Preparation and Biodegradation of Nanocellulose Reinforced Polyvinyl Alcohol Blend Films in Bioenvironmental Media

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Authors' contributions

This work was carried out in collaboration between all authors. Author NI designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SJP and AR managed the analyses of the study. Author AKC managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Solution casting method was used to prepare nanocellulose reinforced polyvinyl alcohol (PVOH) from Oil palm empty fruit bunches. Different environmental test were used to investigate the biodegradability of the composite in soil and compost as well as in water and acidic solution. The morphology of the composite was investigated by scanning electron microscopy. The composite film with nanocellulose and without nanocellulose were compared, nanocellulose modified PVOH film showed more highly degradable by soil and compost as well as in enzymes. From the biodegradation study it was observed that the rate of degradation of the composite depend on the nanocellulose content. Surface morphology study of the composite exposed the distribution of nanocellulose in the PVOH.

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1. INTRODUCTION

Now a day the effect of synthetic polymer materials has become an environmental issue. These materials take more than thousand years to decompose in soil, which is the major part of environmental pollution [1]. Nowadays, biopolymers have drawn more and more interest because of increasing environmental concern and decreasing fossil resources. This evolution motivates academic and industrial researchers to develop novel materials labelled as "environmentally- friendly", i.e., materials produced from alternative resources, with lower energy consumption, biodegradability and non-toxicity [2]. Depending on the raw material the environmental friendly polymer materials divided into two groups: Synthetic degradable polymers and natural renewable polymers. Chitosan, cellulose and starch are the sources of natural renewable polymers. Since biopolymers are biodegradable and the main products are obtained from renewable resources such as agro resources, they represent an interesting alternative route to common nondegradable polymers for short-life range applications (packaging, agriculture, biomedical etc.). Nevertheless, until now, some of the biopolymers (e.g. polylactic acid, which is fully biodegradable) are costly compared to conventional thermoplastic and they are sometimes too weak for practical use. Therefore, it appears necessary to extend the search for fully biodegradable polymers, which are economically accessible and industrially accepted [3]. Composites are novel materials with drastically improved properties due to the incorporation of small amounts (less than 10 wt. %) of nano-sized fillers into a polymer matrix. They offer high surface area, more than 200 m^2/g, i.e., a huge interface with the polymer (matrix), which governs the material properties [4]. The final behavior can be considerably improved by the strong and extensive polymer-nano filler interactions, as well as, good particle dispersion [4]. In tune with the current environmental concerns, the researchers are interested in biocomposites area, which is a solution for various industrial as well as ecological problems. Moreover, since industry is concerned with sustainable developments, the production cost of biocomposites goes on decreasing, which will allow strong developments of biopolymers-based materials [3]. Biocomposites are obtained by adding nanofillers to biopolymers, resulting in very promising materials since they show improved properties with preservation of the material biodegradability, without eco-toxicity. These materials are mainly destined for biomedical applications and different short-term applications, e.g., packaging, agriculture or hygiene devices. They thus represent a strong and emerging answer for improved and eco-friendly materials.

A necessary pre-requisite for extending their utilization is their biodegradability in natural environments, where they may serve as a source of carbon and energy for a variety of microorganisms [5]. Biodegradation studies are usually carried out in soil or compost. In particular, enhanced biodegradation of these materials may occur in the presence of compost, a complex biological environment, in which microbial diversity is relatively high and where there is an increased degradation potential [6]. According to ISO, CEN definition [7], biodegradation is the degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of the exposed material and resulting in the production of carbon dioxide, water, mineral salts (mineralization) and new microbial cellular constituents (biomass) [8].

In the present paper, biocomposites prepared by reinforcing nanocellulose in a matrix of polyvinyl alcohol (PVOH) is discussed. The nanocellulose is isolated from oil palm empty fruit bunches (OPEFB) which is a renewable resource [9]. It is not only biodegradable but also biocompatible [10]. In the present study, nanocellulose was incorporated into the PVOH matrix, which further facilitated the degradation process.

2. MATERIALS AND METHODS

Poly (vinyl alcohol) (Kuraray PVA-220S) was obtained from Kuraray Co., Ltd. (Singapore). Oil palm empty fruit bunch (OPEFB) fibers were purchased from Sabutek Sdn. Bhd., Malaysia. OPEFB underwent a sieving process to obtain fiber particles in the range of 4 to 6 mm. The fiber particles were then sent for grinding and sieving to obtain powder with diameter size between 100 and 150 µm. Hydrogen peroxide and formic acid were obtained from Fisher Scientific (USA). All other solvents and chemicals (analytical grade) were used as received [1].

2.1 Pretreatment of OPEFB Fibers

OPEFB fibers were first washed several times with 1.0 wt% washing detergent to remove all the contamination and dirt. Next, the OPEFB raw fiber was dried in an oven (SOV 70B, Thermoline) at 100±2°C until constant weight was achieved. The fiber was then dewaxed with ethanol (70% v/v) using a Soxhlet apparatus (Favorit) for 6 h. This step was followed by washing the dewaxed fibers with distilled water to remove the traces of alcohol. Later, the dewaxed fibers were suspended in a mixture of 100 mL of 10% NaOH and 100 mL of 10% H_2O_2. The mixture was autoclaved at 1.5 bar and 120°C for 1 h. Finally, the fibers were separated from the dark brown supernatant and washed thoroughly with clean water [1].

2.2 Extraction of OPEFB Nanocellulose

During the extraction process, 5 gm fiber were soaked in a mixture of 20% formic acid and 10% hydrogen peroxide, which was prepared in a 1:1 ratio (v/v). The mixture was placed in a water bath at 85°C for 2 h [1].

The delignified fibers were sent through a filtration process, and the samples were washed thoroughly with 10% formic acid prior to cleaning with distilled water. The extracted nanocellulose was light yellow in color. The nanocellulose was prepared as a suspension by re-suspending it in 10% hydrogen peroxide (pH 11) at 60°C for a duration of 90 min. The nanocellulosic unit is shown in Fig. 1(a) and scanning probe microscopic (SPM) image of the nanocellulose in Fig. 1(b).

2.3 PVA/Nanocellulose Composite

PVA-based composite films were prepared by the solution casting method. A 10 wt% aqueous solution of PVA was prepared by stirring at 1,000 rpm at room temperature to avoid clumps. Subsequently, the PVA solution was continuously stirred at 90°C for 2 h, then sonicated for 5 min. Various compositions of PVA/nanocellulose composites were prepared with a nanocellulose content ranging from 1 to 7 wt%. The solutions were then poured into a mold and dried at room temperature for 7 days before being demolded. The thickness of the films was controlled to approximately 150 µm. The resulting thin composite films were then dried in an oven at 50°C for 1 day.

2.4 Morphological Analysis

The cross-section of the fractured surface morphology of the sample was examined by using a scanning electron microscope (Hitachi S-3400N, Thermo Scientific) with an accelerating voltage of 10 kV. The composite film was soaked in nitrogen liquid for 10 seconds. Then, the sample was fractured immediately to get a freeze-fractured surface. Before the SEM observation was done on the sample film, the cross-section surface of the fractured film was sputter-coated with a gold layer for 1 h to avoid electrostatic charging and poor image resolution.

2.5 Enzymatic Testing

An enzymatic mixture containing certain amounts of distilled water, α-amylase and β-amylase were placed in a conical flask. The dried samples were cut into 3 × 3 cm square specimens, and the
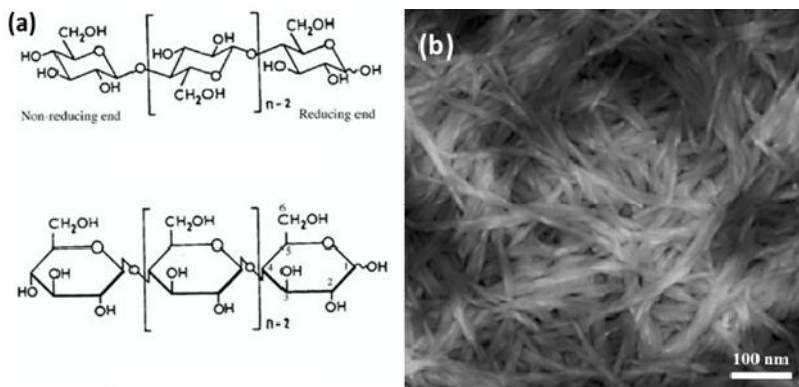

Fig. 1. (a): Nanocellulose unit.   (b): SPM of nanocellulose

samples were then weighed accurately using a digital balance and immersed in a conical flask. The flasks were placed in a shaking incubator at a rate of 120 rpm for 60 hours at 30°C. The samples were removed and rinsed with distilled water to remove the enzymatic mixture and dried in a desiccator under vacuum for 24 hours before being weighed and then the degree of enzymatic degradation [DED (%)] was calculated.

2.6 Soil Burial Test

Two different pots were filled to their approximate capacity of 10 L with soil and compost. The samples were cut into 30 × 50 mm pieces and buried in the soil at a depth of 10 cm. The soil was placed in the laboratory, and the moisture of the soil was maintained by sprinkling water at regular time intervals. The excess water was drained through a hole at the bottom of the pot. The degradation of the samples was determined at regular time intervals (7 days) by carefully removing the sample from the soil and washing it gently with distilled water to remove soil from the film. The sample was dried under vacuum until a constant weight was obtained. Weight loss of the sample over time was used to indicate the degradation rate of the soil burial test.

2.7 Water Solubility Testing

For the water solubility testing, the dried films were immersed in distilled water and an acidic solution made from 0.2 M H_2SO_4 at room temperature (25°C). After equilibrium was reached (24 hours), the moisture on the surface of the film was removed and the weight of the film was measured. The swelled films were dried again for 24 hours at 60°C.

3. RESULTS AND DISCUSSION

3.1 Surface Morphological Study

Fig. 2 shows the surface structure of pure PVOH and NCC modified PVOH composite films and Fig. 2(a) shows pure nanocellulose. During the casting method, the bubble trapped in the voids of the PVOH films. With the increase of the NCC content in the composite, the phase changed and the amorphous NCC finely dispersed with PVOH matrix. Cryo-fractured surface was caused for adding more than 70% of NCC and the surface became rougher and brittle. PVOH was finely distribute in the NCC matrix, but the NCC convinced remarkably at the same moment. After studying SEM micrograph, it is clear that 70/30 PVOH/NCC composite is suitable for the well dispersion of NCC in the matrix.
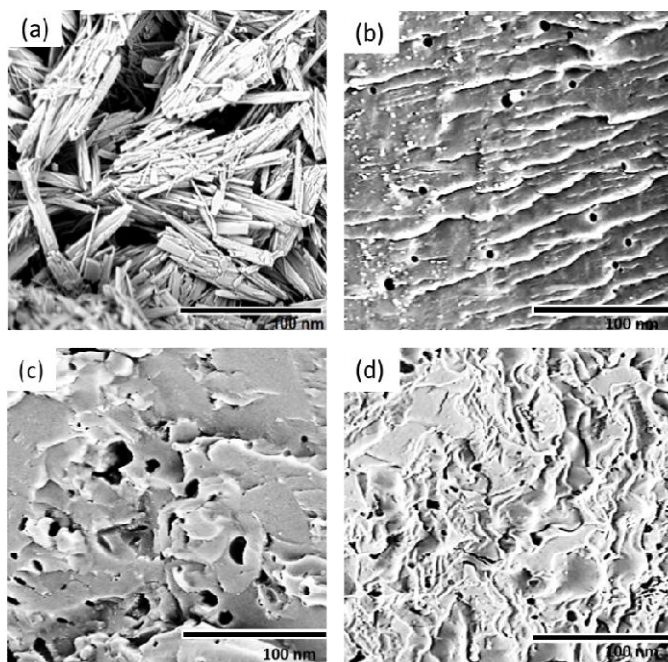

Fig. 2. SEM micrographs of (a) NCC, (b) PVOH/NCC, (c) 70/30 PVOH/NCC and (d) 30/70 PVOH/NCC

3.2 Enzymatic Testing

Fig. 3 shows the weight loss of the composite by enzyme degradation. The composites immersed in the enzyme media for 80 hours to observe the degradation rate. The graph represent that with increasing the cellulose content the rate of degradation also increase. Pure PVOH degradation rate was slower than the NCC modified PVOH composite. The 30/70 weight percent of PVOH/NCC showed higher degradation rate, which indicated 95% weight loss after 80 hours of insertion in the enzyme media. The NCC modified PVOH films can absorb more of the enzyme solution than pure PVOH because of the –OH groups of NCC that enhanced the absorption rate of enzyme in to the composite films [11]. With the increasing of NCC content in the composite, the enzyme absorption rate also increased.

3.3 Soil Burial Test

Figs. 4 and 5 show the weight loss of the composite in soil and compost. The composites buried in soil and compost for 10 weeks to observe the degradation rate. The graph represent that with increasing the cellulose content the rate of degradation also increase. Pure PVOH degradation rate was slower than the NCC modified PVOH composite. The 30/70 weight percent of PVOH/NCC showed higher
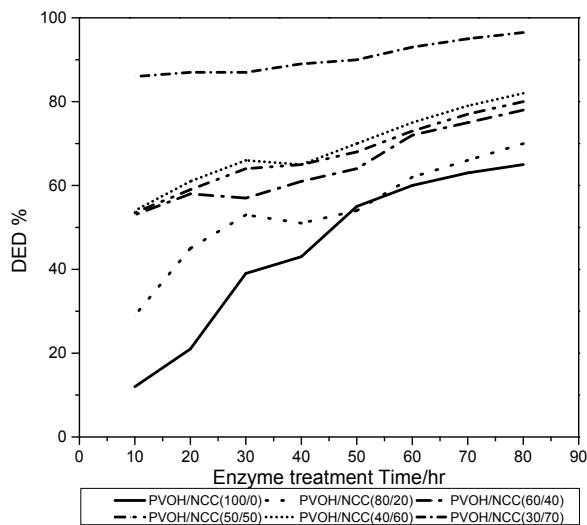
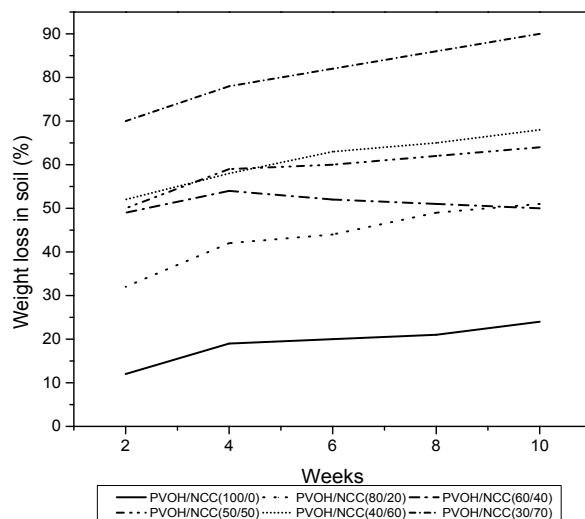**Fig. 3. Enzymatic degradation of PVOH (100/0) and PVOH/NCC films using α- and β-amylase**

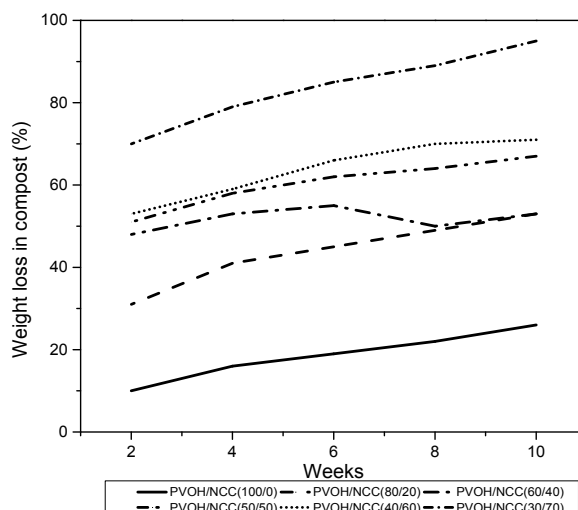**Fig. 4. Weight loss of PVOH/NCC films after 10 weeks in soil**

Fig. 5. Weight loss of PVOH/NCC films after 10 weeks in compost

degradation rate, which indicated 90% weight loss after 10 weeks of burial in soil and compost [12]. NCC is more biodegradable than PVOH. Biodegradation rate increase in compost than oil because compost usually made from organic compound. Generally, compost made from different kinds of plant and animal decomposition. For that reason the nutrients present in compost can degrade the NCC modified PVOH rapidly than in normal soil [10].

3.4 Kinetic Studies of Water Absorption and Water Solubility Testing

Figs. 6 and 7 show the moisture absorption rate of the composite in distilled water and in acidic media. The composites insertion in water and acid for 40 hours to observe the moisture absorption rate. The graph represent that with increasing the cellulose content the rate of moisture absorption also increase. Rate of moisture absorption for the pure PVOH was slower than the NCC modified PVOH composites. The 30/70 weight percent of PVOH/NCC showed higher absorption rate, which indicated 140% moisture absorption after 40 hours of insertion in water and acidic media [13].

Fig. 8 shows the water solubility rate of the composite in distilled water and in acidic media. The graph represent that with increasing the
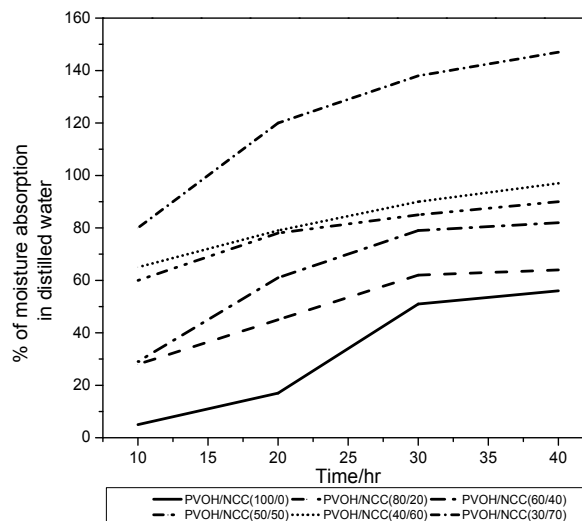

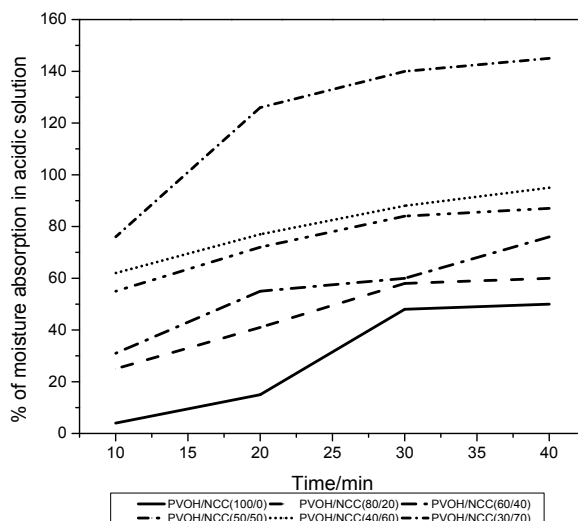**Fig. 6. Effect of nanocellulose on water uptake of PVOH composites in distilled water**

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Fig. 7. Effect of nanocellulose on water uptake of PVOH composites in an acidic solution
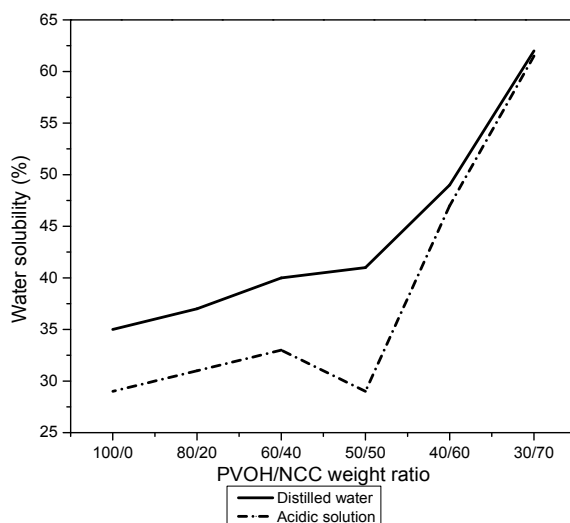

Fig. 8. Water solubility of PVOH/NCC films in distilled water and in an acidic solution

cellulose content the rate of water solubility also increase. Rate of water solubility for the pure PVOH was slower than the NCC modified PVOH composites. The 30/70 weight percent of PVOH/NCC showed higher solubility rate, which indicated 60% for both of in water and acidic media [14]. For other weight ratio of PVOH/NCC the solubility rate in water is higher than in acid because the concentration of acid is higher than of water.

4. CONCLUSION

Biodegradation rate of pure PVOH is slower than NCC modified PVOH composite. In case of enzyme, soil and compost the rate of degradation of the composite is increase with increasing the percentage of NCC content in the composite. The rate of water absorption in water and acidic media also depend on the NCC content in the composite. PVOH/NCC composites were more soluble in the distilled water medium relative to the acidic solution. From the surface study of the composite, it can be summarize that the dispersion of NCC in 70/30 of PVOH/NCC matrix showed better than other ratios. So this research shows that the biodegradation of the composite depends on the percentage of NCC.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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