Electrospinning of Ultrafine Cellulose Fibers and Fabrication of Poly(butylene succinate) Biocomposites Reinforced by Them

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ABSTRACT: In this study, electrospinning conditions for ultrafine cellulose fibers was systematically studied and poly(butylene succinate) biocomposites reinforced by the ultrafine cellulose fibers (cellulose/PBS biocomposite) were fabricated. The ultrafine cellulose fibers were electrospun from cellulose (DP = 700) solutions in N-methylmorpholine-N-oxide hydrate (85/15 w/w) at 100°C. The optimal electrospinning concentration of the cellulose solutions was determined to be 7 wt % and the average diameter of the resulting cellulose fibers was 560 nm. The cellulose I structure of the native cellulose was converted to the cellulose II structure after electrospinning. The ultrafine cellulose fibers showed a reinforcing effect in the cellulose/PBS biocomposite, suggesting that they have potential applications as reinforcement fibers for biocomposites. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1954–1959, 2008

Key words: cellulose; N-methylmorpholine-N-oxide (NMMO); electrospinning; crystal structure; poly(butylene succinate) (PBS); biocomposite

INTRODUCTION

As one of the most abundant renewable polymer resources, cellulose has been widely used for fibers and films.[1,2] To produce cellulose fibers and films, cellulose is dissolved in common solvents after chemical modification or metal complex formation at extreme alkaline pH, because of its strong intra- and intermolecular hydrogen bonds. The chemical modification of cellulose with carbon disulfide (CS_2), which is known as the viscose rayon process, was formerly the most widely used technique for the production of cellulose fibers. The most versatile and commercially successful method which has been developed as an environment-friendly process involves the direct dissolution and spinning of cellulose using N-methylmorpholine-N-oxide (NMMO) hydrates.[3–6]

Recently, electrospinning has attracted a great deal of attention, because electrospun ultrafine fibers have a broad range of applications in affinity membranes, tissue engineering scaffolds, drug deliver carriers, biosensors, chemosensors, protective cloths, reinforced nanocomposites, etc.[7–13] Therefore, it is expected that electrospun ultrafine cellulose fibers can find various applications because of their good thermal stability, chemical resistance, biodegradability, etc. Ultrafine cellulose fibers can be prepared by the electrospinning of cellulose/NMMO hydrate solutions, a method which has recently been reported by other researchers.[14–16] However, the effects of the electrospinning variables and the characterization of the resulting ultrafine cellulose fibers have not been systematically studied. In this study, ultrafine cellulose fibers were electrospun from cellulose/NMMO hydrate solutions at 100°C after determining the optimal concentration for electrospinning, and their crystal structure and thermal stability were characterized. Furthermore, ultrafine cellulose fibers reinforced poly(butylene succinate) (PBS) biocomposites were fabricated and characterized to evaluate their potential use as a reinforcement material in a biodegradable polymer matrix. In this study, PBS was employed for the biodegradable polymer matrix because, as one of the most promising biodegradable aliphatic polyesters, it has excellent melt processability and thermal and chemical resistance.

EXPERIMENTAL

Materials

Cellulose (DP = 700) was purchased from Hanil Synthetic Fiber (Taegu, Korea) and used without further purification. NMMO (97%) was purchased from Aldrich. PBS (EnPol G-4500), which has a melting point of about 115°C, a specific gravity of 1.22, and a melt index of 29 g/10 min (ASTM D1238), was kindly supplied by IRe Chemical (Wonju, Korea).

Electrospinning

For the electrospinning of the ultrafine cellulose fibers, a mixed solvent consisting of NMMO/distilled water (85/15, w/w) that is equivalent to a molar ratio of 1/1.148 was first prepared at 80°C, and then cellulose was dissolved in the mixed solvent at 80°C. The concentrations of cellulose were in the range of 3–9 wt %. The electrospinning setup utilized in this study consisted of a syringe and needle (ID = 0.84 mm), a ground electrode (d = 21.5 cm, a stainless steel sheet on a drum whose rotation speed can be varied), and a high voltage supply (Chungpa EMT, CPS-40K03). The temperatures of the syringe containing the cellulose solutions were maintained in the range of 90–150°C by using a heating oil circulator. The needle was connected to a high voltage supply that can generate positive DC voltages of up to 40 kV. The distances between the needle tip and the ground electrode, viz., the working distances, were in the range of 15–20 cm. The positive voltages applied to the cellulose solutions were in the range of 25–30 kV. The electrospinning solution was delivered via a syringe pump to accurately control the mass flow rate. The mass flow rates of the solutions were in the range of 1–5 mL/h. The solidified ultrafine cellulose fibers collected on an aluminum foil were carefully washed in distilled water and dried in a vacuum oven at 50°C for 24 h.

Biocomposite fabrication

The pulverized PBS powder was dried at 100°C for 2 h in a conventional oven before use. The PBS powder and the ultrafine cellulose fibers with dimensions of 50 mm × 50 mm were stacked alternatively in a stainless steel mold having cavity dimensions of 50 mm × 50 mm, and then molded in a compression manner using a hot-press (Carver 2518). The mixture was first melted at 135°C for 15 min, and then a pressure of 1000 psi was applied for 10 min and retained until the mold was naturally cooled down to ambient temperature. The thickness of the resulting biocomposites was ∼ 3 mm. The content of the ultrafine cellulose fibers was 20 wt %.

Measurement and characterization

The solution viscosities of cellulose in the mixed solvent consisting of NMMO/water (85/15, w/w) were measured using a Brookfield digital viscometer (Model DV-E) equipped with a heating cell (Thermosel, Brookfield 106). The morphologies of the ultrafine cellulose fibers and fracture sections of the biocomposites were observed on a scanning electron microscope (SEM; Hitachi S-2350) after applying a gold coating. The average diameters of the ultrafine cellulose fibers were determined by analyzing the SEM images with a custom code image analysis program. The thermogravimetric analysis (TGA) was performed using a Perkin-Elmer TGA-7 thermal analyzer at a heating rate of 10°C/min under an N_2 atmosphere. The crystalline structures of the ultrafine cellulose fibers were analyzed on a wide angle X-ray diffractometer (WAXD) (Model Rigaku D/max-IIB, Rigaku). Dynamic mechanical analysis (DMA) was performed on a TA Instruments DMA Q800 from −100 to 100°C at a heating rate of 2°C/min with a purging liquid N_2 gas. The specimen dimensions were 35 mm × 10 mm × 1.5 mm. The specimen was deformed in a single cantilever bending mode at a fixed frequency of 1 Hz and an oscillation amplitude of 0.2 mm.

RESULTS AND DISCUSSION

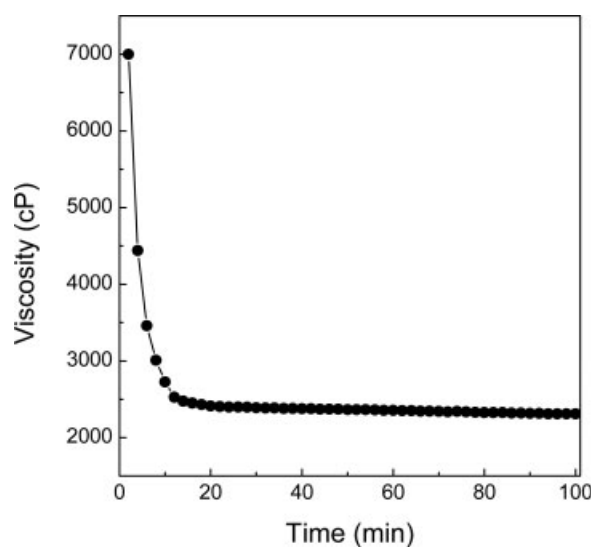### Electrospinning of ultrafine cellulose fibers

In electrospinning, the viscosity of the spinning dope has to be controlled to produce continuous ultrafine fibers. Below a critical concentration, the surface tension is the dominant factor and only a bead or beaded-fiber form is produced, whereas above the critical concentration, continuous ultrafine fibers are obtained and their morphologies are affected by the solution concentration.[17–19] Most polymer solutions can be electrospun at room temperature; however, the electrospinning of cellulose/NMMO hydrate solutions has to be carried out at elevated temperatures because of the higher melting temperatures of NMMO hydrates. Therefore, to find the optimal viscosity of the cellulose/NMMO hydrate solutions, both the concentration of cellulose and the electrospinning temperature have to be considered. The electrospinning of cellulose/NMMO hydrate solutions can be performed in the temperature range of 70–130°C.[14–16] In this study, considering the thermal degradation of both cellulose and NMMO, the electrospinning of the cellulose/NMMO hydrate solutions was carried out at 100°C.

Figure 1 shows the viscosities of the cellulose/NMMO hydrate solutions at various concentrations of cellulose at 100°C. The viscosities of the cellulose solutions increase rapidly at a cellulose concentration
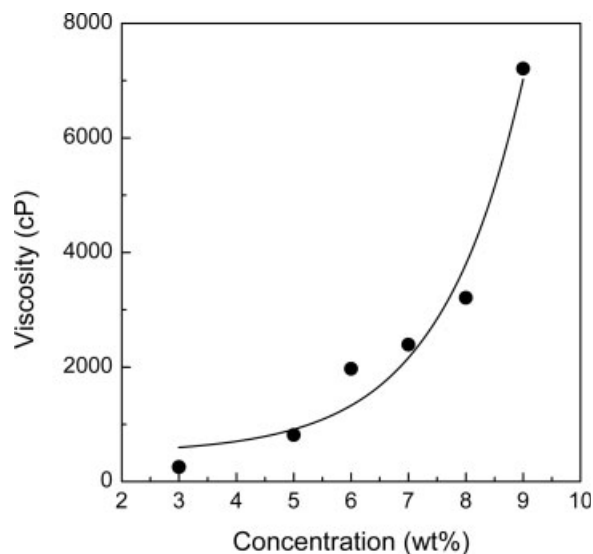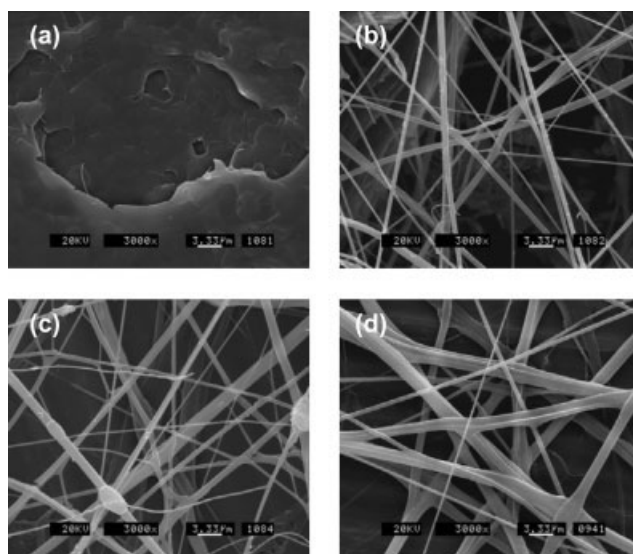
Figure 1 Solution viscosities of the cellulose/NMMO hydrate solutions at various concentrations of cellulose at 100°C.

Figure 3 SEM micrographs of ultrafine cellulose fibers electrospun from (a) 3 wt %, (b) 5 wt %, (c) 7 wt %, and (d) 9 wt % cellulose/NMMO hydrate solutions.

of ~ 7 wt %, indicating that the extensive chain entanglement of the cellulose occurred in this concentration range. Stabilized charged jets were ejected and ultrafine cellulose fibers were formed as the solvent was evaporated and solidified. Figure 2 shows the variation in the viscosity of the 7 wt % cellulose solution with time at 100°C. After a certain induction period required for the melting of the cellulose/NMMO hydrate, the viscosity of the 7 wt % cellulose solution reaches a constant value and remains almost constant for 100 min, indicating that the cellulose chains were not thermally degraded at the electrospinning temperature of 100°C. Figure 3 shows the SEM micrographs of the ultrafine cellu-
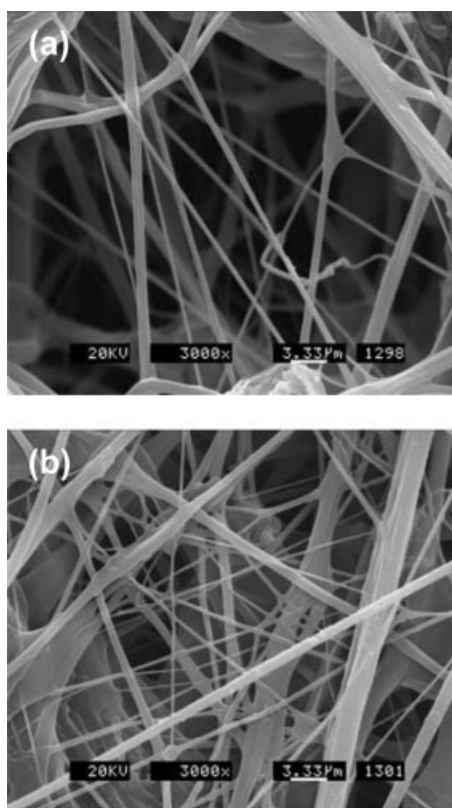
lose fibers electrospun from different concentrations. The working distance was 15 cm and the positive voltage was set at 30 kV. The mass flow rate of the solutions was 3 mL/h. Ultrafine cellulose fibers were obtained from the 5 wt % cellulose solution. The average diameters of the cellulose fibers electrospun from the 5, 7, and 9 wt % cellulose solutions are 450 ± 120, 560 ± 200, and 1080 ± 400 nm, respectively. Although finer cellulose fibers could be produced from the 5 wt % cellulose solution, the charged jets were insufficiently stable to obtain a continuous fibrous structure. Therefore, as expected, the optimal concentration for the formation of ultrafine cellulose fibers was 7 wt %. Figure 4 shows the variation in

Figure 2 Variation in solution viscosity of the 7 wt % cellulose solution with time at 100°C.
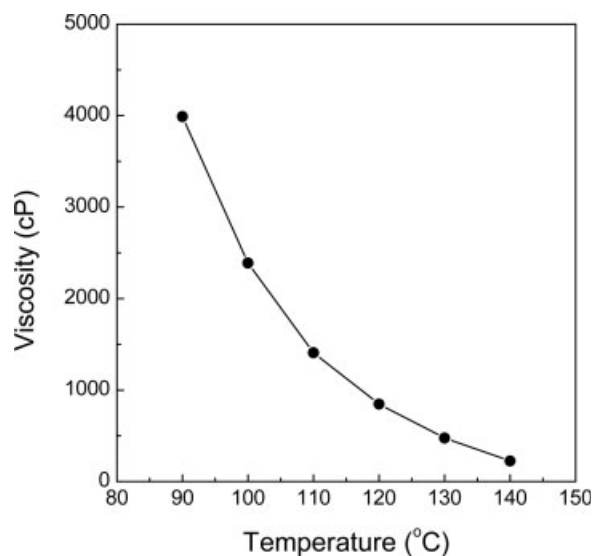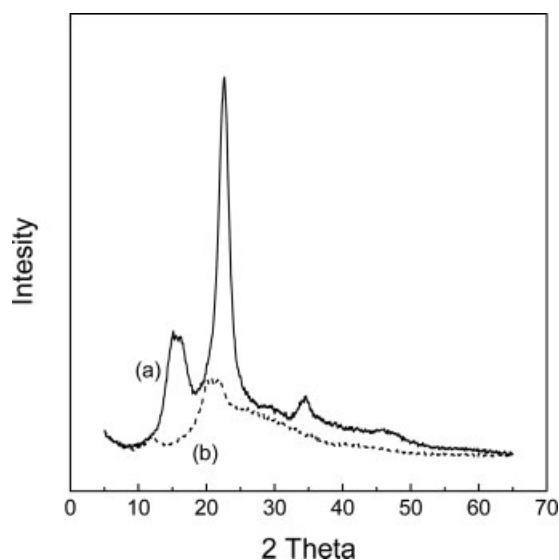

Figure 4 Viscosities of the 7 wt % cellulose solution at different temperatures.

the viscosity of the 7 wt % cellulose solution with temperature. The viscosity of the cellulose solution dramatically decreases with increasing temperature. Figure 5 shows the SEM images of the ultrafine cellulose fibers electrospun from the 7 wt % cellulose solution at 90 and 110°C. The electrospinning of the 7 wt % cellulose solution at 90°C required higher voltages because of the higher solution viscosity, which resulted in unstable charged jets and discontinuous electrospinning. The viscosity of a polymer solution is closely related to its surface tension. The surface tension of the polymer solution increased with increasing viscosity. The applied voltage is one of the dominant factors involved in obtaining ultrafine fibers. The voltage required to overcome the surface tension of the polymer solution is increased with increasing viscosity. When the 7 wt % cellulose solution was electrospun at 110°C, part of the electrospun cellulose fibers exhibited a membrane-like structure because of its lower solution viscosity. This result supports the hypothesis that the formation of continuous fiber requires extensive chain entanglements in the polymer solution.

Additionally, the effects of the processing conditions, such as the acceleration voltage, the working distance, and the mass flow rate, on the average di-
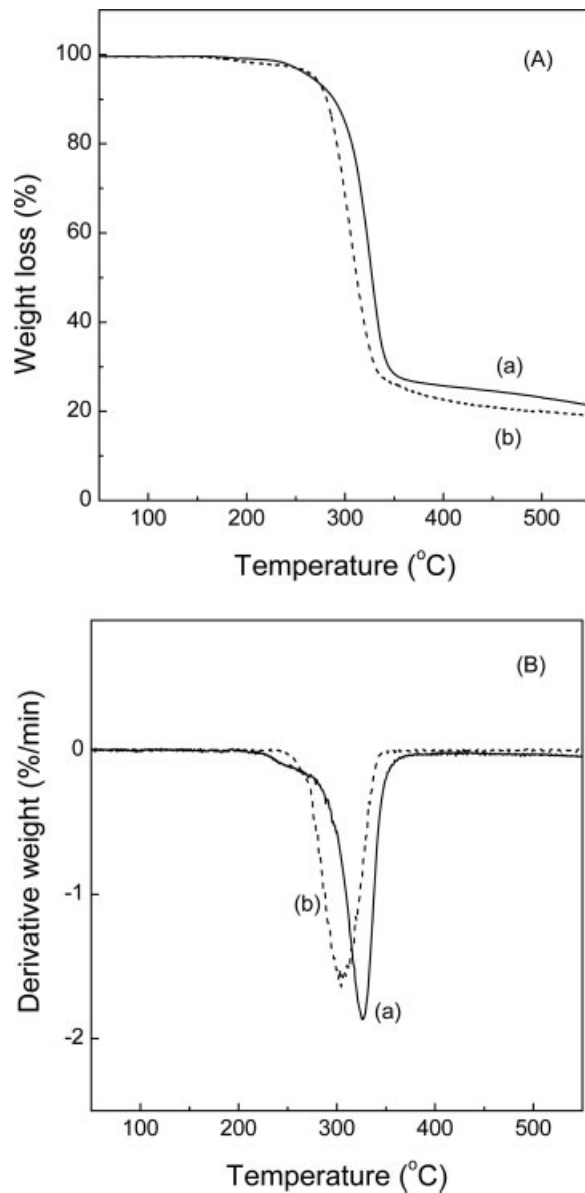

Figure 6 X-ray diffraction patterns of (a) the native cellulose and (b) the ultrafine cellulose fibers.

ameter of the ultrafine cellulose fibers were investigated using the 7 wt % cellulose solution at 100°C. The average diameters of the ultrafine cellulose fibers varied according to the processing conditions. In general, the average diameters of the ultrafine cellulose fibers decreased with increasing acceleration voltage, and increased with increasing mass flow rate or working distance.

Structural and thermal characterization of the ultrafine cellulose fibers

Generally, when native cellulose is regenerated after being dissolved in a suitable solvent or washed after being treated with a highly concentrated NaOH solution, the cellulose I structure of the native cellulose is changed to the cellulose II structure.[20–22] Figure 6 shows the WAXD patterns of native cellulose and the ultrafine cellulose fibers. The native cellulose exhibits the characteristic WAXD peaks at $2\theta = 16.4°$ and $22.6°$ attributed to the (101) and (002) planes of the cellulose I structure, respectively. On the other hand, the ultrafine cellulose fibers shows the WAXD peaks at $2\theta = 12.0°$ and $21.0°$ attributed to the (110) and (002) planes of the typical cellulose II structure, respectively. This result indicates that the cellulose I structure of the cellulose was converted to the cellulose II structure after electrospinning.

Figure 7 shows the TGA and derivative thermogram (DTG) curves of the native cellulose and the ultrafine cellulose fibers. The initial decomposition temperatures (T_{di}), which is defined as the temperature at which the weight loss reaches 5 wt %, are 265 and 269°C, but the maximum decomposition rate temperatures (T_{max}) are 326 and 303°C for the

Figure 5 SEM images of ultrafine cellulose fibers electrospun from the 7 wt % cellulose solution at (a) 90 and (b) 110°C.

Figure 8 Variation in the storage modulus of (a) the PBS matrix and (b) the cellulose/PBS biocomposite with temperature.

rate and the working distance.[16] In the present study, potential use of the ultrafine cellulose fibers as a reinforcement material in a biodegradable polymer matrix was evaluated. Figure 8 shows the changes in the storage moduli of the neat PBS matrix and the ultrafine cellulose fibers reinforced PBS biocomposite (cellulose/PBS biocomposite) in the temperature range of −100 to 100°C. The storage modulus of the cellulose/PBS biocomposite is much higher than that of the neat PBS matrix. This is ascribed to the reinforcing effect imparted by the ultrafine cellulose fibers. Figure 9 shows the variation in the tan δ of the PBS matrix and the cellulose/
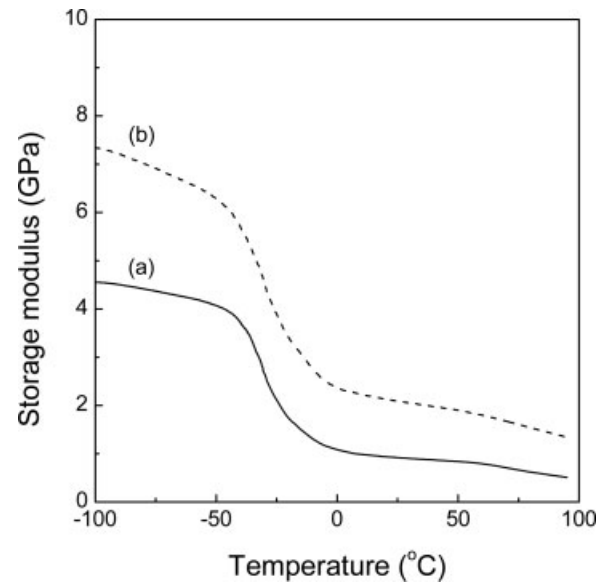

Figure 7 (A) TGA and (B) DTG curves of (a) the native cellulose and (b) the ultrafine cellulose fibers.

native cellulose and the ultrafine cellulose fibers, respectively. The T_{max} of the ultrafine cellulose fibers is comparatively lower than that of the native cellulose. It is considered that this result is related to the crystallinity and crystalline structure of the ultrafine cellulose fibers. As shown in Figure 6, the ultrafine cellulose fibers had a lower crystallinity than the native cellulose.
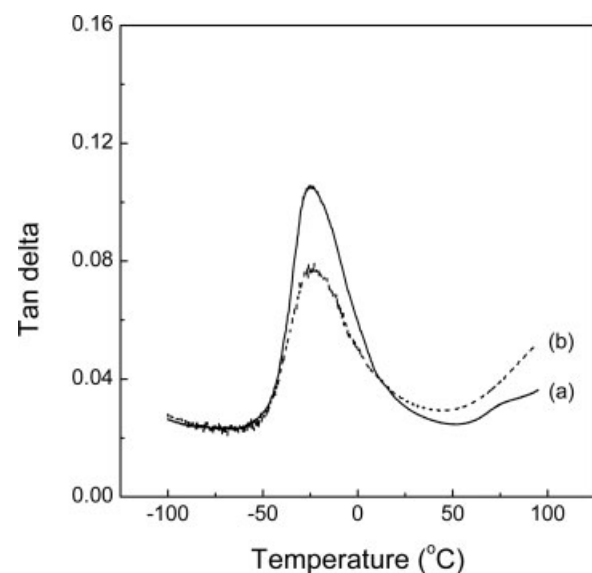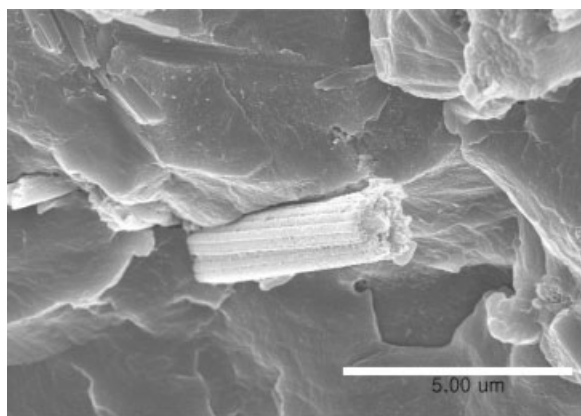
Biocomposite of the ultrafine cellulose fibers

The crystallinity of the ultrafine cellulose fibers was not sufficient for reinforcement fibers. However, it is believed that their crystallinity can be increased by changing process conditions such as the mass flow

Figure 9 Variation in the tan δ of (a) the PBS matrix and (b) the cellulose/PBS biocomposite with temperature.

Figure 10 SEM image of the fractured surface of the cellulose/PBS biocomposite.

PBS biocomposite with temperature. The decrease in the tan δ peak caused by the addition of the ultrafine cellulose fibers indicates that they limited the mobility of the PBS chains. The magnitude of the tan δ peak is associated with the damping properties of composite materials. However, the peak temperature was not significantly affected by the addition of the ultrafine cellulose fibers, meaning that the physical interactions between the ultrafine cellulose fibers and the PBS matrix were not that strong.[23] Figure 10 shows the SEM image of the fractured surface of the cellulose/PBS biocomposite. There is good interfacial bonding between the ultrafine cellulose fibers and the PBS matrix. The uneven surfaces of the cellulose fibers may contribute to the interfacial bonds between the ultrafine cellulose fibers and the PBS matrix in the cellulose/PBS biocomposite. Consequently, these results suggest that the ultrafine cellulose fibers can be used as reinforcements for biocomposites.

CONCLUSIONS

In this study, the electrospinning of the cellulose/NMMO hydrate solutions was carried out at 100°C. The optimal electrospinning concentration of the cellulose solutions was determined to be 7 wt %. The solution viscosity of the 7 wt % cellulose solution remained almost constant at 100°C, indicating that the cellulose chains were not thermally degraded at the electrospinning temperature of 100°C. The average diameter of the cellulose fibers electrospun from the 7 wt % cellulose solution was 560 nm. The electrospinning of the 7 wt % cellulose solution at 90°C was discontinuous due to the higher solution viscosity. When electrospun at 110°C, part of the electro-

spun cellulose fibers exhibited a membrane-like structure because of the lower solution viscosity. The average diameters of the ultrafine cellulose fibers decreased with increasing acceleration voltage, and increased with increasing mass flow rate or working distance. The cellulose I structure of the native cellulose was converted to the cellulose II structure after electrospinning. The ultrafine cellulose fibers showed poorer thermal stability than the native cellulose, probably because of their lower crystallinity. The ultrafine cellulose fibers showed a reinforcing effect in the cellulose/PBS biocomposite. The uneven surfaces in the cellulose fibers may contribute to the good interfacial bonds between the ultrafine cellulose fiber and the PBS matrix.

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