

Polyvinyl Alcohol (PVA) Films Reinforced with Acid Hydrolyzed Cellulose

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Abstract : Cellulose nanofibers from microfibril cellulose (MFC) was prepared by hydrobromic acid (HBr) treatment at different concentrations. Polyvinyl alcohol (PVA) composite films at various loading level of nanofibers were manufactured by a film casting method. The analysis of degree of polymerization (DP), crystallinity (X_c) and molecular weight (M_w) of cellulose after acid treatment was conducted. The mechanical and thermal properties of the cellulose nanofibers reinforced PVA films were characterized using tensile tests and thermogravimetric analysis (TGA). The DP and M_w of MFC by HBr hydrolysis considerably decreased, but X_c showed no significant change. After acid hydrolysis, the diameter of cellulose nanofibers was in the range of 100 to 200 nm. The thermal stability of the films was steadily improved with the increase of nanofiber loading. There was a significant increase in the tensile strength of PVA composite films with the increase in MFC loading. Finally, 5 wt.% nanofiber loading exhibited the highest tensile strength and thermal stability of PVA composite films.

Keywords : MFC, nanocomposite film, PVA, nanofibers

1. Introduction

Cellulose is a carbohydrate polymer consisting of β -1-4 glucopyranose units with degree of polymerization (DP) of about 10,000 [1]. Cellulose is present in amorphous and crystalline state through inter- and

intra-molecular hydrogen bonds [2]. Characteristics of cellulose such as high mechanical properties, low density, biodegradability, and abundant resources have contributed to a rising interest in this material [1].

Many researches have focused on the isolation of these cellulose nanofibers from the plant cells to use them as reinforcing fillers in composite materials [3]. Chemical

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treatment provides chemical changes on the fiber surface and cells, influencing the fundamental properties of the resultant composites. Especially, acid hydrolysis has been used to remove amorphous regions in isolating the cellulose nanofibers [4]. Microfibril cellulose (MFC) has attracted attention as potential starting material for the cellulose nanofibers reinforced composites.

In general, composites are composed of two or three chemically foreign components. The use of polymer matrix is a method for the preparation of nanocomposites. Water soluble polyvinyl alcohol (PVA) has been widely used as a matrix for preparation of nanocomposites, due to its easy process, high optical clarity and biocompatibility [5,6]. The hydroxyl groups on PVA are expected to lead a strong hydrogen bonding with the polar surface of the cellulose nanofibers.

The cellulose nanofibers from microfibril cellulose (MFC) with HBr hydrolysis and the resultant PVA films reinforced with the cellulose nanofibers were prepared in this study. The objectives of this study were to examine the effect of HBr concentration on the chemical characteristics of the cellulose nanofibers and to investigate the effect of filler loading the mechanical and thermal properties of the resultant PVA composite films.

2. Materials and methods

2.1. Materials

Microfibril cellulose (MFC) was used as a starting material for the preparation of nanofiber materials. MFC was obtained from Toyo Roshni Kaishna Ltd., Japan. Polyvinyl alcohol (PVA 1,500) was supplied by Junsei Chemicals Co. Ltd., Japan. Hydrobromic acid (HBr) was obtained from Yakuri Pure Chemicals Co., Japan.

2.2. Preparation of nanocellulose

Five grams of dried MFC were put into a two neck flask with a stirrer and a condenser. Both 1.5 and 2.5M HBr (200 ml) were added slowly with continuous stirring at 100°C for 4 h. The solution was then cooled down to 25°C and treated with an ultrasonic processor (Sonics, U.S.A) for 1 h. The suspension was centrifuged at 6,000 rpm for 20 min and washed five times in distilled water. The suspension was freeze-dried for 48 h, and then the cellulose nanofibers were obtained.

2.3. Degree of polymerization (DP)

The DP of the MFC was determined from the values of intrinsic viscosities determined in 0.75 mol/L cupriethylenediamine (CED) with an Ostwald viscometer. Intrinsic viscosity was determined by the method of Immergut et al. [7]. All experiments were conducted at 30°C with pure solvent as a carrier.

2.4. Morphology

Morphological study for nanocellulose was performed with scanning electron microscope (SEM) (JEOL 6310 and 6700; Jeol Instruments, Tokyo, Japan) systems with an accelerating voltage of 10 and 15 keV.

2.5. Reinforced PVA composite films

Firstly, PVA granules were taken in a three necked flask with a stirrer, a condenser and a thermostat at 80°C. The PVA granules were dissolved in distilled water to a concentration of 10 wt.%, then stirred for 1 h. Thereafter, 1, 3 and 5 wt.% cellulose nanofibers were added to the PVA solution. The stirring was maintained at 80°C for 2 h and ultrasonification was done for 1 h. The films were casted on a glass plate from PVA solution with the nanofibers. The solution was kept in dry oven at 80°C for 4 h, then PVA composite films with nanocellulose were manufactured.

2.6. Thermal properties

The thermal properties of the hybrids were investigated by thermogravimetric analyzer (TGA) (TA Instruments Inc., U.S.A.). Tests were done under nitrogen at a heating rate of 10°C/min in the temperature range of 30 to 600°C. The weight change was determined as a function of temperature. Differential peak temperature (DT_p) was obtained as the maximum derivative temperature of the weight change over time.

2.7. Tensile properties

The tensile tests were conducted using Universal Testing Machine (Zwick Testing Machine Ltd., United Kingdom). Test specimens were molded to 10mm (width) x 0.1mm (thickness) x 100mm (length). Five replicates were tested and the results were presented as an average. Tensile deformation was determined at a crosshead speed of 10mm/min.

3. Result & Discussion

3.1. Chemical characterization

Hydrobromic acid (HBr) at 1.5 and 2.5M concentrations was used for acid hydrolysis of MFC. The X_c of starting MFC was 94.1. After the acid hydrolysis with 1.5 and 2.5M HBr for 4 h, the X_c of MFC showed no

significant change (increase of 0.2 and 0.4%, respectively) (Table 1).

The DP of MFC was 372.7. The acid hydrolysis with 1.5 and 2.5M HBr decreased significantly the DP of MFC (75.5 and 92.1%, respectively). The M_w of nanocellulose was obtained by the multiplication of DP with molecular weight of unit cellulose (181.8).

3.2. Thermal properties of nanocellulose

TGA results of MFC after acid hydrolysis are shown in Table 2. The temperatures at 10% weight loss (T_{10}) and 50% weight loss (T_{50}), and peak temperature (DT_p) before and after acid hydrolysis were represented. The T_{10} and T_{50} of MFC were 316.3 and 346.3°C, respectively. After 1.5 and 2.5M HBr hydrolysis, T_{10} of MFC decreased to 309.2 and 271.7°C, and T_{50} of MFC decreased 354.4 and 334.8°C, respectively. The DT_p of MFC was 341.8. After hydrolysis at 1.5 and 2.5M HBr hydrolysis, the DT_p of MFC increased to 358.6 and 344.8°C. This result may represent that the higher crystallinity is related to the higher thermal stability, compared to starting MFC.

3.3. Morphology

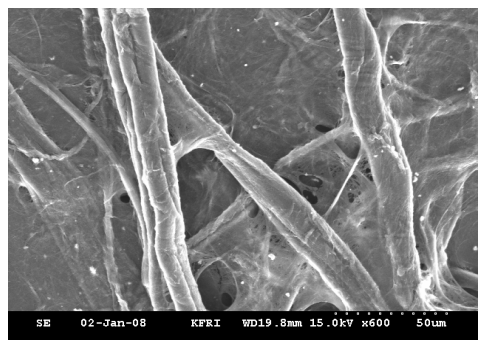
Figure 1(a) is a SEM image of untreated MFC, showing the shape and size distribution of the MFC. Their lengths are 300–500 nm and the diameters are 15–20 nm. Figure 1(b)

Table 1. Chemical characteristics and TGA results of MFC after HBr hydrolysis

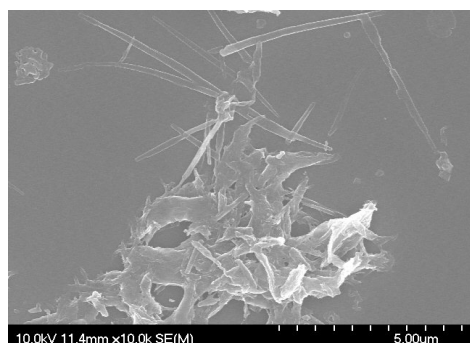
	Chemical characteristics			TGA		
	X_c (%)	DP	M_w	T_{10} (°C)	T_{50} (°C)	DT_p (°C)
MFC	94.1	372.7	60,377	316.3	346.3	341.8
MFC-1.5M HBr	94.3	91.3	14,790	309.2	354.4	358.6
MFC-1.5M HBr	94.5	29.5	4,779	271.6	334.8	344.8

X_c : crystallinity, DP: degree of polymerization, M_w : molecular weight; T_{10} : temperature (°C) at 10% weight loss, T_{50} : temperature (°C) at 50% weight loss, DT_p : differential peak temperature in TGA.

shows the particle size reduction on MFC hydrolyzed by 2.5M HBr. The exposed diameter of the cellulose nanofibers is in the range of 100 to 200 nm.



(a)



(b)

Fig. 1. SEM images of a) untreated MFC ;
b) MFC treated with 2.5M.

3.4. Tensile properties of PVA composite films

The tensile modulus of PVA composite films were represented in Figure 2. The tensile modulus of neat PVA film was 1,065 MPa. As the loading of MFC hydrolyzed with 1.5M HBr increased from 1 to 5 wt.% (based on PVA weight), tensile modulus of PVA composite films increased from 14.7 to 71.5%. For MFC hydrolyzed with 2.5M HBr, the tensile modulus of PVA composite films increased up to 104.5% with increase of filler loading from 1 to 5 wt.%. The improved tensile modulus may be attributed to the

increased stiffness of the composite films by the addition of the cellulose nanofibers.

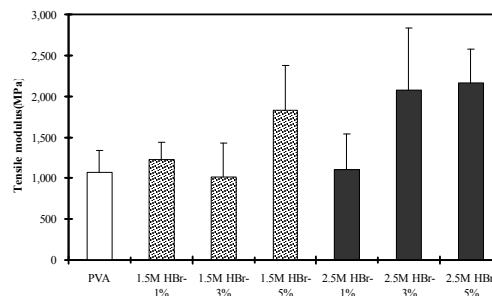


Fig. 2. Tensile modulus of neat PVA and cellulose nanofibers reinforced PVA films at 1, 3 and 5 wt.%.

The tensile strength of PVA composite films was represented in Figure 3. The tensile strength of neat PVA film was 49 MPa. The tensile strength of PVA composite films was increased linearly as the loading of MFC with 1.5M HBr increased from 1 to 5 wt.%. For example, the tensile strength of the PVA composite film with 1 and 3 wt.% nanofibers showed the same strength as neat PVA, but increased 22.4% with 5 wt.% nanofibers. Film prepared with 5% loading of MFC modified with 2.5M HBr showed the highest tensile strength (70% higher than neat PVA). PVA composite films prepared by loading of cellulose treated with 2.5M HBr possess higher tensile strength, compared to cellulose treated with 1.5 M HBr. There may be some specific reasons for increase in the tensile strength for PVA films reinforced with the cellulose nanofibers. Because of high density of hydroxyl groups at the fibril surface, there may be a uniform dispersion of the nanofibers in the PVA matrix. Secondly, a strong hydrogen bonding between the cellulose nanofibers and PVA matrix can form a network. The intermolecular forces between the nanofibers and the base PVA matrix may enhance the tensile strength of the film.

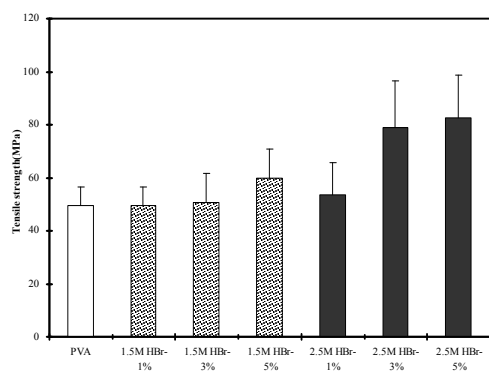


Fig. 3. Tensile strength of neat PVA and cellulose nanofibers reinforced PVA films at 1, 3 and 5 wt.%.

3.6. Thermal properties of PVA nanocomposite films

The effect of cellulose nanofiber loading on the thermal stability of PVA film was seen in their initial decomposition temperature (IDT) of composite films. The IDT of neat PVA film is 240°C. As shown in Figure 4, major difference in the thermal behavior is witnessed for PVA composites films with MFC by 2.5M HBr. Highest thermal stability of PVA films are observed at 5 wt.% loading of MFC. A different of about 20°C in IDT is seen for PVA films with MFC hydrolyzed by HBr, compared to the neat PVA. In case of PVA film with the nanofibers, first stage weight loss is similar to that of PVA and the TGA curves overlaps with each other.

A significant change in the second stage was displayed. The cellulose nanofibers reinforced films undergo slow thermal decomposition, compared to the pure PVA film. At 5 wt.% nanofiber loading level, the decomposition temperature at 50% weight loss was almost 60–70°C higher than neat PVA film, indicating the highest thermal stability. This result may indicate that the enhanced thermal stability due to strong hydrogen bonds between the hydroxyl group of the cellulose nanofibers and neat PVA.

At the third stage, no particular trend is

seen in all the films. The 5 wt.% nanofibers loaded PVA film coincides with the pure PVA film. Both 1 and 3 wt.% nanofibers reinforced films showed better stability in final stage decomposition, compared to the 5 wt.% nanofibers added PVA film.

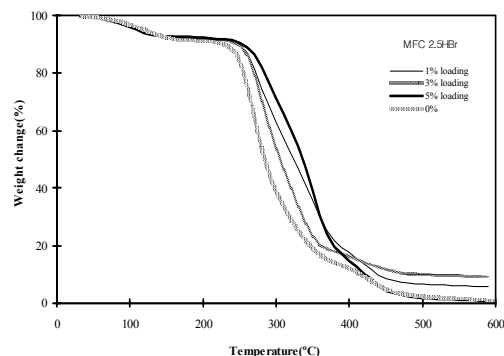


Fig. 4. TGA thermograms of cellulose nanofibers (treated with 2.5M HBr) reinforced PVA films at 0, 1, 3 and 5 wt.%.

4. Conclusion

Cellulose nanofibers were prepared by HBr hydrolysis of MFC. PVA composite films were prepared by reinforcement of the nanofibers into PVA matrix at different filler loading levels. The DP and M_w of cellulose by acid hydrolysis showed a significant decrease, whereas the X_c showed a small decrease. After acid hydrolysis, the diameter of the cellulose nanofibers was in the range of 100 to 200 nm. The cellulose nanofibers loaded films undergo slow decomposition as compared to the pure PVA film. At 5 wt.% loading level, the decomposition temperature at 50% weight loss was almost 60–70°C higher than neat PVA film. There was a significant increase in the tensile strength of PVA composite films with the increase in nanofiber loading.

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