

Influence of SW-CNT on lignin-based nanofibrillated cellulose biofilms: chemical, thermal, thermo-mechanical, and morphological properties

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Keywords

SW-CNT
CNF
lignin
biofilm
thermo-mechanical property

Abstract

This study examined the single wall-carbon nano tube (SW-CNT) effect on the lignin-based nanofibrillated cellulose (CNF) biofilms. For that purpose, CNF and lignin-based CNF interacted with hydrophilic SW-CNT through the casting process to form films. After the formation of the films, chemical, thermal, thermo-mechanical and morphological characterization was conducted by using FT-IR, TGA, DMA, and SEM, respectively. At the end of the study, some minor shifts, and new vibrations were observed after lignin. Higher thermal stability was seen after the SW-CNT, whereas the value lowered with the lignin. DMA reveals that the SW-CNT make it increases both Tg and storage modulus. Also, SEM reveals that all films formed an entangled network in the matrix. As a result, it was seen that those biofilms could be easily prepared and applied in many industrial areas according to necessary.

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Introduction

Lately, many materials have been used in a wide range of applications with ever-increasing industry demand. Materials which mostly preferred by industry are biopolymers owing to their biodegradability properties. The most popular biopolymer is cellulose which consists of anhydroglucose units and has been used in applications thanks to its prospective mechanical properties. The cellulose with different types, which are nano fibrillated cellulose (CNF) and nano crystalline cellulose (CNC) is isolated or synthesized from plants or bacteria via a “top-down” and “bottom-up”

process (Klemm et al, 2011). Of those types, the CNF has attracted much interest as it reveals a higher aspect ratio, more flexibility and stronger interfacial adhesion over CNC. Therefore, it has been applied in numerous fields ranging from bioactive paper to electronic films (Lin and Dufresne, 2014). In addition to CNF, lignin has attracted many interests as it exhibits a high elastic modulus compared to cellulose and hemicellulose. Lignin which consists of aromatic-based structures like phenylpropanoid units (*p*-hydroxyphenyl (H), guaiacyl alcohol (G), and syringyl alcohol (S) are found in a three-dimensional network and has important biological functions such as water transport, mechanical support, and resistance to various stresses. Besides, lignin is also one of the most frequently researched materials after cellulose, owing to its renewability, abundance, sustainability as well as other features such as its stabilizing effect, reinforcing effect, and UV absorption (Kun and Pukanszky, 2017).

Though many materials have been used with nano cellulose and lignin, there is a limited study related to single wall carbon nanotube (SW-CNT). SW-CNT are viewed as rolled-up structures of single sheets of graphene and individual carbon structures have sp^2 hybridization of carbon atoms along with diameters between 0.7 and 10 nm as well as high length/diameter ratio. Besides, SW-CNT reveals a high young modulus and thermal/electrical conductivity. For that purpose, there has been many studies related to the SW-CNT (Osmani et al, 2014).

In a study, Wang et al. (2014) conducted the axial strength of MW-SW-CNTs and reported its elastic modulus values ranging from 200 to 400 GPa; the bending modulus is to 14 GPa, as well as compression strength is about 100 GPa. In another study, Wong et al. revealed that the high deformation of SW-CNTs allows it to break when tensile strength reaches 18% (Wong et al., 1977). Treacy et al. measured the elastic modulus of MW-SW-CNTs to be 1TPa, on the same level as a diamond. They stated that the mechanical strength of the SW-CNT is 100 times higher of steel when compared with steel, but the density is only one sixth of the steel (Treacy et al, 1996). Therefore, it is believed that the incorporation of SW-CNT into matrix may be able to enable to higher mechanical properties (Wang et al., 2014). However, though many studies related to SW/MW-CNT, there is no SW-CNT based biofilms containing the CNF and lignin. Therefore, in this study, the SW-CNT was used to investigate the chemical, thermal, thermo-mechanical and morphological properties of the lignin based CNF film and CNF film. It is thought that this study will make extra contribution researchers studying on biofilms.

Methods and materials

Pulp preparation

500 g of *Eucalyptus camaldulensis* chips were cooked in a digester (sulphidity charges, 28%; active alkali, 18%; and wood/liquor, 5:1) (Uniterm Rotary Digester, Uniterm Lab.) to obtain kraft pulp. Afterward, the obtained kraft pulp was screened to 0.15 mm and bleached using the oxygen-chlorine dioxide-alkaline-peroxide (ODEP) process. The pulps' viscosity (SCAN-CM 15–62 standard) and kappa number (Tappi T236) were determined for each bleaching stage. Then, the kraft pulp was delaminated for mechanical fibrillation by using a blender (2% w/w, 5 min interval, 30°SR) (NuBlend, Waring Commercial) and high-pressure homogenizer (first, one-pass, diameter of 200 μm , 96.5 MPa; second, five-pass, diameter of 100 μm , 165.5 MPa, Z-shaped chamber size, 2% w/w) using a microfluidizer (M-110Y, Microfluidics Corp.).

Sulpho lignin preparation

The obtained alkali lignin (alkali, Powder, 370959, Sigma) was converted to sulfoxide lignin via a chemical sulphide reaction in order to gain hydrophilic properties. For that purpose, the alkali lignin was reacted 2 g of sodium sulfide (407410-50G, Sigma) at 70 °C, 90 min. Following reacted with 30 ml NaOH (0.8 M) (> 99.9, Merck) and 1.5 ml formaldehyde (15512-2.5L-R, ≥ 34.5 wt. %, Sigma) in 400 rpm 30 min at the RT.

Film preparation

For the films, 20 ml at 10 wt.% of the CNF suspension, 20 ml Disodium 2,2'-(1,1'-biphenyl)-4,4' diyldivinylene bis(sulphonate) modified SW-SW-CNT (302, Tuball) and 20 ml sulpho lignin was added and mixed at 80°C prior to sonication for 2 min. Finally, the solution was cast onto a glass plate with controlled leveling, and then dried for seven days at room temperature. Then, Films were designated as C (CNF), CS (CNF+SW-SW-CNT), and CSL (CNFSW-CNT+ Lignin).

Characterization

Chemical alterations were investigated with ATR-FTIR (IR Prestige-21, Shimadzu) by putting on the attachment to investigate and elucidate chemical alterations as vibrations in the range of 4000 to 600 cm^{-1} with a resolution of 4 cm^{-1} , and 20 scans. Thermal stability was determined with a thermogravimetric analysis (TGA) device equipped with a thermal analysis data station (Shimadzu, DTG 60). For that purpose,

approximately 10 mg of films were gently placed in the Pt pan. Then, films were exposed to heat from 25 to 800°C at a 10°C/min heating rate and under a 75 ml/min N₂ (nitrogen) atmosphere. DTMA tests were carried out to determine the thermo-mechanical characteristics of the produced films. The tests were performed in tension mode at a controlled heating rate of 10°C/min. The temperature was increased from 30°C to 250°C at an oscillatory frequency of 1 Hz. Morphological analysis of films was carried out with an SEM (Quanta 250, FEI) to investigate the surfaces and cross-sectional distribution of films.

Results and discussion

Chemical characterization

FTIR spectra of the C, CS and CSL films were given in the Fig. 1.

CH asymmetric and symmetric vibrations sourced from methylene groups in the structures were seen at 2926 and 2854 cm⁻¹ for CSL while those vibrations were seen as overlap for C film at 2901 cm⁻¹. Aromatic CH vibration was observed at 1594 cm⁻¹ for CSL that is related to aromatic ring found in lignin. C₁-O-C₅ inter molecular vibrations were seen at 1162 cm⁻¹ for C and CS. However, those vibrations were not observed in the CSL. Intra molecular C₁-O-C₄ vibrations were seen at 1030 cm⁻¹ both CS and C.

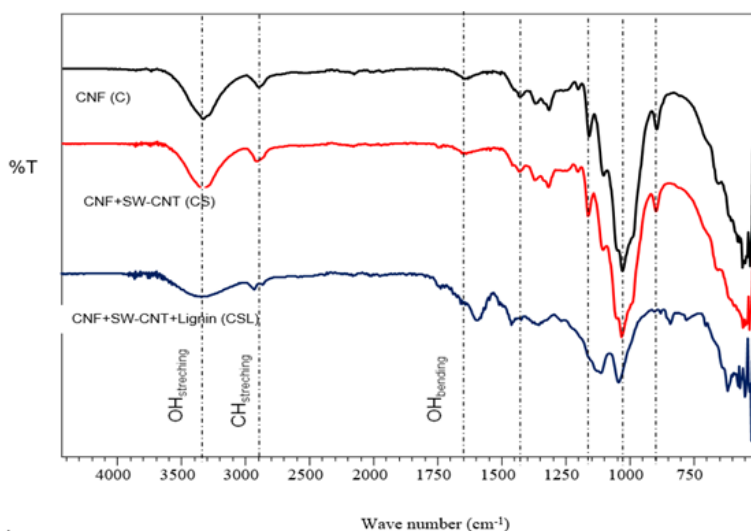


Fig. 1. FTIR spectra of the C, CS and CSL films

However, that vibration were shifted to higher wavelengths and observed at 1040 cm^{-1} for CSL. This circumstance reveals that cellulose structure exposed chemical alteration after adding the lignin to the polymer matrix. In addition to $C_1\text{-O-C}_4$ vibration, glycosidic deformation that sourced from ring stretching OH were observed for the CS and C while that no vibration was observed in that region for the CSL.

Thermal analysis

Thermogram of the films is given in Fig. 2.

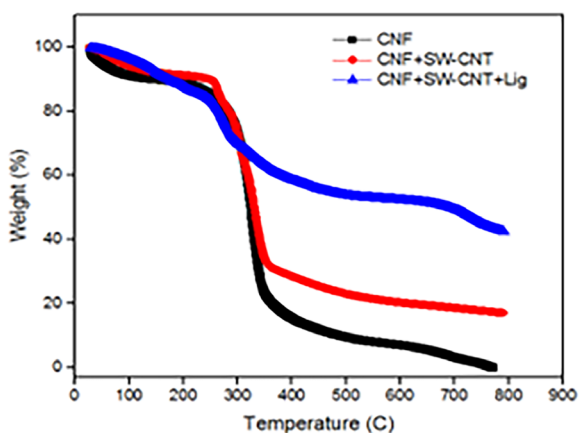


Fig. 2. Thermogram of the C, CS and CSL films

Thermal degradation curves revealed mostly similar behavior for the C and CS films. Those thermograms were seen as a single stage whereas for the CSL film was observed as no one stage. T_{50} % degradation values were investigated in detail for determining thermal stability. It was observed that the lowest thermal stability was seen at CSL whereas the highest stability was seen at CS. Therefore it can be said that carbon nano tube (SW-CNT) enabled higher thermal stability. This circumstance reveals that higher energy was needed to destroy the interaction of molecular chains. This may be attributed to the fact that SW-CNT comprises a large amount of folded-up molecules and required higher energy to move (Sun and Liu, 2021). Besides, this circumstance can be explained with lignin. After adding the lignin, chain mobility was restricted in the matrix on the long range (Shimazaki et al., 2007).

Besides, it can be said that the CNF degraded completely, while biopolymers having SW-CNT left some residue.

Mechanical analysis

The thermo-mechanical behavior of films was studied by DMA. The obtained results were given as storage moduli and tan delta in Fig. 3-a and 3-b, respectively.

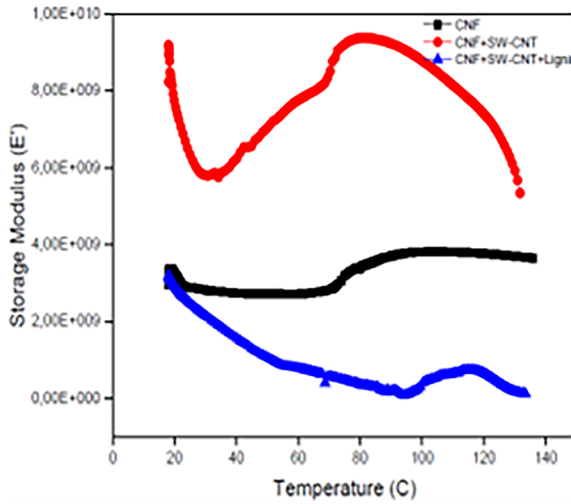


Fig. 3-a. Storage Modulus of the C, CS and CSL films

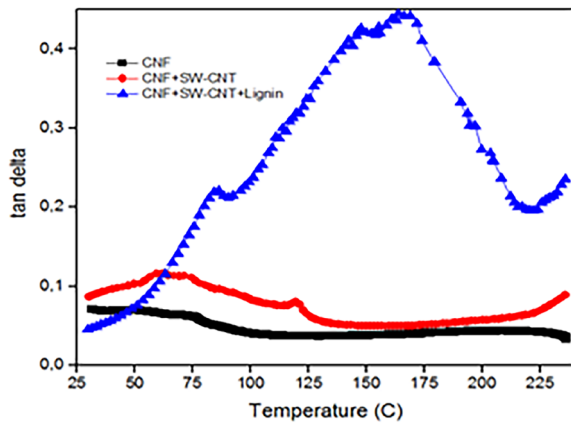


Fig. 3-b. Tan δ of the C, CS and CSL films

When the storage modulus, which give insight into elastic capability and behavior of films for storing energy, investigated in the Figure 3-a, fluctuating behavior were observed for CSL film. This is may be due to single wall graphene lattice which folded-up properties of the carbon nanotube. After lignin, this level lowered that the lowest value was seen in the CSL. Generally, storage modulus increased with SW-CNT due to SW-CNT having stiffness property since SW-CNT enable high modulus in higher temperatures (Jin et al., 2001; Szcześniak et al., 2008).

E' (storage modulus) which is representative of the elastic behaviour and E'' (loss modulus) is the loss modulus indicative of the lost energy due to the resistance to flow of the polymer chains, the ratio between E''/E' is known as $\tan \delta$ (delta), the maximum of this ratio is defined as the T_g (Velasco-Santos et al., 2003).

The storage modulus changes with temperature as the molecular or chain mobility, interfacial interactions altered within the polymer matrix. There is no considerable alteration in the C film that revealed mostly singular behavior. However, after adding the SW-CNT, polymer matrix showed a different behavior that the presence of carbon nanotubes enables CSL films to sustain higher T_g value due to the fact that broad of the $\tan \delta$ peak since carbon nano tube has high elastic modulus and stiffness. The different natures of the SW-CNT and lignin played a major role in determining the extent of $\tan \delta$ broadening whereas in the presence CNF, CSL revealed more broadening peak when compared to C films (Panwar and Pal, 2017).

Morphological properties

Surface pictures of the C, CS and CSL films were taken with SEM as 100 μm and 1 μm dimensions and the obtained pictures were given in Fig. 4.

Fig. 4 depicted the surface morphology of the films. Amorph fibrils particles were observed both C and CS. Also, amorph fibrils in the C film have nano scale and their dimensions were ranged from 20 nm to 50 nm as well as those revealed entanglement network. Also, SW-CNT and lignin was well embedded within the polymer matrix and there is no gross phase for CSL film. In addition, it was seen that there is no considerable aggregation as well as no considerable cracks and voids were observed on the films. Overall, it can be said that SW-CNT and lignin particles were dispersed homogenously in the films.

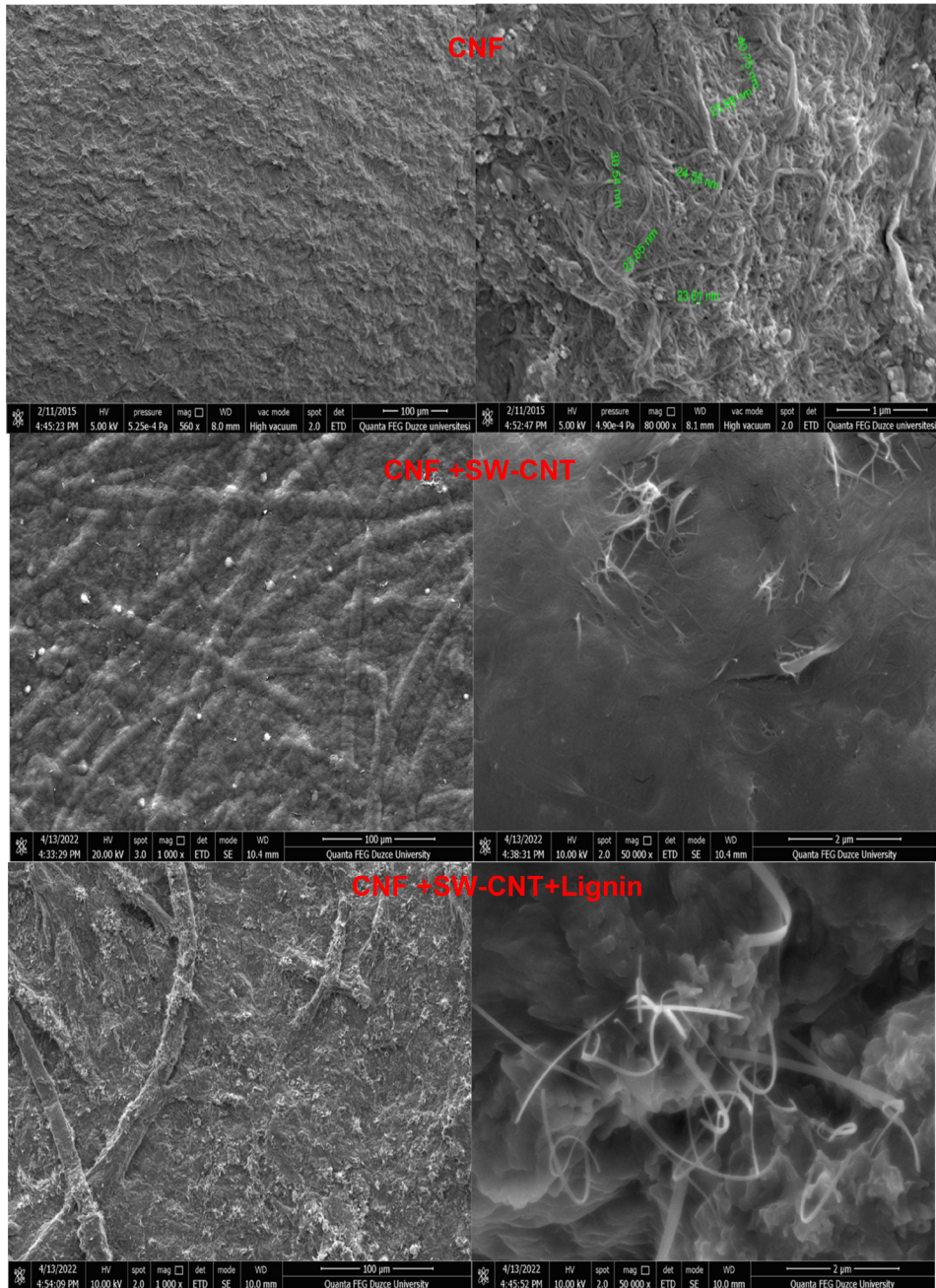


Fig. 4. Surface pictures of C, CS, CSL films

Conclusions

Overall, CNF, CNF+SW-CNT, and CNF+SW-CNT+lignin biofilms have been produced successfully via the casting process. Films had a homogenous surface structures which has fibrils having nano dimensions. In the chemical structure, new vibrations were observed due to the fact that having the aromatic structure of lignin whereas caused the lower thermal stability on the film. Contrary to lignin, SW-CNT enabled higher thermal stability. As for thermo-mechanical properties, SW-CNT enabled higher storage modulus and Tg value. This study reveals that SW-CNT and lignin influenced the film's chemical, thermal, and thermo-mechanical properties differently.

References

- Jin, Z., Pramoda, K. P., Xu, G., Goh, S.H., 2001. Dynamic mechanical behavior of melt-processed multi-walled carbon nanotube/poly (methyl methacrylate) composites. *Chemical Physics Letters*, 337(1–3), 43–47. [https://doi.org/10.1016/S0009-2614\(01\)00186-5](https://doi.org/10.1016/S0009-2614(01)00186-5)
- Klemm, D., Kramer, F., Moritz, S., Lindström, T., Ankerfors, M., Gray, D., Dorris, A. (2011). Nanocelluloses: a new family of nature-based materials. *Angewandte Chemie International Edition*, 50(24), 5438–5466. <https://doi.org/10.1002/anie.201001273>
- Kun, D., Pukanszky B. (2017). Polymer/lignin blends: Interactions, properties, application. *European Polymer Journal*, 93, 618–641. [10.1016/j.eurpolymj.2017.04.035](https://doi.org/10.1016/j.eurpolymj.2017.04.035)
- Lin, N., Dufresne, A. (2014). Nanocellulose in biomedicine: Current status and future prospect. *European Polymer Journal*, 59, 302–325. <https://doi.org/10.1016/j.eurpolymj.2014.07.025>
- Osmani, R.M., Kulkarni, A.S., Aloorkar, N.H., Bhosale, R.R., Ghodake, P.P., Harkare, B.R. (2014). Carbon nanotubes: an impending carter in therapeutics. *International Journal of Pharmaceutical and Clinical Research*, 6(1), 84–96. https://www.researchgate.net/publication/261548910_Carbon_Nanotubes_An_Impending_Carter_in_Therapeutics
- Panwar, V., Pal, K. (2017). Dynamic mechanical analysis of clay–polymer nanocomposites. In: *Clay-polymer nanocomposites* (pp. 413–441). Elsevier. <https://doi.org/10.1016/B978-0-323-46153-5.00012-4>
- Shimazaki, Y., Miyazaki, Y., Takezawa, Y., Nogi, M., Abe, K., Ifuku, S., Yano, H. (2007). Excellent thermal conductivity of transparent cellulose nanofiber/epoxy resin nanocomposites. *Biomacromolecules*, 8, 2976–2978. <https://doi.org/10.1021/bm7004998>
- Sun, N., Di, M., Liu, Y. (2021). Lignin-containing polyurethane elastomers with enhanced mechanical properties via hydrogen bond interactions. *International Journal of Biological Macromolecules*, 184, 1–8. <https://doi.org/10.1016/j.ijbiomac.2021.06.038>
- Szcześniak, L., Rachocki, A., Tritt-Goc, J. (2008). Glass transition temperature and thermal decomposition of cellulose powder. *Cellulose*, 15(3), 445–451. <https://doi.org/10.1007/s10570-007-9192-2>

- Treacy, M.M.J., Ebbesen, T.W., Gibson, J.M. (1996). Exceptionally high Young's modulus observed for individual carbon nanotubes. *Nature*, 381, 6584, 678–680. <https://doi.org/10.1038/381678a0>
- Velasco-Santos, C., Martinez-Hernandez, A.L., Fisher, F., Ruoff, R., Castano, V.M. (2003). Dynamical–mechanical and thermal analysis of carbon nanotube–methyl-ethyl methacrylate nanocomposites. *Journal of Physics. Ser. D: Applied Physics*, 36(12), 1423. <https://doi.org/10.1088/0022-3727/36/12/311>
- Wang, W., Zhu, Y., Liao, S., Li, J. (2014). Carbon nanotubes reinforced composites for biomedical applications. *BioMed Research International*. <https://doi.org/10.1155/2014/518609>
- Wong, E.W., Sheehan, P.E., Lieber, C.M. (1997). Nanobeamme mechanics: elasticity, strength, and toughness of nanorods and nanotubes. *Science*, 277, 5334, 1971–1975. [10.1126/science.277.5334.1971](https://doi.org/10.1126/science.277.5334.1971)