/W at 200 cd/m^2 whilst retained its flexible feature, suggesting that bacterial cellulose nanocomposite is a promising material for the development of substrate for flexible OLED display.

5.2 Introduction

The push towards flexible electronic materials has been evident in the past decade. 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) is a versatile platform system that has attracted worldwide attention [1]. 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 [4-6, 142], the use of conventional polymer substrates has been limited by their coefficient of thermal expansion (CTE).

Okahisa et al. [6] and Choi et al. [8] 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 nanocomposite of nano-sized cellulose and polymeric matrices [9, 10]. 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 [143]. The incorporation of bacterial cellulose into polymeric matrix can be expected to yield a nanocomposite film with much decreased CTE. Bacterial cellulose has the typical thickness and width of 10 and 50 nm [144]. 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 [12, 13]. Bacterial cellulose is also an outstanding reinforcing agent for the design of environmentally friendly nanocomposites. It is renewable and biodegradable. The Young's modulus of its single fibril was measured to be as high as 114 GPa [14]. It also has attractive features of high degree of crystallinity (89 % [15]), high degree of polymerization (14400 [16]), and high specific area (37 m^2/g [17]).

The objective of this work is to develop a transparent and flexible nanocomposite film as a substrate for OLED display. OLED substrates composed of cellulose and polymers have been reported. Legnani et al. [5] prepared OLED substrate from bacterial cellulose sheet deposited with SiO_2. The OLED circuit was fabricated by radio frequency magnetron sputtering. Okahisa et al. [6] fabricated the OLED substrate from acrylic resin and acetylated cellulose nanofibre produced from wood powder. The OLED was fabricated by spin coating, sputtering deposition, vacuum deposition, and chemical vapor deposition. Yano et al. [143] and Nogi and Yano [144] created substrates from acrylic resin and bacterial cellulose pellicle. Iwamoto et al. [145] reported a substrate prepared from acrylic resin and kraft pulp. In this work, the nanocomposite substrate is composed of fibrillated bacterial cellulose and polyurethane (PU)-based resin. This work is an extension of our prior arts, which are the processing of bacterial cellulose [10] and the production of

nanocellulose from cellulosic biomass [9]. The aim of this work is to prove that our prior arts can be developed into a flexible OLED substrate. The nanocomposite was designed to comply with 'Green concept' [23-25], which was defined as the design of product and process that minimize the use and the generation of hazardous materials. The fabricated nanocomposite was characterized in terms of optical properties, thermal properties and dimensional stability to assess its potential as a substrate for the flexible OLED display. After OLED was fabricated upon the nanocomposite substrate via thermal evaporation technique, the performance of the fabricated OLED was evaluated through current density-applied voltage-luminance (I-V-L) relationship. The current and power efficiency were analyzed a function of luminance.

5.3 Methods

5.3.1 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 0.1M NaOH at 80 °C for 20 minutes to remove any remaining microorganisms, medium component and soluble polysaccharides, following Toyosaki et al. [28]. The purified bacterial cellulose was then thoroughly washed with distilled water until neutral pH.

5.3.2 Fabrication Of Bacterial Cellulose Nanocomposite

To fabricate the nanocomposite, the bacterial cellulose sheet was first prepared from bacterial cellulose 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 bacterial cellulose suspension was adjusted to achieve a bacterial cellulose disc with the dried weight of 0.25 g. The filtration was continued until the wet sheet of bacterial cellulose was formed. The wet sheet was then dried between two Polyterafluoroethylene membranes under the applied pressure of 58 psi, following

the paper handsheet formation standard SCAN C 26:76. The dried bacterial cellulose sheet was then impregnated with PU resin and cured under UV at 25 mW/cm^2 for 3 minutes. 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 %.

5.3.3 Organic Light Emitting Diode (OLED) Fabrication

OLED device was fabricated in a Kurt J. Lesker LUMINOS cluster tool with a base pressure of $\sim 10^{-8}$ Torr. Bacterial cellulose nanocomposite was ultrasonically cleaned with deionized water and ethanol followed by UV ozone treatment. The device structure was: copper (Cu) (200 nm)/ Molybdenum trioxide (MoO_3) (1.5 nm)/ 4, 4' – N, N' – dicarbazole – biphenyl (CBP) (50 nm)/ tris (8 – hydroxy – quinolinato) aluminium (Alq_3) (50 nm)/ Lithium fluoride (LiF) (1 nm)/ Aluminum (Al) (100 nm). The Cu anode layer was first deposited in a separate metallization chamber with a base pressure of $\sim 10^{-7}$ Torr. Then, patterned molybdenum oxide film was thermal vapor deposited using a shadow mask and treated by ex situ oxidation with UV ozone for 30 minutes. The substrate was then loaded into the cluster tool again to complete other layers. The organic layers and LiF layer were deposited in a dedicated organic chamber with a base pressure of $\sim 10^{-8}$ Torr. The Al cathode line was consequently deposited in a separate metallization chamber with a base pressure of $\sim 10^{-7}$ Torr. The thickness of each layer was precisely controlled via a calibrated quartz crystal microbalance.

5.4 Results And Discussions

5.4.1 Bacterial Cellulose Nanocomposite Preparation And Characterization

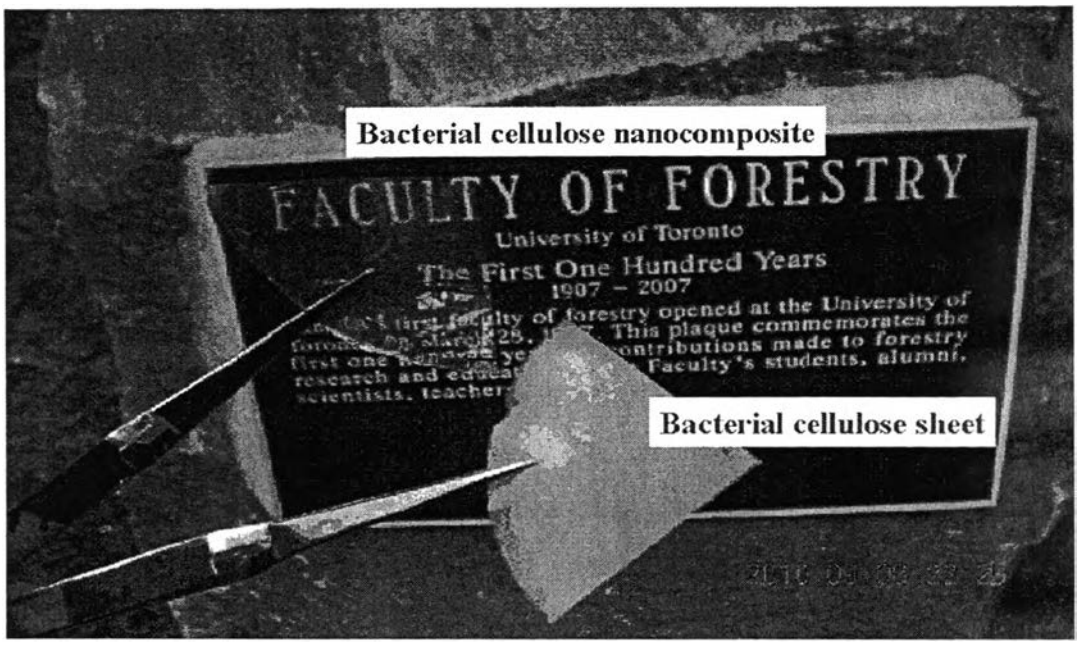

Figure 5.1 Optical transparency of bacterial cellulose nanocomposite film and bacterial cellulose sheet.

Bacterial cellulose microfibril is 10 nm in width and 50 nm in thickness [11], which is smaller than one-tenth of the visible light wavelength (400 – 800 nm); therefore it is free from light scattering [12, 13]. However, Figure 23 shows that the bacterial cellulose sheet is not optically transparent and that the nanocomposite is clearly much more optically transparent. Bacterial cellulose sheet can be considered as a three-dimensional network structure of nano-sized fibers with air interstices in between. The opacity of the bacterial cellulose sheet can be ascribed to the light diffraction at the interface between the cellulose fiber and the air interstices. On the other hand, the bacterial cellulose nanocomposite did not contain air interstices; the interstices were replaced with the PU-based resin of which the refractive index (RI) is close to that of the bacterial cellulose. The matching RI of the PU-based resin and the cellulose means that the light diffraction at the interface between the two components will be restricted and that the transparent film can be achieved. The RI of the nanocomposite and the neat PU-based resin were measured as showed in Figure 5.2 and Table 5.1. In comparison, the RI of cellulose has been reported as

1.618 along the fiber axis and 1.544 in the transverse direction [144]. In Figure 5.2, it can be observed that RI decreases as the wavelength increases – such relationship complies well with the Cauchy relation [85]. Here the PU based resin also helped to encapsulate the bacterial cellulose sheet and protect it from moisture and the surrounding atmosphere. Cellulose is highly hydrophilic, whilst moisture is known to greatly reduce the lifetime of OLED devices [8]. Effective moisture and air barrier properties are vital to the performance of OLED.

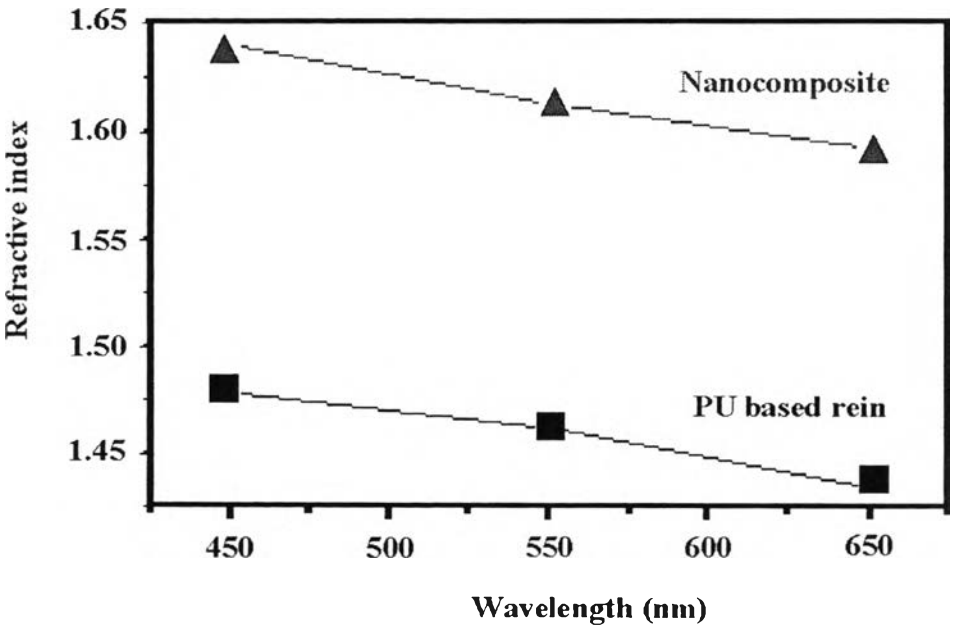

Figure 5.2 Refractive indices of neat PU based resin and bacterial cellulose nanocomposite as a function of wavelength.

The smooth surface of the bacterial cellulose nanocomposite also contributed to the transparency of the film as the light diffraction at the surface will be uniform. On the contrary, the relatively-rougher surface of the bacterial cellulose sheet will make light diffracts in a more random fashion. Figure 5.3 illustrates AFM images of bacterial cellulose sheet (Figure 5.3a) and bacterial cellulose nanocomposite (Figure 5.3b) taken with lateral contact mode. In this work, five AFM images were taken at different areas on the sample, all of which revealed comparable topologies. The

AFM scan size (40 μm x 40 μm) implied the uniformity of the surface roughness. It can be observed that the smoothness of the bacterial cellulose sheet was immensely improved after the impregnation of PU resin. The sheet roughness reduced from 2.711 μm to 33.33 nm as the micron-scale pores of the bacterial cellulose sheet was filled with the resin.

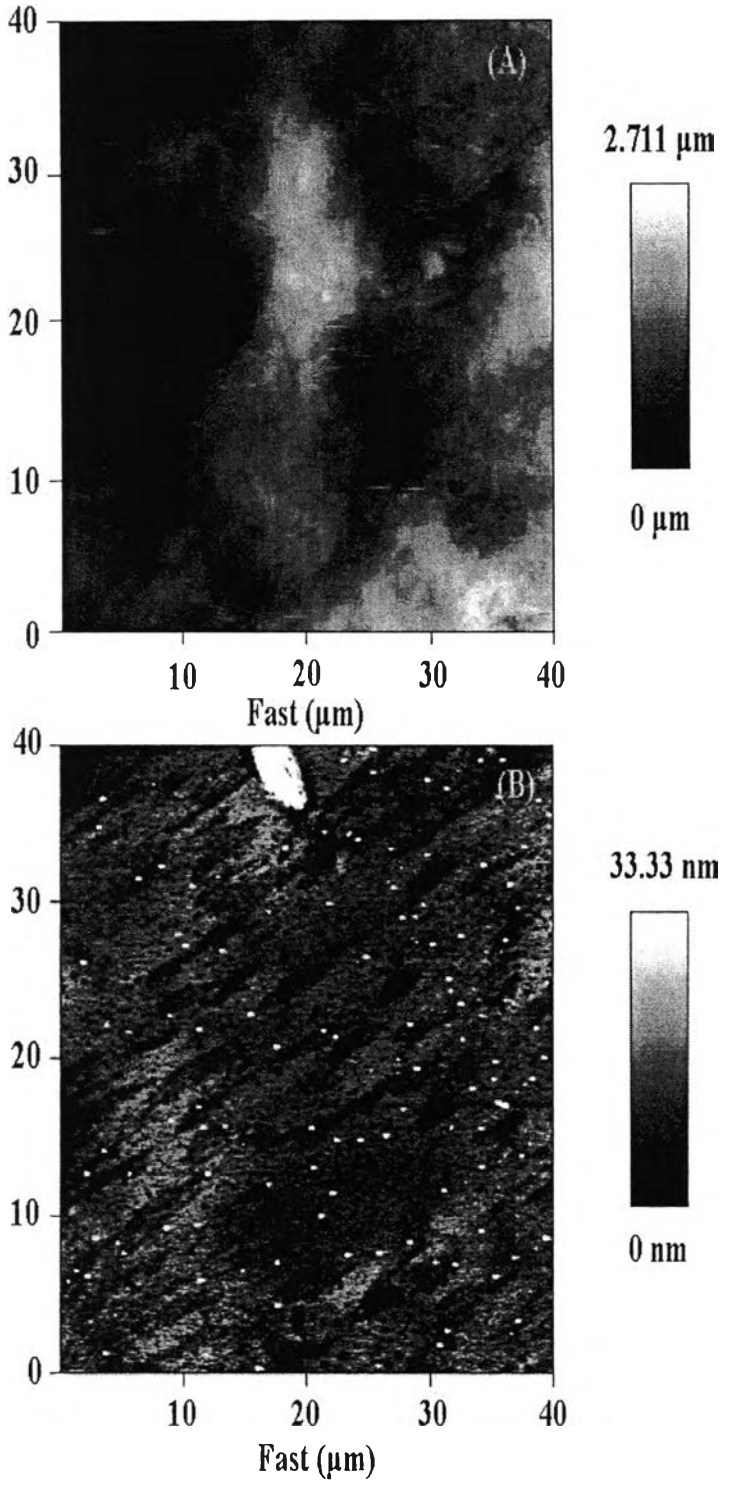

Figure 5.3 AFM investigation of (A) bacterial cellulose sheet and (B) bacterial cellulose nanocomposite

Table 5.1 Thermal and optical properties of bacterial cellulose, neat PU resin, and nanocomposite.

	Bacterial Cellulose	**PU Resin**	**Nanocomposite**
Glass Transition Temperature (C°)	-	16	16
Degradation Temperature (°C)	350 [10]	265	345
CTE (ppm/K)	0.1 (Fiber) [11] 4 (Sheet)	18	50
RI	1.618 (Axial) [144] 1.544 (Transverse) [144]	1.478 at 450 nm 1.462 at 550 mn 1.433 at 650 nm	1.640 at 450 nm 1.613 at 550 nm 1.592 at 650 nm

[10] Juntaro 2009

[11] Yano et al. 2005

[144] Nogi and Yano 2008

The light transmittance of neat PU-based resin and bacterial cellulose nanocomposite were demonstrated in Figure 4.4. Bacterial cellulose nanocomposite offered high transmittance of in the range of 75 – 87 % in the visible light wavelength (400 – 800 nm). Such high light transmittance satisfied the transparency criteria for the OLED substrate of 80 %, according to Choi et al. [8], suggesting the nanocomposite as a potential candidate for flexible OLED substrate.

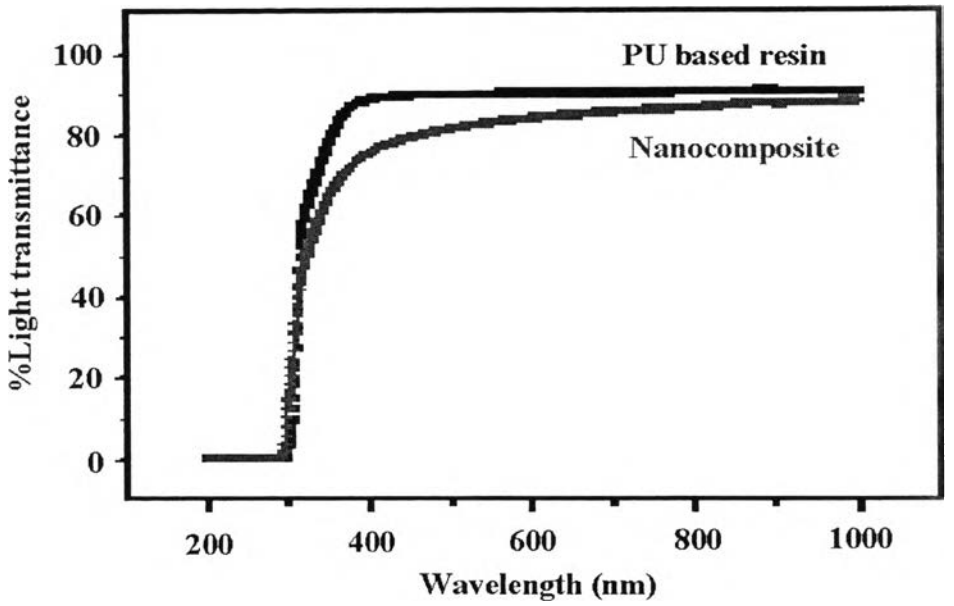

Figure 5.4 Regular transmittance spectra of PU based resin and bacterial cellulose nanocomposite.

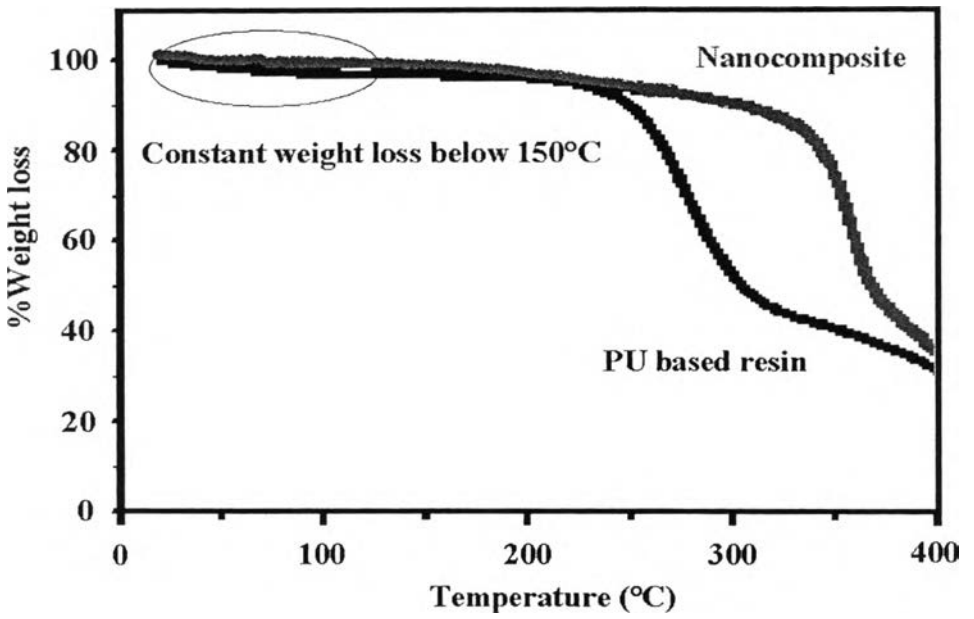

Figure 5.5 TGA thermogram of neat PU based resin and bacterial cellulose nanocomposite.

Thermal properties of the neat PU based resin and the nanocomposite were analyzed with TGA and DSC (Figure 5.5, Figure 5.6 and Table 5.1). The thermal decomposition behaviors of the PU based resin and the bacterial cellulose nanocomposite showed that both samples were thermally stable up to 150 °C. TGA revealed the PU based resin had the degradation temperature of 265 °C while the nanocomposite had the higher degradation temperature of 345 °C. In comparison, pure bacterial cellulose had the degradation temperature of 370 °C. The incorporation of bacterial cellulose into the PU-based resin led to an improvement in the degradation temperature, which can be ascribed to the strong interaction between bacterial cellulose and the PU-based resin, i.e. hydrogen bonding between the hydroxyl groups in cellulose and oxygen atoms in urethane unit. On the other hand, DSC revealed that bacterial cellulose did not significantly affect the glass transition temperature of the PU resin. Both the PU resin and the nanocomposite expressed glass transition at approximately 16 °C (Figure 5.6).

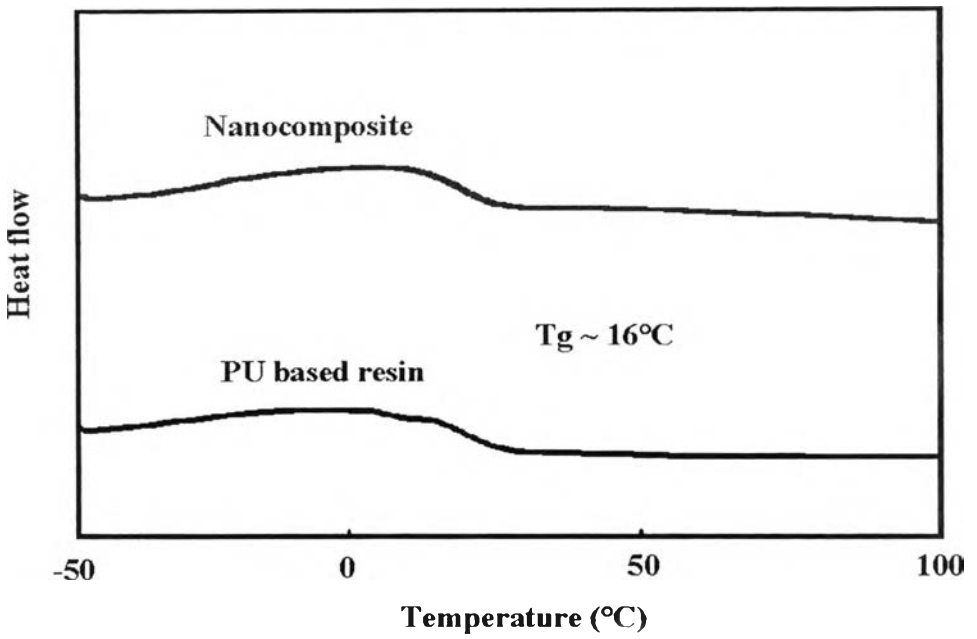

Figure 5.6 Heat flow curve of neat PU based resin and bacterial cellulose nanocomposite.

The dimensional stability of the nanocomposite was measured in terms of coefficient of thermal expansion (CTE). The CTE of bacterial cellulose fibril has been reported as 0.1 ppm/K in the axial direction. The low CTE is stable up to 120 °C [143]. In this work, bacterial cellulose in the sheet form and neat PU based resin exhibited CTE of 4 and 50 ppm/K respectively (Table 5.1). The bacterial cellulose sheet drastically reduced the CTE of nanocomposite to an ultimate value of 18 ppm/K, which is below the criteria for the OLED substrate of less than 20 ppm/K [6, 8]. This result suggested bacterial cellulose nanocomposite as a promising candidate for flexible OLED substrate.

5.4.2 Organic Light Emitting Diode (OLED) Performance

In this section, the potential of bacterial cellulose nanocomposite as flexible OLED substrate was evaluated. Each layer of the OLED was fabricated via vapor deposition technique. In this technique, reacting material will evaporate and crystallize into the form of epitaxial thin film, depositing onto the substrate surface.

This deposition technique is widely accepted as one of the most effective methods in creating thin film with uniform thickness. After the OLED was successfully fabricated on the flexible nanocomposite substrate, the fabricated OLED could emit light when it was flat (Figure 5.7a), and bended (Figure 5.7b). The ability of the fabricated OLED to emit light even when it was bended suggested its potential as an alternative substrate to the commonly-used glass sheet with additional feature of flexibility. Here the flexibility of the fabricated OLED is showed only qualitatively. Note that to quantitatively assess the flexibility of the OLED is not in the scope of this work. OLED was operated under forward bias voltage - Cu and Al acted as anode and cathode respectively. Holes were injected from anode into the highest occupied molecular orbital (HOMO) state and started to move towards the emitter CBP layer. On the other hand, electrons were injected from the cathode into the lowest unoccupied molecular orbital (LUMO) state of the organic layers and started to move in the opposite direction towards the emitter CBP layer at the same time. Both holes and electrons accumulated at the emitter CBP due to large energy barrier. Recombination of holes and electrons formed 'exciton,' leading to photoemission in the CBP layer. Note that all the experiments were performed at ambient atmosphere without device encapsulation.

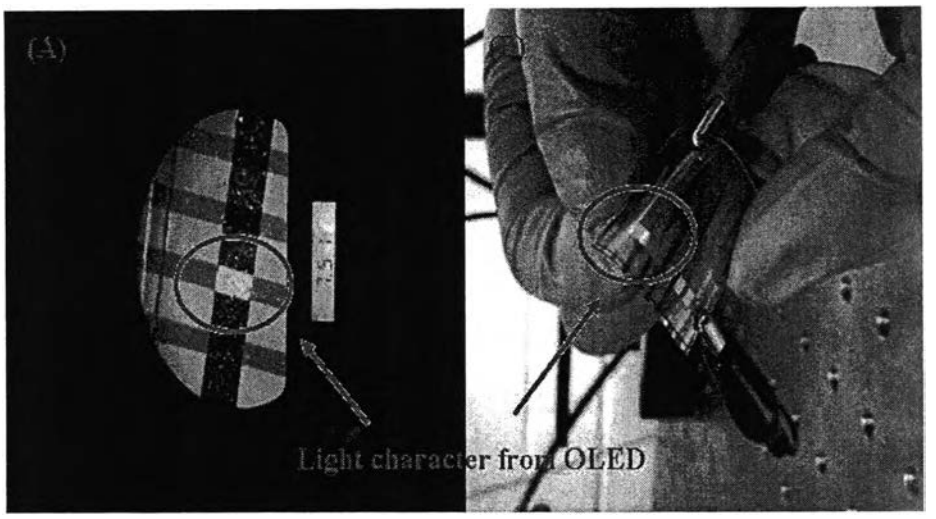

Figure 5.7 Organic light emitting diodes (OLED) on bacterial cellulose nanocomposite.

Figure 5.8 showed the current density and luminance as a function of applied voltage (I-V-L) of the successful OLED. Light emission from CBP was observed for the applied voltage in the range of 0 to 16 V. It was important to note that the small operational voltage of the device is preferred to prevent the destruction of the device. In this work, the fabricated OLED started to give photoemission at the low voltage of approximately 12 V, which was comparable to the OLED fabricated on commercial glass substrate. The effective performance of the device can also be ascribed to the uniform layer thickness. The smooth surface is also a vital key in enhancing the device lifetime and efficiency.

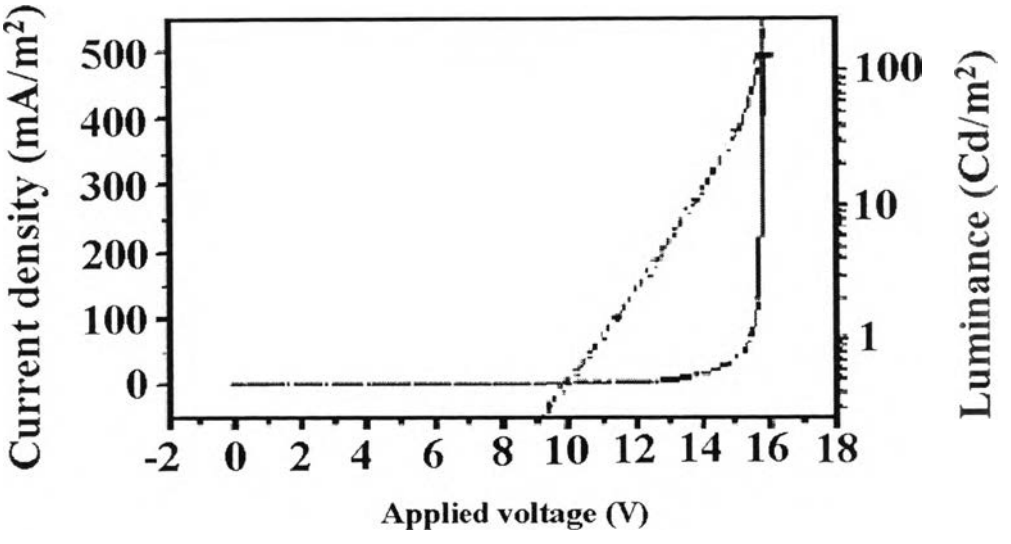

Figure 5.8 I-V-L characteristic of OLED.

The efficiency of the OLED is illustrated in Figure 5.9. The luminance of the OLED was approximately 100 cd/m^2 at 16 V, and increased with the applied voltage up to 200 cd/m^2. The current and power efficiency reached maximum at 0.085 cd/A and 0.021 lm/W at 200 cd/m^2 respectively. The luminance efficiency started relatively high and remained stable up to 200 cd/m^2 and then dropped rapidly.

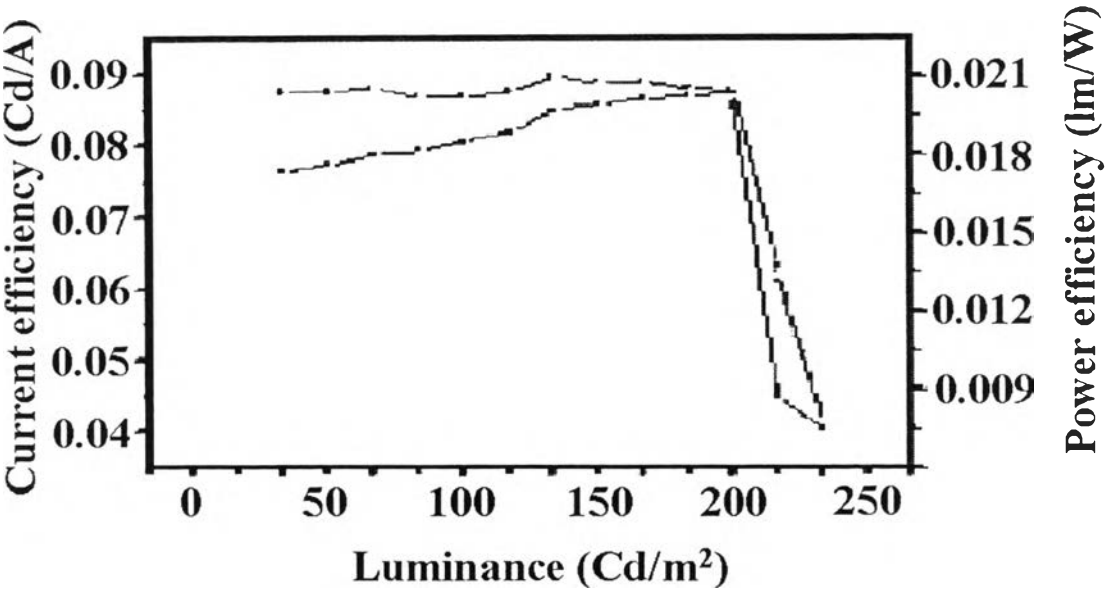

Figure 5.9 Efficiency vs luminance characteristic of OLED.

5.5 Conclusion

Transparent and flexible nanocomposite composed of bacterial cellulose and PU based resin was successfully prepared and used as a substrate for OLED. The nanocomposite had appealing features of flexibility, optical transparency, high light transmittance of up to 80 % and dimensional stability in terms of CTE of as low as 18 ppm/K. These features satisfied the criteria for the OLED substrate. After OLED was successfully fabricated on the nanocomposite via thermal evaporation deposition, it exhibited promising performance; it could emit light even when it was bended. This work proves that bacterial cellulose nanocomposite is a promising environmentally friendly candidate for the substrate of flexible OLED display.

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