

Biodegradable Polyvinyl Alcohol Composite Film Reinforced by Crystalline Nanocellulose from Rice Straw

Yen T. H. Nguyen, Tuyen Boi Ly, Bup A. T. Bui, Phung K. Le*

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology (HCMUT), VNU-HCM, Ho Chi Minh City, Vietnam
 phungle@hcmut.edu.vn

Polymer films show the best versatility, low cost, and permeability in packaging purpose. On the contrary, these synthetic materials have a lengthy environmental half-life, cannot be broken down by natural microbes, and increase the formation of solid waste. The synthetic polymer polyvinyl alcohol (PVA) is completely dissolves in water and harmless. It has several uses, including controlled medication delivery systems, polymers recycling, film creation, and packaging. Using PVA and crystalline nanocellulose (CNC) as raw materials, PVA/CNC nanofiber membranes were prepared by solvent casting. Fourier transform infrared spectroscopy (FTIR), Scanning electron microscopy (SEM), Water vapor permeability (WVP), thermogravimetric analysis (TGA), and tensile strength were used to describe the characteristics of the film. The tensile strength of the PVA/CNC composite film improved significantly: with 2 % CNC content, the tensile strength 157.6 % increase compared to original PVA. The WVP of PVA markedly reduced 32.4 % after adding 4 % CNC. These properties are suitable for applications in various technologies such as food and packaging.

1. Introduction

Petrochemical-based plastics such as polyolefins, polyesters, and others have become increasingly popular as packaging materials due to their ability to be produced in large numbers at a low cost and their distinguishing characteristics (excellent tensile, tear strength, and thermal resistant). They do, however, have a very low water vapour transfer rate and are completely non-biodegradable. This resulted in environmental contamination, which caused major ecological pollution issues. As a result, organizational and commercial activities are required to fulfill the increasing need for plastics while simultaneously making the whole supply chain environmentally friendly, from raw material selection through manufacturing, consumption, and eventual recycling of plastic products (Montanari et al., 2023). To keep up with this trend, environmentally degradable plastics have been used to replace non - degradable plastic materials synthesizing from fossil fuel sources in the production of sustainable food packaging items. Because biopolymers films are very susceptible to environmental variables including light, temperature, humidity, etc. as well as having low mechanical qualities (Haghighi et al., 2020). Many studies have been published to develop biodegradable films (Said et al., 2023).

There are many useful properties of PVA for food packages films, including high hydrophilicity, strong chemical stability, and great film forming capabilities (Yang et al., 2020). PVA is susceptible to environmental influences and is easily disintegrated by water, just like other biofilms. Effort to enhance the properties of PVA films have been conducted. Nanocomposite films incorporating zinc-oxide nanoparticles and starch-PVA showed improved water barrier, and mechanical properties as the nanofiber content increased (Jayakumar et al., 2019). Cellulose nanocrystal (CNC) is stiff, hydrophilic, high in aspect ratio and rod-shaped crystal cellulose whiskers with diameters spanning from 1 to 20 nm and lengths varying from tens to hundreds of nanometers (Trache et al., 2017). CNC has a high surface area (150 - 250 m²/g) and a low index of expansion under temperature, making it ideal for tissue creation, fillers for injection hydrogels, and pharmaceutical carriers (Kim et al., 2021).

In this study, PVA film is reinforced by CNC at different concentrations to create biodegradable film which had good mechanical property. From there, it is possible to evaluate the influence of CNC concentration on properties of PVA film and propose suitable application direction for PVA film.

2. Materials and methods

2.1 Materials

Cellulose nanocrystal (CNC) was attained from treatment of rice straw from An Giang Province, Vietnam. All the reagents, including sulfuric acid (H₂SO₄), polyvinyl alcohol (PVA) and glycerin (C₃H₈O₃) were purchased from commercial suppliers and used without further purifying.

2.2 Preparation methods

2.2.1 CNC recovery

Cellulose was recovered from rice straw following a previously mentioned process with > 90 % purification (Vo et al., 2022). Cellulose hydrolysis used 62 % H₂SO₄ solutions at a solid: liquid ratio of 1 g : 12 mL with continuous mixing controlled at around 40 – 42 °C for 2 h, attained cellulose nanocrystal suspensions. The reaction was halted by diluting the solution by 10 folds and centrifuging with 4,000 rpm. The final solution was neutralized by dialysis with water changed every 6 h. The resulting CNC material was measured by dynamic light scattering (DLS) to be around 20 – 30 nm in diameter and around 250 nm in length.

2.2.2 Preparation of the PVA – CNC films

PVA was diluted in purified water at 6 % (w/w) for 3 h with magnetic stirring at 80 °C. The film-forming mixtures were obtained by mixing PVA solution and CNC at different mass ratio (0 - 10 %CNC w/w total solution, corresponding to PVA 0 – PVA 5). Then, the mixture was added 0.05 g glycerine. All film-forming combinations were created at room temperature using a Hielscher UP400St ultrasonication (Germany) at 200 kW for 5 min. The mixture films were cast in a inox tray (11 cm x 15 cm) and heated up at 60 °C for 24 h to dry. The films were taken off the tray and placed in a zip bag.

2.3 Characterization

2.3.1 Morphology of films

Surface morphology of PVA films was characterized by a scanning electron microscope (SEM) (Prisma E, US) at 10 kV.

2.3.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FT-IR) was operated in the 4000 - 500 cm⁻¹ range using a Bruker ALPHA II (Germany). Each sample received 16 scans with a spectrum resolution of 2 cm⁻¹. It was employed as a diamond-enhanced attenuated total reflectance (ATR) attachment.

2.3.3 Mechanical tests

Tensile strength testing was accomplished at 25 °C using a Testometric X350 (UK) machine using the ASTM D882 standard. The test was executed at 50 mm/min using a 1 N load cell. The films were cut into 1 cm x 7 cm piece to run this test.

2.3.4 Thermogravimetric analysis (TGA)

The evaluation of thermal stability used an METTLER TOLEDO 3+ Large furnace (Switzerland). The samples were placed in alumina pans and heated at a rate of 10°C/min, from 30 to 500°C under nitrogen atmosphere (50 ml/min).

2.3.5 Water vapor permeability

Water vapor permeability (WVP) tests were according to a modified version of the standard ASTM E96/E96M-16. Film samples with diameter of 90 mm are wrapped onto plastic cup filled with 40 mL of distilled water. The cups were tightly sealed with a plastic lid (50 mm open mouth). The weight of each cup was monitored every hour in 8 h. The experiments were conducted in triplicate.

The water vapor transmission rate (WVTR) can be defined as Eq(1):

$$WVTR = \frac{G}{tA} \quad (1)$$

G is the change in weight (g), t is the time (h), A is the test area (m²), WVT: Water vapor transmission (g/h.m²). The water vapor permeability is calculated by Eq(2):

$$WVP = \frac{WPTR.L}{\Delta P} \cdot 100\% = \frac{WVTR.L}{S(R_1 - R_2)} \cdot 100\% \quad (2)$$

L is the thickness of the sample (m), ΔP is the vapor pressure difference (Pa), S is the saturation vapor pressure at test temperature (Pa), R_1 is the relative humidity in the dish, R_2 is the relative humidity at the vapor sink, WVP is the water vapor permeability of sample (g./m.h.Pa).

3. Results and discussion

3.1 Synthesized CNC properties

The surface morphology of CNC was shown by the SEM image (Figure 1a). CNC was rod-shaped particles with a particle size of about 20-30 nm in diameter and about 250 nm in length, and exhibited high uniformity and stability.

Figure 1b showed that the obtained CNC samples all have transmission peaks typical of cellulose I. The $3,333\text{ cm}^{-1}$ peak corresponds to the elongated OH group, the $2,901\text{ cm}^{-1}$ peak corresponding to the CH group; the $1,633\text{ cm}^{-1}$ peak belonging to water adsorbed onto cellulose, the $1,430\text{ cm}^{-1}$ peak relating to the CH_2 group movement; the peak $1,161\text{ cm}^{-1}$ corresponding to the C-O-C bond extending from the glycosidic bond; and the 898 cm^{-1} representing the β -glycosidic bond in cellulose I. Due to be hydrolyzed by sulfuric acid, the CNC appeared to have a peak at 801 cm^{-1} corresponds to the S-O-C bond (Sahlin et al., 2018).

The thermal stability of CNC was shown in Figure 1c. CNC was degraded in three main thermal steps (Onbattuvelli et al., 2020). Since the CNC material is dispersed in water, at under $100\text{ }^\circ\text{C}$, the large volume of water would be evaporated, retaining 10 % of the original mass. Between 220 and $350\text{ }^\circ\text{C}$, cellulose decomposition and oxidation occurred, which lost about half of the remaining mass. Finally, coal residues decomposed in the temperature range of 350 to $470\text{ }^\circ\text{C}$, more than 4 % of the remaining volume of CNC remained stable.

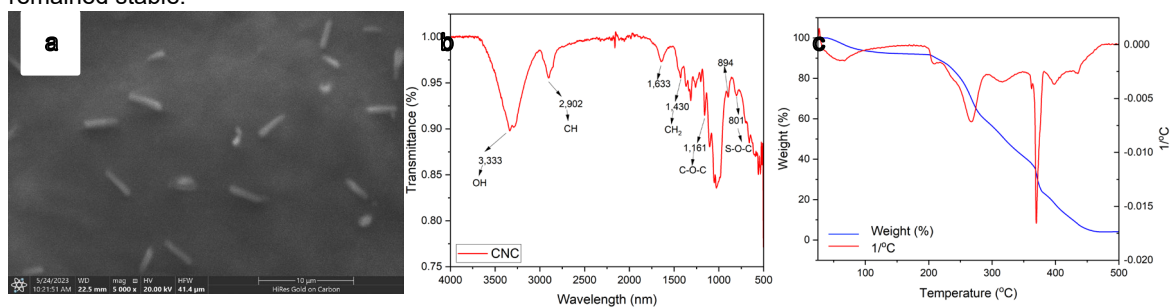


Figure 1: SEM image (a), FTIR spectra (b), and TGA-DTG analysis (c) of CNC

3.2 Morphology of films

The surface morphology of PVA - CNC films were presented in Figure 2. Both PVA 0 and PVA 2 film showed homogeneity and a relatively smug surface. On the surface of the two films, there are some large circular spots of a few micrometres in size, which can be explained by the hydrophilic PVA film, which is prone to moisture, causing water accumulation on the surface. The PVA 2 film was slightly rough with appearance of white spots which were the dispersed CNC particles. There was no conglomeration or macroscopic phase separation which demonstrated how excellent CNC dispersed in PVA matrix.

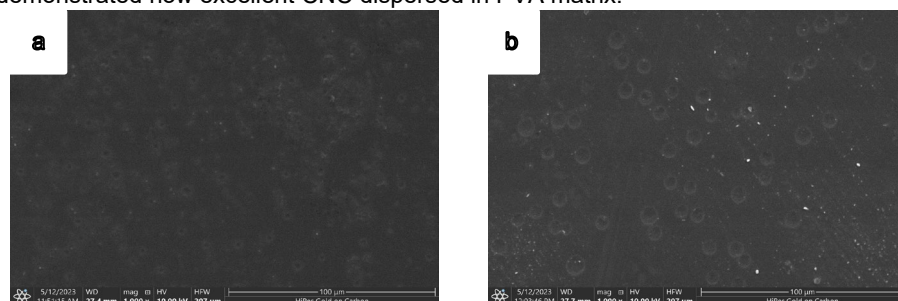


Figure 2: SEM images of (a) PVA 0 and (b) PVA 2

3.3 Fourier transform infrared spectroscopy (FTIR) of films

Figure 3a showed chemical structure of PVA - CNC films. Both PVA films containing CNC and without CNC showed a broad peak at $3,300\text{ cm}^{-1}$ related to (O-H stretching), $2,900\text{ cm}^{-1}$ corresponding to CH_2 alkyl

asymmetric stretching, $1,730\text{ cm}^{-1}$ (residual C=O stretch vibration), $1,240\text{ cm}^{-1}$ corresponding to (C-C and C-O stretching vibration), $1,020\text{ cm}^{-1}$ related to (C-O-C stretching), 840 cm^{-1} (C-C and C-O stretching vibration) (Roy and Rhim, 2021). Even when adding CNC to the films, the peaks of films were not shifted, indicating that there was no chemical reaction between PVA and CNC, CNC was added to the films as a filler, reinforcing the films.

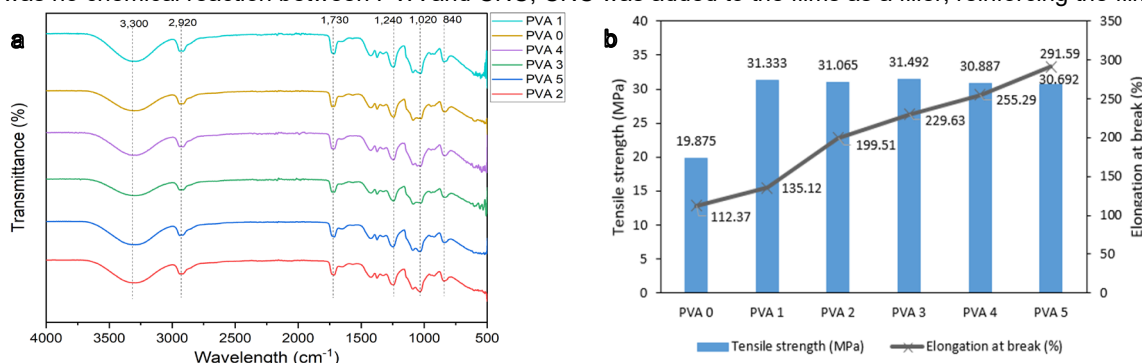


Figure 3: (a) FTIR spectra and (b) mechanical properties of PVA – CNC films

3.4 Mechanical tests

(Abdullah et al., 2017) showed that degree of hydrolysis, molecular weight, and the amount of plasticizers of PVA directly influenced its mechanical properties. For instance, it has been reported that the tensile strength (TS) and elongation break (E %) of PVA were respectively 28.6 MPa and 148 % (Roy and Rhim, 2021), 13.69 MPa and 195.5 % (Lin et al., 2020), or 26 MPa and 232 % (Yang et al., 2020).

In this study, the effect of concentration of CNC (0, 2, 4, 6, 8 and 10 %) on mechanical characteristics of PVA films was shown in Figure 3b. These results indicated that the concentration of CNC had a significant impact on the mechanical characteristics of the original PVA (PVA 0). The tensile strength (TS) value of PVA increased from 19.875 MPa (PVA 0) to 31.333 MPa (PVA 1 increased 157.6 % PVA 0) by adding 2 % CNC. The explanation was that initially, when adding CNC to the PVA film, the CNC has a reinforcing effect, resisting the pull force, causing the TS value of PVA 1 to increase sharply. CNC concentration continued to increase, TS value remained quite stable in 2 samples PVA 2 and PVA 3 (31.065 MPa and 31.429 MPa), then, slightly decreased in 2 samples PVA 4 and PVA 5 (30.887 MPa and 30.692 MPa). The total crystallinity of PVA-CNC films increased or the accumulation rate of CNC in PVA films increased as the CNC content increased, which could be the reasons for this phenomenon. Excessive CNC concentration disrupted the interaction in the PVA matrix, which might reduce the mechanical properties of the film. (Sarwar et al., 2018). Adding reinforcement may increase the amount of faults in films, such as bubbles trapped during films preparation, resulting in a drop in tensile strength (Bacha et al., 2022). As the CNC concentration increased, the elongation of the PVA films increased continuously, from 112 % (PVA 0) to 292 % (PVA 5). This was a marked improvement of the mechanical strength of the PVA film when CNC was added.

Table 1 showed the comparison to the mechanical properties of PVA from other related studies. PVA film in this study showed a significantly higher tensile strength and elongation at break comparing with the other PVA film reinforcing by CNC from natural. This PVA film has even greater tensile strength than common films such as polypropylene, low-density polypropylene and polyvinyl alcohol.

Table 1: Comparison of the mechanical properties with other related studies

| Film | Additive | TS (MPa) | E (%) | References |
|--------------------------|-----------------------------------|----------|--------|--------------------------|
| PVA | 6 % CNC from straw | 31.492 | 229.63 | This study |
| PVA | 9 % CNC from date palm mat fibers | 30.99 | 60 | (Khatun et al., 2023) |
| Low density polyethylene | 0 | 12.71 | 121.40 | (Mousavian et al., 2021) |
| Polyvinylchloride | 0 | 10.34 | 46.16 | (Patil and Jena, 2021) |

3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) and Derivative thermogravimetry (DTG) of PVA films after 500 °C tests were shown in Figure 4. Weight loss after tests of PVA films ranged from 6 - 8 %, no obvious difference between

samples with different CNC concentration. During the test of PVA films, three main weight loss regions are observed. In the region 30 °C to 130 °C, all the films showed first weight loss which can be attributed to the loss of evaporation on the surfaces of PVA films. The mass decreased in the first period about 12 %. The second stage of losing weight occurs in the temperature range of 260 °C to 380 °C, owing mostly to the dehydration process and the generation of volatile matter. Weight reduction in this range was around 61 – 70 %. The third degradation was above 380 °C, included the breakdown of carbonaceous materials (Wang et al., 2018). When CNC concentration increased, the second step and third step tended to be further apart: the temperature in second step tended to decrease, and third step tended to increase, resulting in slightly less thermally stable PVA/CNC film.

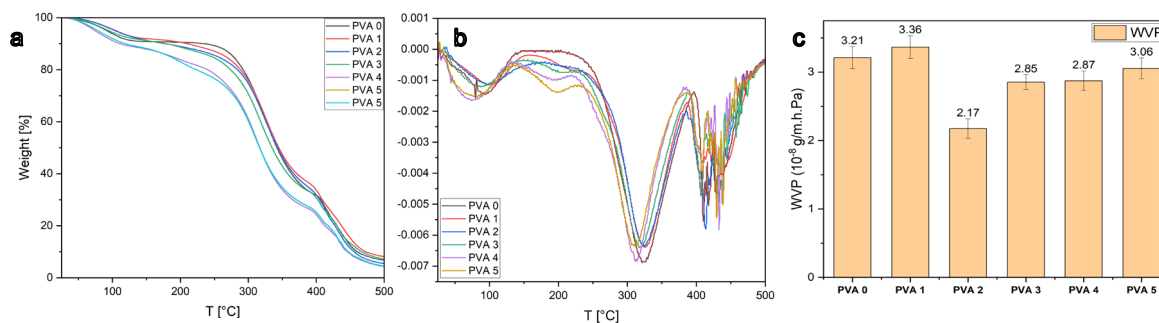


Figure 4: TGA (a), DTG (b) and water vapor permeability (WVP) (c) of PVA/CNC films

3.6 Water vapor permeability

The water vapor barrier feature of a wrapping material is critical in reducing moisture transmission between packed goods and the external environment (Ren et al., 2017). In applications for food packaging, limiting the water vapor permeability would reduce the moisture loss of food, preserving their qualities. Films commonly used to wrap food have different WVP such as polyvinylchloride of $0.35 \text{ g.mm/day.KPa.m}^2$ ($1,458.10^{-8} \text{ g/m.h.Pa}$) (Suzuki et al. 2020) and low density polyethylene of $5.25.10^{-5} \text{ g.m/m}^2.\text{d.Pa}$ ($2.188.10^{-6} \text{ g/m.h.Pa}$) (Zia et al. 2019). Figure 5 illustrated the WVP values of PVA films with varying levels of CNC. The incorporation of the different CNC sharply decreased the WVP of the film, after that increased again (even bigger than the original PVA film). The PVA 2 film reached a minimum WVP value ($2.17.10^{-8} \text{ g/m.h.Pa}$, 32.4 % decrease compared to original PVA. WVP value declined because as the content of nanocellulose in the film matrix grows, so does the film's hydrophilicity, which is related to the hydrogen bonding connecting to water (Solhi et al., 2023). The increase in WVP could be due to the high CNC concentration, which were not evenly distributed in the PVA lattice, causing agglomeration, or it could also be influenced by the high crystallinity of the CNC.

4. Conclusions

Biodegradable film composites were successfully prepared using cellulose nanocrystals reinforced with polyvinylalcohol. Polyvinylalcohol films had homogeneous and relatively smooth surface with white cellulose nanocrystals particles equally dispersed. Even when adding cellulose nanocrystals to the polyvinylalcohol films, the peaks of the polyvinylalcohol films were not shifted, indicated by FTIR. The heat resistance of polyvinylalcohol films decreased a bit when the amount of cellulose nanocrystals increased significantly. On the other hand, there is a noticeable change in tensile strength and water vapor permeability. Tensile strength of 2 % cellulose nanocrystals film increased 157.6 % compared to the original polyvinylalcohol film. Water vapor permeability of 4 % cellulose nanocrystals film decreased 32.4 % compared to the original polyvinylalcohol film. This proves that with a small amount of cellulose nanocrystals, it has a significant impact on the characteristics of polyvinylalcohol films, demonstrating that it will save materials throughout the material production process. Based on the enhanced mechanical and water vapor permeable qualities, synthesized films are highly suited to food packaging applications, which promises eco-friendly and healthy wrappers for consumers.

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