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Physical and Electrical Properties of Sustainable Substrate Thermoplastic Starch/Nanocellulose Fibre/Stannous Oxide

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ABSTRACT

Indonesia and Malaysia are prominent suppliers of oil-palm and sugar palm resources within the Southeast Asian region. The substantial starch and fibril components found in these plants hold significant potential for utilization in the industrial market as a viable alternative to polymer-based substrates. To achieve this, a series of adjustments is necessary, encompassing considerations related to physical, mechanical, and even electrical characteristics. Therefore, this research primarily focuses on conducting physical assessments, including parameters such as water absorption rates and thickness swelling. Additionally, it involves examining the morphology of the plants using field emission scanning electron microscopy (FE-SEM). Simultaneously, the electrical properties are assessed using a two-point probe method to determine the resistance and conductivity of thin films. Through this research, it was found that, the incorporation of nanocellulose-fibril (NCF) and SnO to the thermoplastic starch biofilms, the improved physical and electrical of biofilms. Among all, biofilms 4SnO/1NCF/TPS showed improved electrical properties compared to other compositions.

1. Introduction

Malaysia was included in the top 10 Asia country along with Philippines and India are responsible for 81% of annual global marine plastic release in 2019 [1]. Over the last few years, the distressing state of the Earth's environment has signalled an alert [2] with one of the concerning factors being that these abandoned plastic takes around 10 to 1000 years to degrade, contingent upon a given condition [3]. The worst-case scenario occurs when it finally broke down into microplastic and consumed by sea life then eventually goes into human digestive system [4,5]. According to Malaysia Plastics Sustainability Roadmap (2021 – 2030), approximately 64% of plastics made up of PET, PP, LDPE/LLDPE and HDPE were neglected without any proper disposal system that triggering

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environmental issues. In an attempt to address this misery, the academia has taken a smart measure in fabricating biopolymer to replace a synthetic one. The term "biopolymer" here refers to a bio-based substance made from natural resources such starch [6,7], chitosan [8,9], silk [10,11] and cellulose [12,13]. The good reason behind the action is biopolymers such as cellulose, chitin, lignin and hemicellulose were discovered as the most abundant materials [14,15].

According to Quanjin Ma *et al.*, fibre-reinforced composites are increasingly gaining popularity as a replacement for conventional materials [16], and in recent years, numerous research groups have focused on developing sustainable substrates composed of thermoplastic starch (TPS) with nanocellulose as the reinforcing agent [17-19]. In 2019, Fazeli *et al.,* focusing on plasma treatment modification on starch-based polymers. Since starch have poor mechanical qualities by themselves, adding natural plant fibres from diverse species improves those capabilities [20]. Along with the fact that modified TPS thin films potentially match up with polymer's mechanical properties, we might as well study on the electrical properties by adding a conducting element to the thin films. S. Chen *et al.,* had conducted research on fabricating flexible sensor composing carbonized bacterial nanocellulose and wood-derived cellulose nanofibril composite aerogels [21]. With that being said, this research will be focusing on fabricating TPS with nanocellulose fibre (NCF) with addition of stannous oxide (SnO) to discover the electrical and physical properties of the substrate through V-I testing, water absorption, thickness swelling and Field emission scanning electron microscopy (FE-SEM) analysis to examine the surface morphology part.

2. Methodology

2.1 Materials

Nanofiber cellulose (NCF) suspension made from Oil Palm Empty Fruit Bunches (OPEFB) was the raw material utilized to make this substrate, and it was purchased from ZoepNano Sdn. Bhd. in Serdang, Selangor, Malaysia. While thermoplastic starch used was made up of sugar palm starch from PT Kofta Unitrada, Tangerang (Indonesia) and lastly the stannous oxide, Tin (II) Oxide was bought from Sigma-Aldrich with particle size ≤60 micron.

2.2 Fabrication of Bio-Nanocomposite Thin Films

Method used to fabricate bio-nanocomposite thin films is casting method according to Ilyas *et al.,* [22] with few modifications made. The formula calculated to prepare the films suspension corresponds to Table 1, TPS took 95 wt.% out of the whole composition and left 5 wt.% for both SnO and NCF with varied ratio accordingly.

Table 1
The composition for different substrate's formulation

Sample	TPS (wt.%)	SnO (wt.%)	NCF (wt.%)
0SnO/5NCF/TPS	95	0	5
1SnO/4NCF/TPS	95	1	4
2SnO/3NCF/TPS	95	2	3
3SnO/2NCF/TPS	95	3	2
4SnO/1NCF/TPS	95	4	1
5SnO/0NCF/TPS	95	5	0

Suspension for 0SnO/5NCF/TPS were prepared by sonicating 5 wt.% of NCF with 180ml distilled water for 30 minutes. This step is essential to ensure all NCF will not accumulate in the suspension later on. After a while, the sonicated NCF were placed on hot-plate stirrer then 7g of TPS (95 wt.%) with 1:1 plasticizer composing sorbitol and glycerol (30 wt.% of TPS) were added and stirred at 1000rpm, 85℃ for another 30 minutes. This suspension has 0 wt.% SnO, which means SnO was not included in these thin films. The final step is to let the suspension cooled down before poured 150ml of it into rectangular petri dish to make sure it dispersed well with no bubble trapped in. Placed the petri dish in oven and let it dry over night at 45℃. Films with different loading of SnO and NCF were labelled as 1SnO/4NCF/TPS, 2SnO/3NCF/TPS, 3SnO/2NCF/TPS, 4SnO/1NCF/TPS and 5SnO/0NCF/TPS.

2.3 Water Absorption

According to the standard ASTM D570-98 procedure, water absorption testing was conducted. The peeled thin films were prepared into 1.5cm x 1.5cm cut and immersed in distilled water. The initial mass of dry condition thin films was recorded as 0 minute (0min), and the next consequent 30 minutes for 4 hours then labelled as 30min, 60min, up to 240min. Finally, all data were tabulated and calculated according to Eq. (1) to finalize the percentage of water absorb.

$$\text{Water absorption (\%)} = \frac{W_f - W_i}{W_i} \text{ x } 100 \quad (1)$$

Where, W_f is the final weight after every 30 minutes immersion and W_i is the Initial weight of dry film.

2.4 Thickness Swelling

According to the standard ASTM D570-98 procedure, water absorption testing was conducted. The peeled thin films were prepared into 1.5cm x 1.5cm cut and immersed in distilled water. The initial thickness of dry condition thin films was recorded as 0 minute (0min), and the next consequent 30 minutes for 4 hours then labelled as 30min, 60min, up to 240min. Finally, all data were tabulated and calculated according to Eq. (2) to finalize the percentage of thickness swelling.

$$\text{Thickness Swelling (\%)} = \frac{T_f - T_i}{T_i} \text{ x } 100 \quad (2)$$

Where, T_f is the final thickness after every 30 minutes immersion and T_i is the initial thickness of dry film.

2.5 Two-Point Probe

The conductivity of the samples was measured by a two- point probe method. Limited voltage ranges from 0V to 7.0V with fixed distance between probes. The value of resistance obtained through Ohm's Law in Eq. (3) while the conductivity (σ) of the thin films was calculated according to Eq. (4).

$$V = IR \quad (3)$$

Where V is the voltage applied, I stand for current flow and R is the resistance of the thin films

$$\text{Conductivity } (\sigma) = \frac{L}{(R)(A)} \quad (4)$$

Where, L is the fixed distance between 2 probes, R is the resistance obtained from I-V curves graph and A is the area of the thin films.

2.6 Field Emission Scanning Electron Microscopy (FE-SEM)

The surface morphology of the thin films was scanned using Zeiss Supra 55VP In-lens. All substrates were coated with Iridium (Ir) to avoid electron charging and promotes homogeneous images. The resolution limited to 3.00 Kv acceleration voltage with magnification around 2.00 – 3.00 KX.

3. Results

3.1 Water Absorption

Bio-based nanocomposite were known with high hydrophilic properties with the act of affinity towards water [23,24] . Since starch is the key components here, there is high chance that it will form numbers of hydrogen bond due to presence of hydroxyl groups [25,26]. Nevertheless, with the addition of metal oxide, stannous oxide might slightly abrupt the substrate since SnO is hydrophobic unlike nanocellulose. Figure 1 exhibits the rate of water absorption for six prepared thin films after being immersed for at least 4 hours. There is a rapid increase in water uptake for all six samples at the first 30 minutes of immersion time. Sample 0SnO/5NCF/TPS with highest NCF contents absorbed highest water uptake, approximately 40% of the thin films. Sample 5SnO/0NCF/TPS consist only SnO and TPS, it can uphold water slightly over 25% which marked the lowest record. The substrate seems to reach equilibrium state as the result is almost consistent for the remaining 210 minutes.

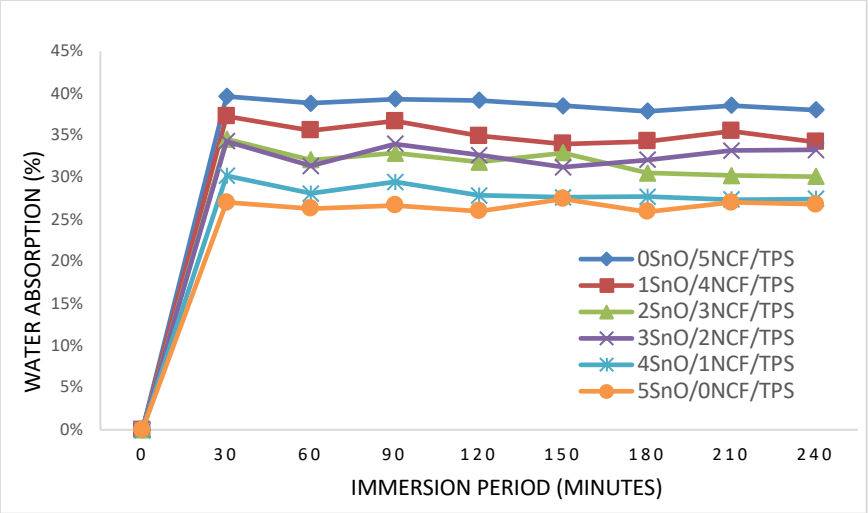


Fig. 1. Rate of water absorption for substrate Thermoplastic Starch/Nanocellulose Fibre/Stannous Oxide

3.2 Thickness Swelling

Figure 2 shows the rate of thickness swelling for all six thin films after 240 minutes immersed in distilled water. The trend observed are noticeable similar to the water absorption test when substrate 0SnO/5NCF/TPS attain as the highest rate of swelling right after 30 minutes immersion time

followed by 1SnO/4NCF/TPS, 3SnO/2NCF/TPS, 2SnO/3NCF/TPS, 4SnO/1NCF/TPS and 5SnO/0NCF/TPS. According to the previous study by Radzi *et al.,* the amount of water uptake for both water absorption and thickness swelling are dependent to the void formed, density and bond between matrix of the substrate [27]. It is safe to claim that substrate 5SnO/0NCF/TPS gained lowest swelling rate due to fewer void as diameter of SnO itself is taking up space.

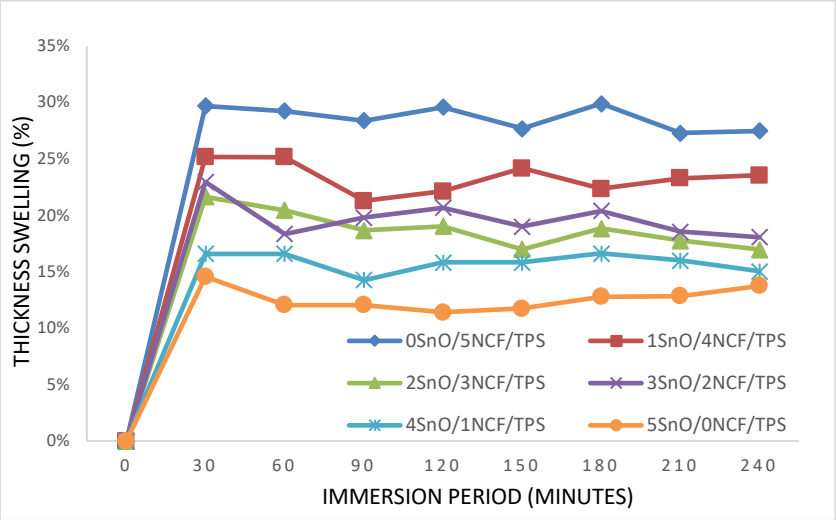


Fig. 2. Rate of thickness swell for substrate Thermoplastic Starch/Nanocellulose Fibre/Stannous Oxide

3.3 Current-Voltage (I-V) Curves

Starch and nanocellulose were known as weak conductors or rather being called insulators. With a view of fabricating conductive substrate, adding a metal oxide like SnO is given to enhance the conductivity value. Hence, a two-point probe test has been performed to gain conductivity and resistivity of the thin films. The raw data were recorded and presented as Current-Voltage (I-V) Curves in Figure 3 below to obtain the resistance of the thin films from the slope of the graph below.

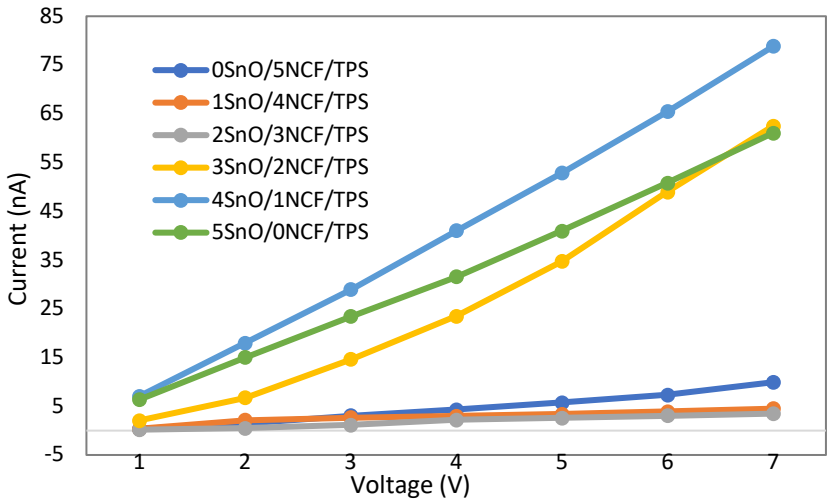


Fig. 3. Current-Voltage (I-V) curves for conductivity test using two-point probes

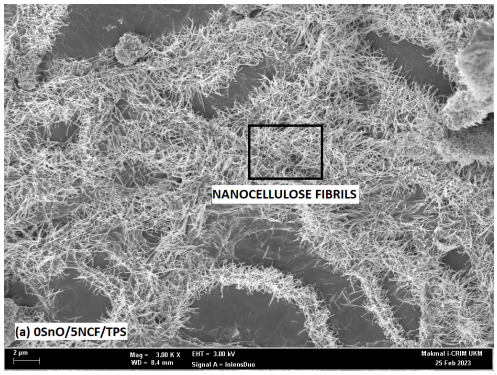
Meanwhile Table 2 concluded the resistance and conductivity that were calculated from graph in Figure 3. Substrate 4SnO/1NCF/TPS marked the highest conductivity of $1.8538X10^{11}$S/m despite having 1 wt.% of nanocellulose. Meanwhile substrate 2SnO/3NCF/TPS has the lowest conductivity with highest resistance of $2.1244X10^{-9}\Omega$.

Table 2
The resistance and conductivity calculated for different formulated substrates

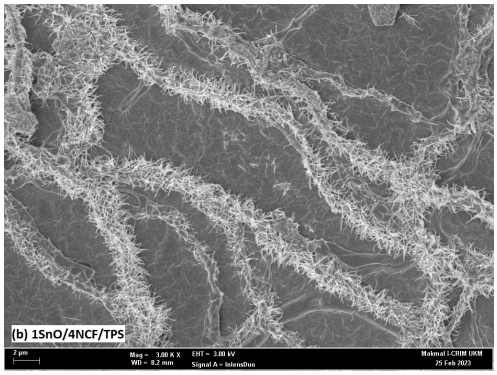
Sample	Resistance, R ($10^{-9}\Omega$)	Conductivity, σ (S/m)
0SnO/5NCF/TPS	0.8713	2.0404E+10
1SnO/4NCF/TPS	1.4023	1.2678E+10
2SnO/3NCF/TPS	2.1244	8.3684E+9
3SnO/2NCF/TPS	0.1450	1.2261E+11
4SnO/1NCF/TPS	0.0959	1.8538E+11
5SnO/0NCF/TPS	0.1222	1.4548E+11

3.4 Field Emission Scanning Electron Microscopy (FE-SEM)

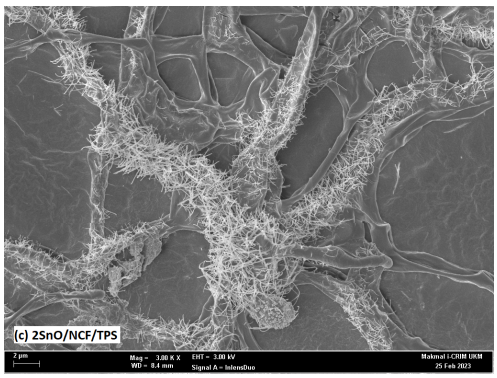
The surface microstructure of the thin films was observed to determine the existence and distribution of both SnO and NCF on the morphological surface. Figure 4 (a)-(f) shows images from FE-SEM analysing the coarse surface with varies SnO and NCF content in TPS thin films with magnifications of 3.00K X. The network of NCF is well distributed in Figure 4 (a) since it has the highest NCF content without any SnO element added. However, it is hard to identify the appearance of SnO for the rest of the images.



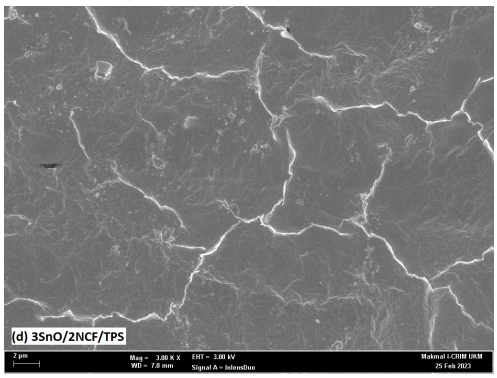
(a)



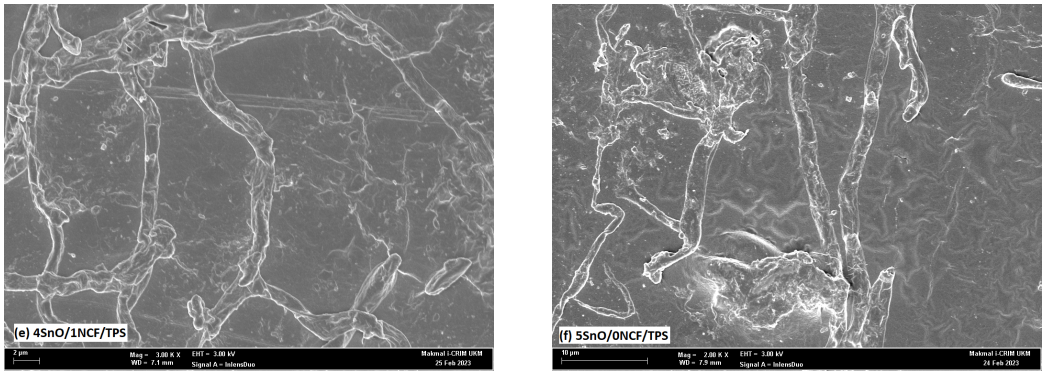
(b)



(c)



(d)



(e) (f)

Fig. 4. Microscopy images of FE-SEM for varies NCF and SnO loading (a)-(f)

In view of that, an energy-dispersive X-ray analysis (EDX) was exported to validate the presence of SnO in substrate 5SnO/0NCF/TPS (Figure 5).

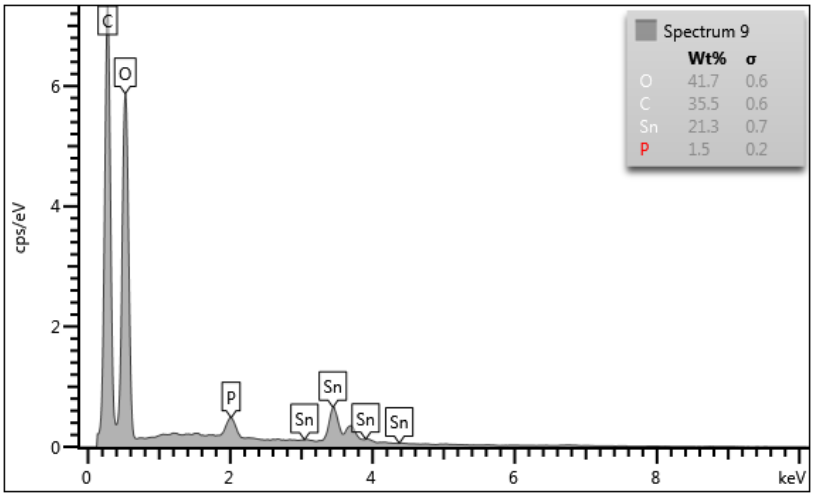


Fig. 5. EDX spectrum for substrates 5SnO/0NCF/TPS

4. Conclusions

Starch-based with nanocellulose reinforcer is highly potential to replicate polymer substrate as results shows the addition of NCF and SnO improves the water barrier properties of the substrate. During water absorption and thickness swelling test, substrate with highest SnO content marked the lowest rate for both tests. It shows that the addition of SnO increases the hydrophobic behaviour within the substrates. The distribution of NCF can be seen clearly through FESEM while observing the surface and morphological parts. Meanwhile the content of SnO is validate through EDX graph. Adding SnO into the thin films does alter the electrical properties as sample 4SnO/1NCF/TPS portrays the best electrical behaviours among even with present of nanocellulose.

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