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Development of chemically grafted multiwall carbon nanotube onto cellulose fiber sheet and polyurethane based resin composite for an active paper

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Abstract

Cellulose fibers (CFs) and carbon nanotubes (CNTs) were successfully developed on polyurethane substrate as a flexible composite paper. With small amount of CNTs, the composite was prepared by a suction filtration method. The existence of CNT additive in cellulose matrix was investigated based on the correlation of mechanical properties, thermal stability, and electrical properties. Although the highly transparent cellulose sheets impregnated with polyurethane were successfully fabricated, the low transmittance was obtained as the increasing of CNT additive. However, the dielectric properties of composite were enhanced with an addition of CNTs in the composite paper. The electrical conductivity was increased from the insulator to 4.91×10^{-4} $S \cdot cm^{-1}$ at small amount of CNTs of 5 wt%. In addition, the minimal amount of CNTs of 1.5% showed the transmittance of 35%, adequate dielectric constant, and the conductivity of 5.59×10^{-7} $S \cdot cm^{-1}$. The role of CNTs with well distribution presents as a polar cluster of well-defined electrically charge in cellulose composite.

1. Introduction

The push towards to the development on bio-based material has been evident for a decade. Numerous approaches have been extremely developed by means of many strategic techniques for utilization of bio-based material for engineering sector such as active packaging, automotive part, medical device as well as electronic component [1-3]. One of the most important applications was focused on the utilization of bio-based material in electronic device. It was remarkable to note that utilization of flat glass sheet was commonly employed as a substrate. Although it provided significance in term of device efficiency, it was therefore limited due to brittleness and processing cost. Utilization of flat glass sheet was also inefficient due to large amount of product with respect to processing time. The development on flexible electronic substrate was therefore considered for device efficiency. From the fundamental point of view, it was remarkable to note that flexible electronic substrate was suitable for short processing and large amount of product and been able to be fabricated by roll to roll (R2R) and printed process. In order to overcome this technical issue, transparent plastic was pushed to develop as flexible substrate for electronic device. Numerous transparent plastics were encouraged due to low cost and flexible technique of fabrication. However, in the particle use, utilization of flexible plastic was still limited due to thermal expansion when device was operated, and its influence was therefore affected on device lifetime [4].

To solve this issue, cellulose fiber was considered for flexible electronic device substrate. It was important to note that cellulose exhibited low thermal expansion, high stiffness as well as high chemical stability. The development of cellulose based composite for electronic device has been extensively gained many interests in order to replace flexible plastic in electronic device [5-6]. Moreover, utilization of cellulose based composite was also encouraged on the support of Green concept; which was referred to the support of process of non-toxicity and hazardous reagents [7]. Therefore, utilization of cellulose based composite was encouraged to develop due to socio-economic purpose.

Cellulose based substrate has been considered for many electronic device researches such as sensor, paper displays, supercapacitors and solar cell [8-9]. Typically, Indium Tin Oxide (ITO) glass and Fluorine Tin Oxide (FTO) glass are used for optoelectronic device substrate. Special properties of oxide glass are electrically conductive and optically transparent, good uniformity of optical transmissivity, but liable to break or shatter easily [10]. To use as a supporting layer for flexible optoelectronic device, it has succeeded in using cellulose nanocrystal substrates (CNC) for recycled device [11,12]. Consequently, many researchers have developed transparent and conductive cellulose substrate by adding high conductivity materials into cellulose, so called active paper.

Many types of conductive materials such as polyaniline (PANI), polypyrrole (PPy), graphene oxide, silver nanowires, and carbon nanotube (CNT) are considered for cellulose composited materials with the advantages of cellulose and additive [13-17]. One of the promising materials is carbon nanotube with excellent mechanical properties and composited paper was lowered to 200 $\Omega \cdot sq^{-1}$ [18]. Moreover, the

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CNTs/cellulose composite fiber show the multifunctional sensing abilities [19]. Recently, high conductivity composite nanopaper of 200 S·m^{-1} has achieved by using single-wall nanotube (SWNTs) and nanocellulose fiber (CNF) [20]. Moreover, using NaOH treatments, the conductivity of CNTs/CNF can be enhanced to be 17 S·m^{-1}, but with 50 wt% CNTs [21]. Most previous works showed that the transmittance of CNTs/cellulose composites was rather low. Because the conductivity enhancement is required, the carbon nanotube is also used at high concentration, which reduce the transparent property of CNTs/cellulose composite. Nevertheless, the transparent and conductive SWNTs/TEMPO-Oxidized nanocellulose (TOCN) was achieved with the resistance of 1.2 kΩ and transmittance of 70% at the wavelength of 600 nm [22]. In that work, the CNTs/TOCN was coated on polyethylene terephthalate (PET) films and the special nanocellulose type is required. Alternatively, to fabricate the highly transparent cellulose composite, the resins is frequently used to enhance the transparent property [23]. The polyurethane (PU) is one of the promising resins with low density, thermal conductivity, moisture permeability and dimensional stability [24,25]. Recently, the cellulose/PU composites enhanced the transparency up to 90% and mechanical properties [24]. However, the cellulose/PU composites are still lack of conductive

In this work, chemically grafted multiwall CNT onto cellulose was developed. Modified cellulose fiber and polyurethane resin-based composite was successfully prepared. The mechanical properties, electrical conductivity and optical transparent were characterized based on the various amount of CNTs concentration. Then, properties of composite materials will be discussed on the electronic substrate approaches.

2. Materials and Methods

2.1 Materials

Cellulose fiber was received as a gift from SCG packaging public company limited, Thailand. It was stored in desiccator in order to prevent the moisture adsorbent. Multiwall carbon nanotube (MWCNT, purify 90%, averaged diameter: 10 nm.) is purchased from NANOGEN company, Thailand. Polymer used in this research is an aliphatic polyester based urethane di-acrylate (PU) oligomer blended with 10% with SR256, 2(2-ethoxyethoxy) ethyl acrylate. It is a highly flexible oligomer offering good weather ability from SARTOMER company.

2.2 Methods

2.2.1 Cellulose suspension

The cellulose pulp with the width of 10 cm and length of 10 cm was rip and peel to be thin sheets. Then the thin sheets were mixed with deionized water (DI water) 500 mL for 5 days under the mechanical stirring of 500 rpm. The obtained cellulose suspension was concentrated and subsequently washed with distilled water [17,26].

2.2.2 Composite Preparation

The cellulose and carbon nanotube composite were prepared in the following manner. Cellulose of 0.188 g was suspended in DI water of 500 mL and stirred for 30 min, then the cellulose suspension was obtained. After that, the carbon nanotube (CNT) powder was added into the cellulose suspension and mixed it with ultrasonic bath for 30 min, and then mechanical stirred for 30 min. Then, the carbon nanotube will be chemically grafted on the cellulose by the formation of covalent bonds between cellulose and CNT. In previous report, the C=O and C-O-C bond stretching of the ester was observed [27]. According to previous work [22], the mechanical and electrical properties can be affected by the aspect ratio of CNT and cellulose. Herein, the concentration of CNT in the cellulose matrix was set at 0.5, 1.5, 2.5 and 5.0 wt%. The solvent was removed from the solution through filtration with a Buchner funnel fitted with membrane filter (0.1 mesh, 90 mm diameter) for overnight [28]. The filtration continued until a wet sheet of cellulose/carbon nanotube composite formed. The wet sheet was then dried between two membranes under an applied pressure of 1 kPa for 2 days. Polyurethane (PU) gel was prepared by mixing of PU and α-Hydroxyketone at the concentration of PU of 10 wt% and then casted on transparent plastic sheet by doctor blade technique. The freestanding CFs/CNT composited film was placed on the PU gel. The CFs/CNT on PU film was vertically kept and dried in ambient for 24 h, and then UV post-cured for 3 h. Finally, the CFs/CNT composited film on PU substrates can be achieved.

2.3 Characterization Techniques

2.3.1 Field emission scanning electron microscope (FE-SEM)

The morphological properties of the CFs/CNT composites were investigated with FE-SEM (Hitachi, S-4800) at an acceleration voltage of 2 kV. Prior to the investigation, the samples were stored in desiccators for reduced humidity. Each sample was placed on carbon tape and sputtered with gold particles before being analyzed. The root mean square surface roughness of CFs/CNT composite sheets were estimated using SurfCharJ plugin [29] on the ImageJ software.

2.3.2 UV-vis spectroscopy

The light transmittance spectrum of the conductive cellulose films was measured at wavelength from 200 nm to 1000 nm by using a UV-Visible spectrometer with a SHIMADZU; UV-2600.

2.3.3 Thermogravimetric Analysis (TGA)

The TGA characteristics of the CFs/CNT composite were investigated by TGA (MET- TLER TOLEDO, TGA/DSC3+1600, Switzerland). Each sample was heated at a heating rate of 10°C·min^{-1} under nitrogen atmosphere from room temperature to 700°C.

2.3.4 Differential scanning calorimetric (DSC)

DSC (DSC 204F1 Phoenix) of the PU and CFs/CNT composite was performed in the temperature range of 10°C·min^{-1} under nitrogen atmosphere from -100°C to 350°C. 10 mg of samples were tested.

2.3.5 Mechanical properties determination

The sample was cut into the rectangle with the width of 20 mm and the gauge length of 30 mm. The thickness was 0.07-0.09 mm. The testing speed was 5 mm·min^{-1} and the test was carried out 3 times per sample. The tensile tests were conducted using as Instron Universal material testing machine (Instron 55R4502, S/NH 3342) equipped with a 100 N load cell.

2.3.6 Dielectric properties

The dielectric constant and loss tangent were measured using a precision LCR meter (Agilent 4294A) at room temperature and at various frequencies ranging from 10^2 Hz to 10^6 Hz. Prior to analysis, samples were coated on both sides with silver paint.

2.3.7 Conductivity

The samples were cut with the dimension of 50 × 50 mm^2. Four Point Probe System was used to characterize the conductivity properties of CFs/CNT substrate. The cylindrical four-point probe head (Jandel Engineering Limited) were used with the Jandel RM3000 test unit.

3. Results and discussion

3.1 Field emission scanning electron microscopy (FE-SEM)

Figure 1 shows that the morphological properties of CFs/CNT on PU substrates with various CNT concentration have no significant differences. Because the CFs/CNT sheets were submersed on the PU gel during the preparation process, the CFs/CNT sheets were embedded in the PU substrates. Moreover, the diameter of CNTs is significantly smaller than that the diameter of macro cellulose fiber. Thus, from Figure 1, the existence of CNTs is difficult to identify. At higher magnification, it is clearly seen that the CNTs was immersed in the PU surface as shown in Figure S1. However, the wrinkle on the cellulose fiber surface can be observed when the CNTs were added, indicating that the CNTs may be formed on cellulose structure. In addition, the CNTs may fill the porous structure and form a secondary bond with hydroxyl group of cellulose fiber. From the morphological properties of the composites, the cellulose formed a network, and the surface of the composite illustrates the orientation of the cellulose fibers. The orientation of cellulose fiber was non-uniformed, which presents as a network for the whole figure. The diameter of cellulose fiber was estimated to be 30 μm with a variation in length. The average roughness of all cellulose based CNT composite is approximately 3.749 μm, which is rather close to the roughness of pure cellulose fiber of ca. 3.750 μm. Such rather similar roughness of pure cellulose fiber and cellulose based CNT composite may be caused by the coating of PU resin. However, this surface roughness of cellulose sheets is important when another conductive layer was deposited onto cellulose surface. It can be suggested that the roughness of all celluloses-based CNT composite has similar effect on the performance of flexible electronic device.

3.2 UV-Vis Spectroscopy

Figure 2(a) presents the transmission of cellulose-based composite. With the existence of CNT, the composite became opaque due to the absorption of CNT. It was also remarkable to note that with higher amount of CNT, the light transmittance was significantly low. This phenomenon can be suggested that utilization of cellulose and CNT composite for optical device should be concerned on the existence of CNT and its distribution. The quality of optical device was less when higher CNT was added. It may provide the light scattering and absorption when incident beam of light was interacting onto the surface of cellulose and CNT composite. However, the optical transmittance of more than 35% in the visible region of wavelength can be observed with the CNT ratio of less than 1.5%. This suggested that the cellulose-based CNT composite with high ratio of more than 1.5% is not practical used for transparent electronic substrate.

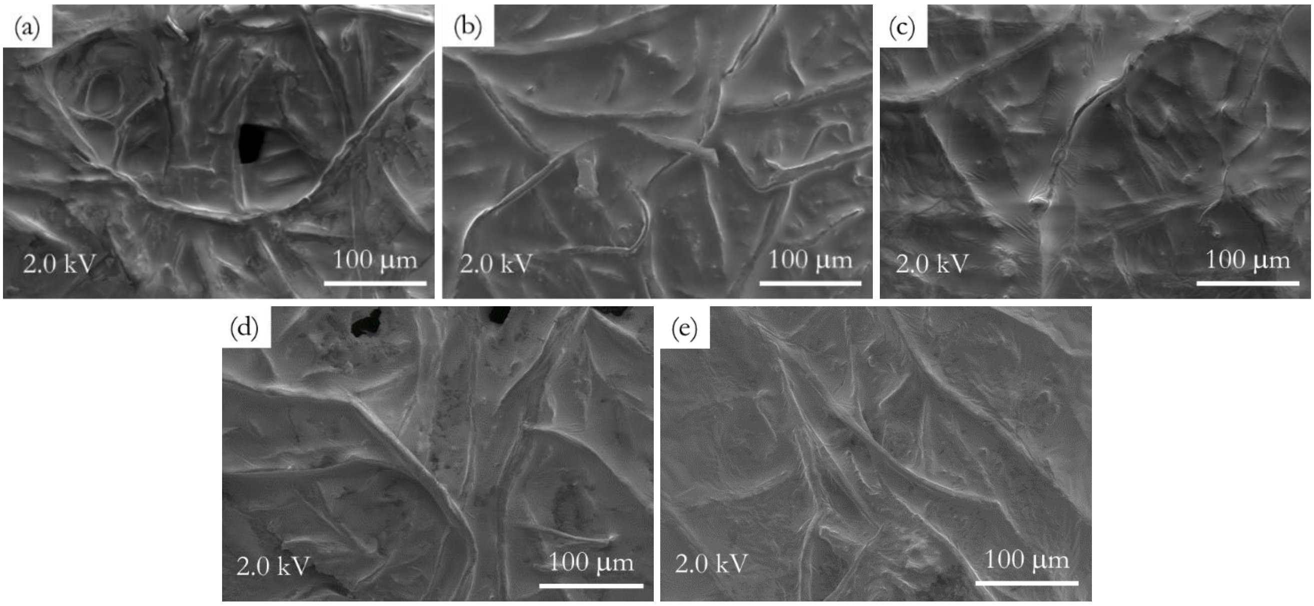

Figure 1. FE-SEM of the CFs/CNT all neat PU resin, (a) CFs without CNT, (b) CFs/CNT 0.5, (c) CFs/CNT 1.5, (d) CFs/CNT 2.5, (e) CFs/CNT 5.0.

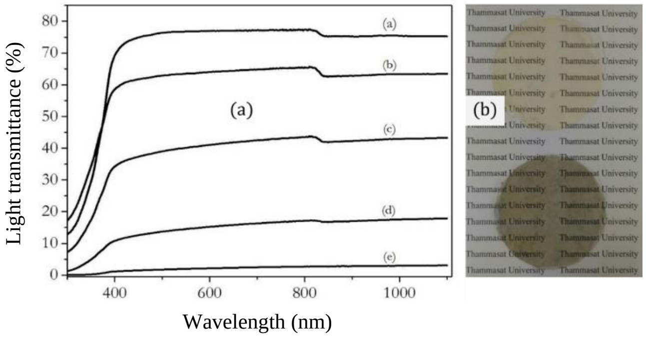

Figure 2. (a) UV – Vis spectroscopy of the CFs/CNT all neat PU resin, (a) CFs without CNT, (b) CFs/CNT 0.5, (c) CFs/CNT 1.5, (d) CFs/CNT 2.5, (e) CFs/CNT 5.0. (b) Image of the CFs/CNT all neat PU resin (top) CFs without CNT and (bottom) CFs/CNT 0.5.

3.3 Thermo gravimetric Analysis

TGA revealed that polyurethane has the degradation temperature of 265°C [22]. All of curves were typically similar. The incorporation of CFs/CNT sheet into the polyurethane resin led to an improvement in the degradation temperature. From Figure 3, it can be categorized into three different regions by weight loss. From room temperature to 250°C, a slightly decrease in weight was observed. Only 10 wt% of weight loss was therefore evaluated. However, the weight loss was occurred due to the evaporation of water and solvent. This was probably due to the presence of moisture onto cellulose fiber surface. As the temperature increased into the region of 250-450°C, the broad region of weight loss was significantly observed. 80% of weight loss was thus determined. In this temperature region, it typically related to thermal decomposition of the composite. The decomposition of cellulose and polyurethane was changed to volatile gas such as CO_2 and NO_x. However, it was remarkable to note that with the existence of CNT, the curve of weight loss was slight shifted to higher. It can be implied that with the presence of CNT, thermal stability of cellulose fiber and polyurethane was therefore increased. Furthermore, when temperature is above 450°C, the weight loss remained constant. All CFs/CNT composites were changed to be char and residual. The percent yield of final product was estimated to be approximately 5-10 wt%. It was notable that with the presence of CNT, the percent of char was slightly higher compare to pristine cellulose fiber and polyurethane composite.

3.4 Differential scanning calorimetric

Figure 4 presents the DSC thermogram of cellulose-based composite. The polyurethane resin expressed glass transition temperature of -70°C and -30°C [28]. These temperatures were indicated as a soft segment and hard segment of polyurethane, respectively. The soft segment was typically related to a polyether and/or polyester polyol while the hard segment was composed of a diisocyanate and chain extender. However, it can be noted that when CFs/CNT was integrated into polyurethane resin, the glass transition temperature regions were estimated to be -65°C and -25°C, respectively. The incorporation of CFs/CNT composite into the polyurethane resin led to increase in the glass transition temperature of polyurethane. It can be explained that for neat polyurethane-based resin, the polymeric chain was easy to move when applied temperature was elevated. The existence of cellulose fiber in polyurethane provided the difficulty of chain movement. From the fundamental point of view, cellulose present high crystalline part and it was subsequently affected onto polyurethane movement when external heat was applied. In addition, the existence of CNT was also affected. It existed as a small particle embedded into cellulose network and filled into polyurethane resin. It presented a high thermal degradation. The glass transition temperature of composite was therefore enhanced with respect to the existence of CNT and cellulose. In case of flexible substrate, CFs/CNT filled into polyurethane composite was successfully prepared.

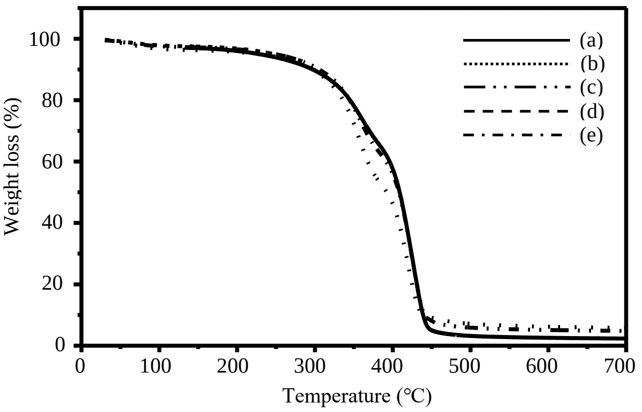

Figure 3. Thermo gravimetric of the CFs/CNT all neat PU resin, (a) CFs without CNT, (b) CFs/CNT 0.5, (c) CFs/CNT 1.5, (d) CFs/CNT 2.5, (e) CFs/CNT 5.0.

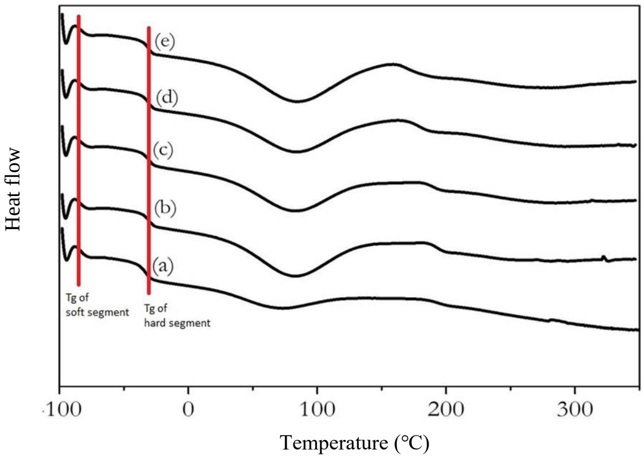

Figure 4. Differential Scanning Calorimetric of the CFs/CNT all neat PU resin, (a) CFs without CNT, (b) CFs/CNT 0.5, (c) CFs/CNT 1.5, (d) CFs/CNT 2.5, (e) CFs/CNT 5.0.

3.5 Mechanical properties

The mechanical properties of the CFs/CNT composite neat PU resin investigated. Table 1 exhibits the tensile strength, Young's modulus, and elongation at break. The tensile strength, Young's modulus, and elongation at break of the composite were significantly increased by the amount of CNT. Also, it clearly sees that the tensile strength and Young's modulus of CFs/CNT composite were enhanced from the CFs neat sheet. However, the elongation at break of all CFs/ CNT

Table 1. Mechanical of the CFs/CNT all neat PU resin.

Composite	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
CFs	1.84 ± 0.05	72.41 ± 7.99	3.89 ± 0.82
CFs:CNT0.5	2.77 ± 0.16	174.86 ± 16.59	2.83 ± 0.20
CFs:CNT1.5	3.01 ± 0.28	221.53 ± 65.76	3.14 ± 0.35
CFs:CNT2.5	4.16 ± 0.26	241.33 ± 39.25	3.34 ± 0.06
CFs:CNT5.0	4.08 ± 0.42	261.19 ± 16.91	3.43 ± 0.08

are lower than that of CFs neat sheet. No significant change on mechanical properties was observed between neat polyurethane and composite. This was probably due to the fact that the amount of CNTs was still less, and it was also embedded into cellulose network and PU substrate. At low amount of CNTs, the crosslink between CNTs and cellulose was not perfectly formed, instead, the CNTs may arrange on the cellulose surface and cause the defects in the cellulose/PU composites. Consequently, the elongation at break of low amount CNTs is low. However, as the amount CNTs increase, the elongation at break is slightly increased due to the crosslink formation between CNTs and cellulose fiber. The mechanical properties were only dependent on amount of cellulose. This material presented as a high stiffness and, consequently, it may discard on mechanical properties.

3.6 Dielectric properties

The dielectric properties of CFs/CNT composite films were investigated. The dielectric constant and loss tangent of the CFs/CNT composite at difference frequency is presented in Figure 5. Notably, the dielectric properties were high at low frequency, and slightly decreased as the increasing of frequency. The phenomenon can be expressed by relaxation behavior. With high region of frequency, the charge has insufficient time of re-orientation under applied external frequency. Although the bacterial cellulose base composite has presented as a lower on dielectric properties [28]. Here, slightly high cellulose-based CNT composites were presented. Recently, the dielectric constants with more than 500 at 10^2 Hz have been investigated from nano fibrillated and micro fibrillated cellulose films [30]. The size of cellulose fiber is very crucial important for dielectric constant as well as the polymer coating [31]. As shown in Figure 5, high dielectric constant and loss tangent can be observed from CFs/CNT 5.0 at all frequency regions. This condition can be explained that CNT was well distributed into cellulose and polyurethane composite. It exhibited as an island-like structure embedded in cellulose network. There is no conductive pathway of CNT along composite structure. This was called as a percolation threshold of dielectric material prior to alteration to conductivity. This composite was successfully designed for flexible electronic. The high dielectric constant represents the high electric polarization material, which probably use as dielectric energy storage [32]. As we expected, the low dielectric constant was obtained at all frequency ranges from CFs neat PU sheet, which represents the insulating property. The increasing of dielectric constant and loss tangent was observed when the CNT amount increased. In case of loss tangent, the energy loss is due to the electric dipole orientation, the ion movement, and the ion oscillation. The existence of PU may affect the dipole orientation and ion movement; hence, the loss tangent is rather low for CFs neat sheet and CFs/CNT at low amount. However, the high amount of CNT may increase the homogeneity and porous of CFs/CNT sheet, consequently, the loss tangent is increased. The increasing of dielectric constant and loss tangent due to the increasing of CNT is coincidence with the previous results [32]. Note that the difference of dielectric constant and loss tangent may be resulted by the difference type and diameter of the CNTs [33].

From Figure 5, high dielectric constant is CFs/CNT composite sheet in condition 5%. It is a dielectric material that can store electrostatic charge. From dielectric properties, refraction index (RI) can be calculated. At high frequency (10^6 Hz), the micro-composite has a higher relative permittivity, presumably because the filler has a high permittivity [34]. Refraction index was calculated from equation $n = \sqrt{\varepsilon_r}$,where ε_r is dielectric constant at high frequency and n is refractive index. The reactive index is presented in Table 2. The PU resin of which the refractive index is close to that of the CFs/CNT [28]. The RI of cellulose has been reported as 1.618 along the fiber and 1.544 in the transverse direction [35]. The matching RI of the PU resin and CFs/CNT means that the light diffraction at the interface between the two components will be restricted. It was suggested that less amount of CNT into cellulose composite presented the good quality on matching RI. There is no light diffraction inside the CNT and cellulose based polyurethane composite structure.

3.7 Conductivity

Electrical properties of conductive CNTs/CFs composites were investigated. The resistance, sheet resistivity, and conductivity of composites is presented in Table 3. Unfortunately, the resistance of neat CFs and CFs/CNT0.5 film cannot be measured due to the non-conductive properties. The low resistance of 10^3-10^4 Ω can be observed at high amount of CNTs in CFs composite. Moreover, the resistance of CNTs/CFs composites at rather similar CNTs amount of 5.0% is lower than that the previous report of CNTs/cellulose nanofiber [32]. But such resistivity at all ratio are rather high as compared to other work with optimized process for CNT network to form on the cellulose fibers [33]. Therefore, the high resistivity in this work may result from the agglomeration of CNTs on the cellulose surface during the fabrication. However, as increasing of CNTs amount, the composites show the tendency of electrically properties as similar as the dielectric results. Here, the conductivity increases sharply with the increasing of CNTs amount, which is consistent with the statistical percolation theory of composite. This indicate that the volume fraction of CNTs at minimal amount of 1.5% may be above the percolation threshold. Because the conductivity at amount of 0.5% was not obtained, thus, the percolation threshold of CNTs on CNTs/ cellulose composites may be in the range between 0.5% to 1.5% of CNTs. Although the conductivities at high CNTs are enhanced, the transparent properties of such high CNTs amount are reduced, which is not applicable for active paper. Interestingly, moderately resistance of order 3×10^6 Ω can be obtained

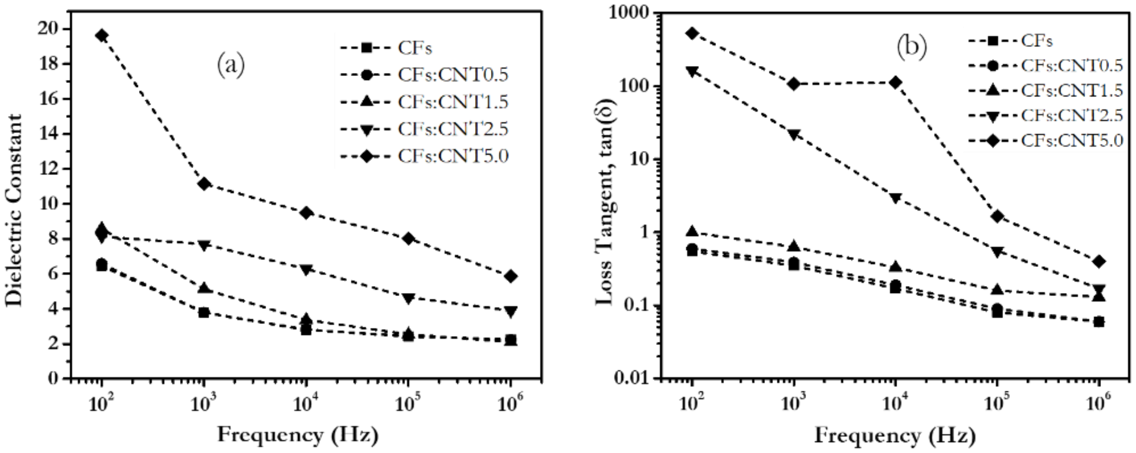

Figure 5. The dielectric constant (a) and loss tangent (b) of the CFs/CNT all neat PU resin.

Table 2. Refractive index of the CFs/CNT all neat PU resin.

Samples	$\varepsilon_r(F = 10^6$ Hz)	Reflective index
CFs	2.23	1.49
CFs:CNT0.5	2.25	1.50
CFs:CNT1.5	2.11	1.45
CFs:CNT2.5	3.90	1.97
CFs:CNT5.0	5.86	2.42

Table 3. Electrical Properties of the CFs/CNT all neat PU resin.

Samples	Resistance (Ω) ×10^3	Resistivity (Ω·cm) ×10^3	Conductivity (S·cm^{-1}) ×10^{-4}
CFs	-	-	-
CFs:CNT0.5	-	-	-
CFs:CNT1.5	3000 ± 732	1880 ± 460	0.00559 ± 0.00115
CFs:CNT2.5	19.5 ± 2.72	12.2 ± 1.70	0.832 ± 0.0127
CFs:CNT5.0	3.26 ± 0.241	2.04 ± 0.151	4.91 ± 0.373

from CFs/ CNT1.5, which also present the high dielectric constants, loss tangent, and translucent. In addition, the optical, thermal, and mechanical properties of composite film of CFs/CNT1.5 reveal that this composite have an opportunity to develop for transparent and flexible electronic device.

4. Conclusions

A new type of flexible and slightly transparent sheet made of cellulose fiber and carbon nanotube composite on PU resin was simply fabricated. The CNTs was formed on the CFs structure and immerse in the PU sheet. The introduction of small amount of CNTs can enhance the mechanical, thermal, and electrical properties. Although, the transmission of CFs/CNT composite was reduced, the fairly transmittance of 35% in all visible regions can be obtained from cellulose fiber based-CNTs composite film with CNTs amount of 1.5 wt%. The CFs/CNT composite film enhance the dielectric and conductivity properties. Compare to the previous work, the lowest sheet resistance of ~300 Ω·sq^{-1} was obtained at the transmittance of ~45% for the SWCNT/nanocellulose [36]. In our work, the resistance of 3 MΩ and transmittance of 35% were achieved, which indicate that the active paper properties of CNTs/macro cellulose composite sheets on PU substate is limited at the CNTs amount of 1.5 wt%. This suggest that an opportunity of active paper in the utilization for flexible electronic substrate, especially the renewable and storage device depend on the size of cellulose and amount of conductive additive.

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