Effect of Cellulose Nanofibers (CNF) as Reinforcement in Polyvinyl Alcohol/ CNF Biocomposite

Rathesh Kumaran Ulaganathan¹, Nur Aiman Mohamad Senusi¹, An’Am’t Mohamed Noor¹, Wan Nazwanie Wan Abdullah², Mohamad Asyraf Mohd Amin³, Mohammad Khairul Azhar Abdul Razab³, Abrar Ismardi⁴ and Nor Hakimin Abdullah⁵

¹Advance Materials Research Centre (AMRC), Faculty of Bioengineering and Technology, Universiti Malaysia Kelantan, 17600 Jeli, Kelantan, Malaysia.
²School of Chemical Sciences, Universiti Sains Malaysia, Minden-Penang, 11800, Malaysia.
³Green Tech Enov, Lorong Tji 34, Taman Jengka Indah, Bandar Tun Razak, Pahang, 26400, Malaysia.
⁴School of Health Sciences, Universiti Sains Malaysia, Health Campus, 16150 Kubang Kerian, Kelantan, Malaysia.
⁵Department of Engineering Physics, School of Electrical Engineering, Telkom University, Jalan Telekomunikasi No. 1 Terusan Buah Batu Bandung, West Java, Indonesia.

E-mail: norhakimin@umk.edu.my

Abstract. This research was targeted to use the planetary ball milling method to extract cellulose nanofibers (CNFs) from commercial microcrystalline cellulose and also to utilize the obtained extracted cellulose nanofibers (CNFs) as reinforcement in polyvinyl alcohol (PVA) thin film. The effect of cellulose nanofibers (CNFs) on the mechanical and physical properties of polyvinyl alcohol (PVA) thin films was investigated. As a result of the study, we found that the thin film's tensile strength is good, and the surface morphology of the CNFs suspension enhances the bonding between the PVA and the reinforcement. Tyndall effect was accurate with the visible light scattering through CNF suspension, and the CNF/PVA thin film exhibited transparent thin film. In contrast, the CNF/PVA composite's mechanical and physical properties are good due to the excellent dispersion and absence of agglomeration of CNFs. The prepared PVA/CNF biocomposite would be a suitable candidate to be implemented as biodegradable food packaging material.

1. Introduction

As of late, there has been a developing consciousness of the significance of the naturally agreeable plan of synthetic products and processes. The idea of maintainability is firmly affecting the substance network, which is more and additional zeroing in on limiting the utilization of hazardous substances also, embracing green manufactured techniques from sustainable, reasonable assets as beginning materials [1]. Cellulose is a characteristic polymer comprising straight homo polysaccharide β-(1,4)-D-glucose units connected together by β-1-4-linkages with plenty of hydroxyl groups and abundant organic polymers [2-4]. It is utilized for different applications since its most plentifully found in
natural resources, climate amicable and biocompatible. Cellulose nanofibers (CNFs) are separated from cellulose utilizing various strategies like high-pressure homogenizer [5], chemically treated hydrolysis [6], corrosive hydrolysis treatment measure [7] and ball milling as a green preparation procedure. Cellulose nanofibers (CNFs) gives excellent mechanical properties [8], enormous explicit region, low coefficient of thermal expansion, ease and accessibility [9], better biodegradability, high angle proportion (L/D), biocompatibility and renewability [10,11].

Ball milling is a mechanical procedure generally used to granulate powders into fine particles and mix materials [12]. Being environmental-friendly and cost-effective, it has found wide application in the industry everywhere in the world. Since this review mostly centres around the conditions applied for the arrangement and functionalisation of nanocellulose subsidiaries by ball mill, as opposed to the apparatus itself, the various kinds of machines accessible in the industry won't be thus depicted. In any case, an overall depiction of the various kinds of gear is accounted for in this segment. Contingent upon the application, there are various sorts of ball mill. Nonetheless, the aim of this study was to apply the planetary ball milling process for CNFs extraction. The planetary ball milling method was chosen because the milling vessels are placed on a rotating supporting disk and they rotate around their own axes. This is an essential parameter for the process's efficiency as a higher distance allows higher kinetic energy and, therefore stronger impacts. Polyvinyl alcohol (PVA) is a water-soluble synthesized polymer, broadly utilized as a lattice to create biodegradable polymer composites because of its biodegradability, biocompatibility, high tractable quality, incredible resistance and adhesive properties.

In this study, CNFs suspension was prepared through ball milling and CNF/PVA film prepared via mixing and mechanical stirring. Since the well-dispersed CNF in distilled water could be used as a dispersing agent for PVA and afforded to form a rigid nano-network structure [13,14], the CNF/PVA film was served as a template to develop thin-film via the casting process. In this process, the CNF/PVA nano-networks provided the composite with both improved mechanical strength and physical property due to the nano-network structures. Furthermore, morphological features and tensile properties were discussed.

2. Experimental

2.1. Materials

Microcrystalline cellulose was purchased from R&M Chemicals, local distributors. Polyvinyl alcohol (PVA, 98-99% hydrolyzed, Mw 31000-50000) was obtained from the laboratory of Universiti Malaysia Kelantan.

2.2. Extraction of cellulose nanofibers (CNFs)

A 1.1g sample of microcrystalline cellulose and 20.9g of deionized water were added to a 45mL zirconia pot containing seven zirconia balls (15mm). Ball milling was conducted in the planetary ball mill at 300 rpm for 0.5 to 8 hours. After ball milling, cellulose slurry was then washed repeatedly with distilled water and centrifuged at 12000 rpm for 0.5 to 3 hours to obtain cloudy precipitation and bring the pH value of cellulose between 6 and 7.

2.3. Preparation of polyvinyl alcohol thin film

PVA granules of 4.4g were added to 100ml of distilled water under the heated condition and magnetically stirred to dissolve the polymer completely. The desired CNFs suspension (4.4g) was then added and sonicated for uniform dispersion of CNFs in PVA solution. The mixture was then poured into petri dishes to allow water to evaporate. Then, the film was demolded and stored. Finally, the thin films were undergone a freeze-thaw process for 6 hours (3 hours per cycle) to improve the thin film’s resistance to deterioration after repeated temperature cycling.
3. Characterization

The surface morphology of the prepared CNFs suspension was characterized using a field emission scanning electron microscope (FE-SEM) operating at 1.5 kV. The tensile strength of the CNFs and PVA thin films were investigated by using a universal material-testing machine (UTM) at room temperature. The sample was cut (in 85 mm length, 25mm width). The average value of the tensile stress, fracture strain, and Young’s modulus was calculated. The tyndall effect of the CNF suspension was determined by using a laser beams. The transparency of the thin film obtained was compared with a random picture.

4. Results and discussion

The Tyndall effect was observed to identify light's scattering through the CNF particles and distilled water, as shown in Figure 1. The laser light was directed towards the universal container (A) with distilled water and (B) with CNF suspension. The distilled water did not show the light beam passing through the water. The CNF suspension allows the light beam to pass through the solution. This appearance of the light beam passing through the solution is referred to as Tyndall effect. In distilled water, the water particles are too small to obstruct the path of light as it passes through and the straight line is not visible. However, the CNF suspension does because it has two phases, the dispersed phase and the dispersion medium. In a colloid, the light scatters into different directions due to the dispersed particles. Tyndall effect was used to determine if the solution is a solution or a colloid.

Morphological analysis of the CNFs suspension was characterized by a field emission scanning electron microscope (FE-SEM). As shown in Figure 2, CNFs suspension under 500x magnification (a) shows a flat and smooth surface, whereas CNFs suspension under 1000x and 2000x magnifications (b), (c) and (d) exhibits a nano-network structure. When the microcrystalline cellulose in optimum content, a nano-network structure can be clearly observed in the CNCs suspension due to the absence of any form of fiber aggregations. In the higher magnifications (2000x), the surface of CNFs suspension can be seen without any visible pores, and the nano-network structures were indistinct inside the bulky polymers.

![Figure 1. Tyndall effect of (A) distilled water and (B) CNF suspension.](image)

Morphological analysis of the CNFs suspension was characterized by a field emission scanning electron microscope (FE-SEM). As shown in Figure 2, CNFs suspension under 500x magnification (a) shows a flat and smooth surface, whereas CNFs suspension under 1000x and 2000x magnifications (b), (c) and (d) exhibits a nano-network structure. When the microcrystalline cellulose in optimum content, a nano-network structure can be clearly observed in the CNCs suspension due to the absence of any form of fiber aggregations. In the higher magnifications (2000x), the surface of CNFs suspension can be seen without any visible pores, and the nano-network structures were indistinct inside the bulky polymers.
Figure 2. Field emission scanning electron microscope (FE-SEM) images of CNFs suspension (a) CNFs 500x (b) CNFs 1000x (c) CNFs 2000x (d) CNFs 2000x.

The transparency of the CNF/PVA thin films prepared were observed in comparison with a clear random picture, for example, the UMK logo (as shown in Figure 3). The prepared thin films were placed on top of the pictures to observe the pictures seen through the transparent thin films. Figure 4 shows the pictures taken during the observation of thin-film transparency. As observed with the naked eye, CNF/PVA thin film exhibited a well transparent thin film compared to PVA thin film.

Figure 3. Transparency of thin film (A) PVA and (B) CNF/PVA.
Due to the rigid nano-network of the CNCs suspension, the mechanical properties induced by the reinforcement of CNCs with PVA were further investigated through tensile testing. Figure 4 shows the stress-strain curve of the CNF/PVA thin film tensile strength. The CNC/PVA thin film exhibits a rigid structure with tensile strength, Young’s modulus, and fracture strain of 25.76 N/mm², 5.579 MPa and 168.035 %. Notably, the CNF/PVA thin film exhibited significantly improved mechanical strength. The reinforcement of CNF into PVA arguably has provided good elastic behaviour of the composite. The tensile properties of CNC/PVA thin films have been listed down in Table 1 below.

![Figure 4. Tensile stress-strain curve of the CNF/PVA thin film.](image)

| Sample Data | Stress (N/mm²) | Strain (%) | Young Modulus (MPa) |
|-------------|----------------|------------|---------------------|
| CNF/PVA (5mm) | 25.76          | 168.035    | 5.579               |

5. **Conclusion**

The study aimed to obtain CNFs reinforced PVA thin films and see break down the impact on mechanical and physical properties. Reinforcement of CNFs expands the hydrogen bonding between the strands and polymers, which brought about better improvement in mechanical and physical properties of the PVA thin films, as seen from tensile test and FE-SEM analysis. Simultaneously, the addition of high concentration CNFs into the PVA grid framework can cause degradation in mechanical and physical properties due to the development of agglomeration. Ball milling causes better cooperation of CNFs with PVA polymer lattice by uncovering more hydroxyl bunches on the surface.

**References**

[1] M. P. Wilson and M. R. Schwarzman 2009 Environ. Health Perspect., 117 10, A386–A434.
[2] F. A. M. Zin, A. M. Noor, M. K. A. A. Razab, N. H. Abdullah, and L. S. Wei 2019 AIP Conference Proceedings 2068 1: 020045.
[3] N. A. Senusi et al 2020 IOP Conf. Ser.: Earth Environ. Sci. 596 012035.
[4] P. T. Anastas and M. M. Kirchhoff 2002 Acc. Chem. Res., 35 9, 686–694.
[5] R.A. Sheldon 2014 Green Chem., 16 3, 950–963.
[6] Hayashi N., Kondo T., and M. Ishihara 2005 Carbohydr. Polym, 61 2:191-197.
[7] Mandal A., and D. Chakrabarty 2011 Carbohydr. Polym , 86 3:1291-1299.
[8] Orts W. J., Shey J., and S. H. Imam et. al 2005 J Polym Environ, 13 4: 301-306.
[9] Nishino T., Matsuda I., and K. Hirao 2004 Macromolecules, 37 20:7683-7687.
[10] Samir M. A. S. A., Alloin F., and A. Dufresne 2005 Biomacromolecules, 6 2:612-626.
[11] Herrick F. W., Casebier R. L., and J. K. Hamilton et. al 1983 J Appl Polym Sci: Appl Polym Symp 43 8:3434-3441.
[12] Moosakazemi, M. R. T. Mohammadi, M. Mohseni, M. Karamoozian and M. Zakeri 2017 Int. J. Miner. Process, 165, 41–49.
[13] Chen, C.; Mo, M.; Chen, W.; Pan, M.; Xu, Z.; Wang, H.; Li, D, Compos 2018 Sci. Technol, 156, 103–108.
[14] Turbak A. F., Snyder F. W., and K. R. Sandberg 1983 J Appl Polym Sci: Appl Polym Symp 5 1:1-193-32.

Acknowledgement
The authors would like to acknowledge the Ministry of Higher Education (MOHE) for the awarded grant to Ts. Dr. Nor Hakimin bin Abdullah namely FRGS (FRGS/1/2019/TK02/UMK/02/2) and UMK for SGPPU (R/SGJP/A1300/00462A/002/2019/00615).