ENHANCEMENT OF WATER RESISTANCE AND MECHANICAL PROPERTIES OF MICROFIBRILLATED CELLULOSE BY GLYCEROL AND HOT-PRESSING TREATMENT

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Abstract

In this work, glycerol and hot-pressing treatment were utilized to enhance the water-resistant and mechanical properties of microfibrillated cellulose (MFC) film. Recently, MFC films have been suggested as promising materials for various applications such as flexible electronics, micro-optical devices, and biosensors. However, their poor water resistance and brittleness prevent the widespread use of MFC films. In this study, the combination of glycerol and hot-pressing treatment was used to overcome these limitations. While the plasticizing effect by glycerol greatly enhances the stretchability and flexibility of the MFC film, hot-pressing treatment improves its water resistance and mechanical strength. The wet strength of treated MFC film using a glycerol solution with a concentration of 2.5% (v/v) (H-MFC/2.5%G) was 41.3 MPa compared to 3.3 MPa of untreated MFC film. Moreover, the strain at break and tensile strength of this film was significantly improved. The present MFC film can be used as an eco-friendly, robust, and flexible platform for advanced applications.

Keywords: *Glycerol; hot-pressing; microfibrillated cellulose; water resistance; wet tensile strength.*

1. Introduction

Cellulose is the most abundant type of renewable organic polymer on the Earth, with an annual biosynthetic production that is estimated to be over 10^{11} tons. Plants, agricultural residue are the common sources of cellulose. The unique hierarchical architecture of natural cellulose consisting of nanoscale fibrils allows the extraction via mechanical and chemical methods, or through a combination of both of these techniques [1]. The results of these processes are nanocellulose materials. Generally, nanocellulose is divided into two main categories: cellulose nanocrystals (also known as cellulose nanowhiskers or nanocrystalline cellulose) and cellulose nanofibrils (also termed microfibrillated or nanofibrillated cellulose) [2]. Cellulose nanocrystals (CNCs) have a width of 3-10 nm and a length of 100-500 nm. CNCs exhibit a rod-like shape and have very limited flexibility compared to cellulose nanofibrils. The nanocrystalline particles are generated by the splitting of amorphous domains, as well as by the breaking of local crystalline contacts between nanofibrils, through hydrolysis with highly concentrated acids [3].

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Microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC) is about 5-100 nm in width and 500-2000 nm in length. Isolated cellulose nanofibrils are long, thin, and flexible formations composed of alternating crystalline and amorphous domains. MFC/NFC is generally produced by the mechanical methods without any pretreatment, or after chemical or enzymatic pretreatment.

Paper made from nanocellulose is typically called nanopaper [4]. Because nanopaper has some excellent properties such as high surface area, superior mechanical strength, high thermal stability, low thermal expansion, high smoothness, high optical transparency, and high oxygen gas barrier [5], it can be considered as a green platform for many advanced applications such as flexible printed electronics [6], micro-optical devices[7], biosensors [8, 9], microfluidic devices [10], and functional membranes [2]. However, brittleness and low water resistance are considered as two critical limitations of MFC films, which hindered their widespread use.

The plasticizers are commonly used to enhance the flexibility and stretchability of the nanocellulose substrates [11-13]. The most commonly used plasticizer is glycerol because it is a cheap, non-toxic, and eco-friendly chemical agent. Glycerol has been shown to effectively increase elongation [12] and oxygen barrier [11]. However, it substantially reduces Young's modulus and tensile strength of the nanocellulose film [11, 12]. Moreover, when glycerol is added to the MFC film, its water resistance is significantly decreased because glycerol can easily absorb water. Hot-pressing treatment is a simple and effective way to improve the water resistance and mechanical strength of nanocellulose film [14]. This treatment produces a denser structure with more hydrogen bonds between nanofibrils, resulting in a strong microstructure with excellent water stability. Although this method is simple and effective to improve the water-resistance and mechanical strength without the use of chemical treatment, the flexibility of the MFC substrate become worse [14].

In this regard, the effects of glycerol and hot-pressing treatment on the mechanical and water-resistant properties of MFC films were investigated. The morphology, water contact angle, and surface energy of the modified MFC substrate were also examined. To incorporate glycerol into the MFC film, a semi-dry MFC substrate made by vacuum filtration was immersed in a glycerol solution. Dry MFC/Glycerol films were prepared by a subsequent hot-pressing process.

2. Methodology

2.1. Materials

A 3.0 wt% aqueous suspension of microfibrillated cellulose (width of 5-100 nm, length of 130 nm to 225 μm) was purchased from the University of Maine. Glycerol

(99%, molecular weight M_w = 92.09) was supplied by Sigma-Aldrich. All materials were used as received without modification.

2.2. Preparation of the MFC samples

The brief information of the prepared MFC samples is shown in Tab. 1.

To make the H-MFC, the MFC suspension was first diluted with deionized water to obtain a suspension of 0.25 wt% MFC. After stirring the suspension for 2 hours with a magnetic stirrer, 300 g of the diluted suspension was filtered through a polyvinylidene fluoride membrane (SVLP09050, Millipore) using a vacuum pump. With this technique, a wet cake containing about 20 wt% MFC, which was sufficiently dried for handling, could be prepared in about 30 minutes. The wet sheet was carefully peeled off from the membrane and placed between two conventional filter papers (01511090; Advantec). Finally, an H-MFC was obtained through a hot-pressing process at 100°C and about 0.15 MPa in 1 hour.

For the plasticized H-MFC, wet cakes were prepared by the same procedure. The wet MFC sheets were immersed in 300 ml of aqueous glycerol solutions (2.5% v/v) for 24 hours at room temperature to obtain the plasticized H-MFC. An excess of aqueous glycerol solution was used to minimize dilution caused by the occurrence of water inside the wet cakes. A similar process was performed to dry plasticized H-MFC by hot-pressing.

The A-MFC and plasticized A-MFC were also prepared as reference cases. The same preparation method was employed to make the wet cakes. The completely dry films were obtained by air-drying of the wet MFC sheets at room temperature (23-25°C) for about 7 days.

Tab. 1. The concentration of glycerol in the plasticized solution and drying methods for preparing MFC films

Case	The concentration of glycerol in the plasticized solution (% v/v)	Drying method
H-MFC	0.0	Hot-pressing
H-MFC/2.5%G	2.5	Hot-pressing
A-MFC	0.0	Air-drying
A-MFC/2.5%G	2.5	Air-drying

2.3. Characterization of MFC samples

All samples were conditioned at 23°C, 50% RH for one week before characterizing.

The surface morphology of the MFC films was analyzed using a scanning electron microscope (SU-70; Hitachi). Samples were coated with platinum to avoid a charging effect.

A tensile test of the MFC films in dry and wet conditions was performed using a tensile test machine (TO-100-1C; Test One). The dog-bone-shaped specimen (40 mm long and 3 mm wide) was carefully cut from the MFC film. The specimens were conditioned at 23°C and 50% RH for 48 hours. For a dry condition test, the grip distance, load cell capacity, and crosshead speed were set to 7.5 mm, 1 kN, and 1 mm/min, respectively. The specimens for the wet condition were first immersed in freshwater at 25°C for 1 hour. They were tested immediately after removing excess water with a blotting paper. The grip distance, load cell capacity, and crosshead speed for the wet condition test were 7.5 mm, 100 N, and 0.5 mm/min, respectively. Wet tensile strength was calculated based on the initial shape of the dry specimen [15]. To obtain Young's modulus, a tensile stress-strain curve was fitted assuming a linear relationship over the 0.5-1% strain range.

To examine water absorption, the strip sample (20×5 mm^2) was immersed in freshwater at 25°C for 24 hours. Before the measurement, the excess water on the surface was carefully removed using blotting paper. The mass of all samples was measured right before and after water immersion. Water absorption was calculated by the following equations:

$$\text{water absorption} = \frac{M_1 - M_0}{M_0} \times 100(\%)$$

where M_0 and M_1 are the mass of the sample before and after dipping into the water, respectively.

3. Results and discussion

3.1. Morphological characterization

Scanning electron microscopy (SEM) was used to analyze the morphology of the MFC films. It is well known that the air-dried MFC film from an aqueous solution exhibits a fibrous structure [16, 17]. As can be seen in Fig. 1(a), the nanofibrils aggregate, producing the porous structure. Because the nanofibrils stack together, the relative motion of these fibrils is very difficult. As a result, the A-MFC shows strong but brittle behavior. A porous structure is also observed in the H-MFC (Fig. 1(b)). It can be seen that the microstructure of the H-MFC is smoother and denser than that of the A-MFC. It can be attributed to the effect of the hot-pressing treatment where nanofibrils are compressed.

The structures of plasticized MFCs are shown in Fig. 1(c), 1(d). It is obvious that glycerol penetrated the pores of the MFC structures. In these SEM images, it is also noticeable that glycerol not only occupied the pores but also covered the nanofibrils. The fibers became thicker and the fine fibrils were not clearly visible. This can be due to

the coverage of glycerol on the fine fibrils and the combination of more nanofibrils to larger and thicker fibers. The plasticized H-MFC exhibited a smoother and denser structure, which is the consequence of the hot-pressing. While there exist fibrous structures in the plasticized H-MFC, no obvious fibers can be observed in the plasticized A-MFC.

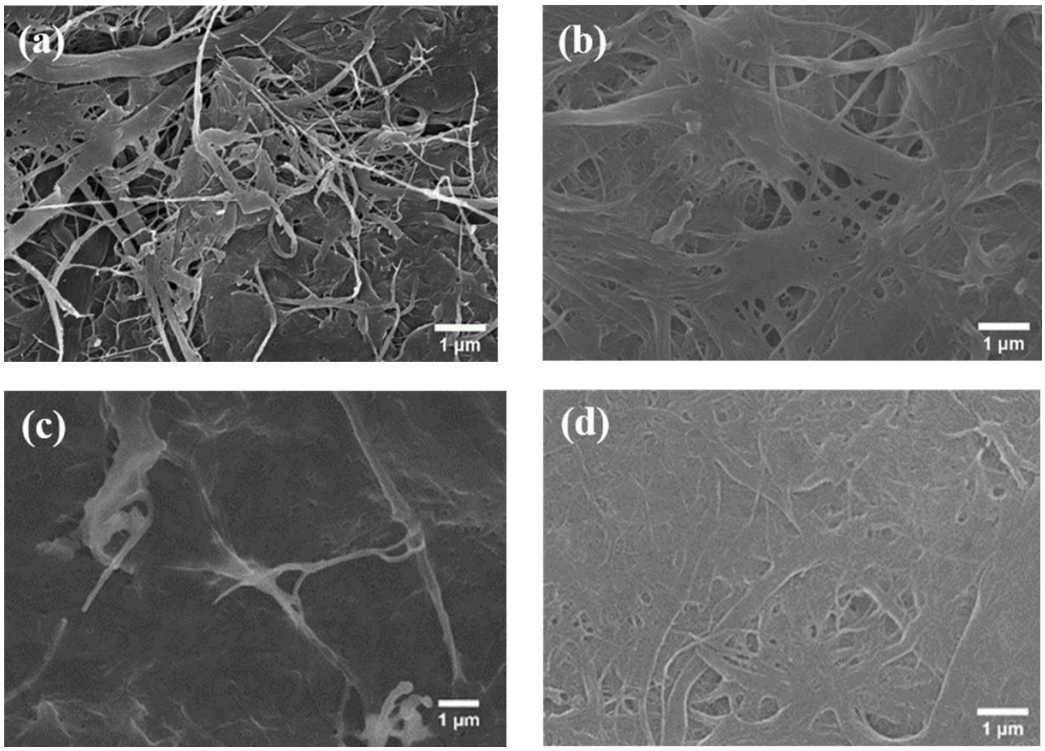

Fig. 1. Scanning electron microscope images of A-MFC (a), H-MFC (b), A-MFC/2.5%G (c), H-MFC/2.5%G (d).

3.2. Mechanical properties

The mechanical properties of MFC films were measured using the tensile test. As can be seen in the stress-strain curve (Fig. 2), the H-MFC showed a higher tensile strength of 130.2 MPa than the A-MFC (95.3 MPa). This improvement is due to the effect of the hot-pressing process to change the microstructure of MFC films. Many reports have demonstrated the effect of glycerol on the mechanical properties of plasticized A-MFC [11-13]. While the elongation increased, the tensile strength and Young's modulus decreased significantly due to the plasticizing effect. Therefore, the film became weaker but more flexible. However, the case of H-MFC/2.5%G showed different behavior. For H-MFC/2.5%G, while the elongation of the sample improved, the tensile strength decreased slightly. The addition of glycerol to H-MFC mainly makes two effects: (i) plasticization by glycerol and (ii) formation of the additional

hydrogen bonds between the hydroxyl groups of nanofibrils and glycerol by hot-pressing. The particular case of H-MFC/2.5%G might be resulted from the positive effect of improving the tensile strength by the additional hydrogen bonds can overcome the negative one of the plasticization.

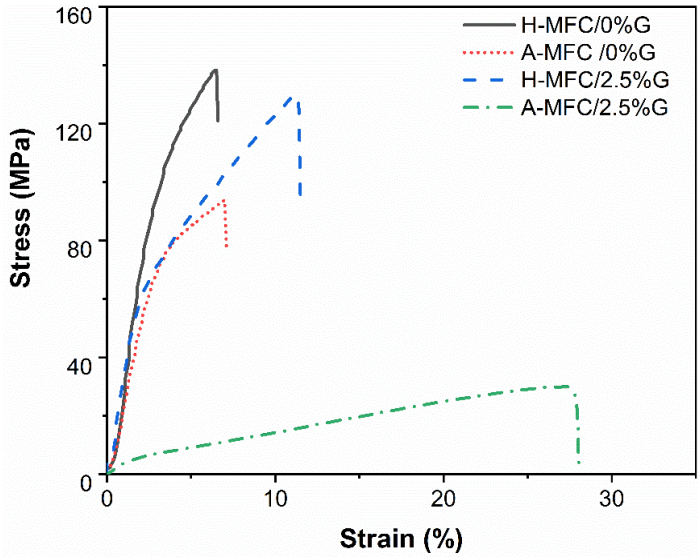

Fig. 2. Stress-strain curves of prepared MFC films.

3.3. Water-resistant properties

Cellulose fibrils can be self-assembled because hydrogen bonds are generated by hydroxyl groups on the surface [18]. Since hydroxyl groups can easily absorb water, hydrogen bonds between hydroxyl groups are quickly broken when cellulose fibrils are immersed in water. Therefore, MFC film becomes weaker after soaking in water and can also break down into individual fibrils [6, 19]. The poor water-resistance of the typical MFC film is one of the critical limitations [6, 19]. In this study, we used a combination of glycerol and hot-pressing treatment to improve the water-resistance of MFC film. Water absorption and wet tensile strength were used to evaluate the water-resistant characteristics of the current MFC film.

The effect of the drying methods on the water absorption is shown in Fig. 3(a). Water absorption of A-MFC was very high, at 137.4%. On the other hand, this value for H-MFC was only 32.3%. This proved that the hot-pressing treatment improved the water-swelling resistance of MFC film. The denser microstructure and additional hydrogen bonds between cellulose nanofibrils resulting from the hot-pressing treatment contribute to this improvement [14].

The effect of glycerol on the water absorption of plasticized H-MFC and plasticized A-MFC is also shown. Glycerol significantly increases water absorption of

the plasticized A-MFC. This can be attributed to the strong water absorption capability of glycerol [20]. For the plasticized H-MFC, the addition of glycerol does not change the water absorption.

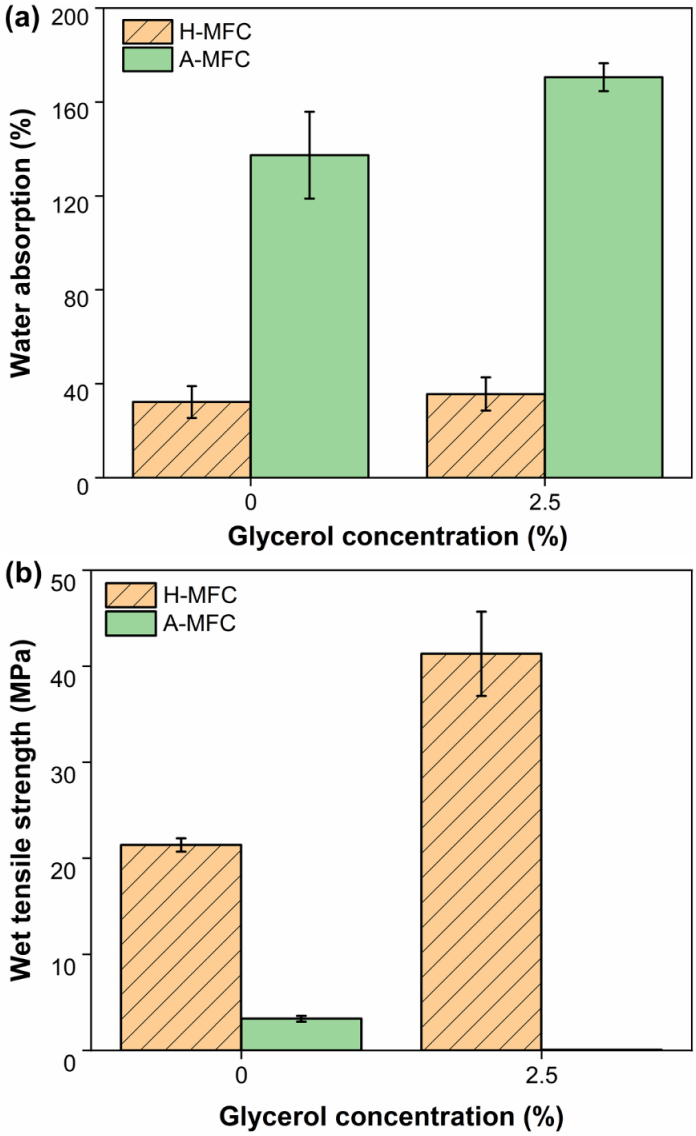

Fig. 3. Water absorption (a) and wet strength (b) of prepared MFC films. An A-MFC/2.5%G film was too weak when immersed in water. Therefore, their wet strength cannot be measured.

Low strength in the wet state is one of the disadvantages of MFC film, which hinders its application [2, 19]. The mechanical strength of H-MFC and A-MFC in the wet state after being immersed in water for 1 hour is shown in Fig. 3(b). Because a hydrogen bond is easily broken by water, the wet tensile strength of A-MFC was found to be very low (~3.3 MPa). The addition of glycerol to A-MFC could significantly

reduce the wet tensile strength. The plasticized A-MFC/2.5%G was too weak to measure their tensile strength in the wet state. The hot-pressing treatment was found to improve the wet tensile strength [14]. As can be seen in Fig. 3b, the wet tensile strength of H-MFC was approximately seven times higher than that of A-MFC. The combination of glycerol and hot-pressing treatment was significantly enhanced the wet tensile strength. H-MFC/2.5%G exhibits the highest wet tensile strength (41.3 MPa), which is about thirteen times compared to that of A-MFC.

4. Conclusions

In this study, glycerol and hot-pressing treatment were used to improve the mechanical properties and water resistance of MFC films. Glycerol was responsible for enhancing flexibility through a plasticizing effect. Hot-pressing treatment formed a denser, smoother structure, subsequently enabling the improvement of the hydrogen bonds between cellulose nanofibrils. The plasticized H-MFC not only showed good flexibility and stretchability due to the plasticization effect of glycerol but also exhibited high strength due to its dense structure and additional hydrogen bonds. Compared to A-MFC, the tensile strength and elongation of H-MFC/2.5%G were improved by 37% and 85%, respectively. In addition, a combination of glycerol and hot-pressing treatment can increase the water resistance of the MFC film. The wet strength of H-MFC/2.5%G was nearly thirteen times that of A-MFC. The materials used in the fabrication of plasticized H-MFC films, and the preparation process itself are environmentally friendly. Consequently, the proposed MFC film can be considered a robust, flexible, and green platform for advanced applications.

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NÂNG CAO SỨC KHÁNG NƯỚC VÀ ĐỘ BỀN CƠ HỌC CỦA MICROFIBRILLATED CELLULOSE (MFC) FILM BẰNG GLYCEROL VÀ ÉP NÓNG

Nguyễn Văn Sơn

Tóm tắt: *Một số nghiên cứu gần đây đã giới thiệu khả năng ứng dụng của MFC film trong các sản phẩm công nghệ cao như flexible electronics, micro-optical devices, biosensors. Tuy vậy, hai nhược điểm chính của MFC film là độ giòn cao và sức kháng nước kém đã hạn chế ứng dụng thực tiễn của nó. Trong nghiên cứu này, glycerol và ép nóng được dùng để hạn chế các nhược điểm trên. Trong khi hiệu ứng dẻo của glycerol được dùng để nâng cao tính đàn hồi của MFC film, ép nóng nâng cao tính kháng nước và độ bền. Độ bền ướt của MFC film đã xử lý với glycerol 2,5% (v/v) là 41,3 MPa so với 3,3 MPa của MFC film ban đầu. Ngoài ra, độ bền và độ dẻo của film được nâng cao đáng kể. Loại MFC film này có thể được sử dụng như vật liệu thân thiện với môi trường, tính chống nước và độ bền cao trong các ứng dụng thực tiễn.*

Từ khóa: Glycerol; ép nóng; microfibrillated cellulose; sức kháng nước; độ bền kéo ướt.

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