1 Introduction

Recently the research and development of bio-based engineering materials have been widely done in North America, Europe, Asia and elsewhere [1-8], because public attention has been focused on various environmental issues such as global warming, waste problems, etc. Hence, many researches have tried to make high-performance materials by using various bio-based resources, such as starch, soy protein and plant fiber, in order to establish a resource-circulating society [9]. Especially the use of natural plant fibers as reinforcement is increasing year by year as their specific strength and modulus are roughly comparable to those of glass fibers [6]. There are many attempts to combine high-strength natural fiber with fully biodegradable resin matrix, resulting in so-called green composites. Most of the green composites therefore exhibit perfect-biodegradability, and their disposal treatment becomes easier than that of glass fiber-reinforced plastics (GFRP).

Cellulose nanofibers (CNFs) are basic structural units of all plants and are among the smallest natural fibers. The Young’s modulus of the CNF has been measured as around 140 GPa [10]; and its tensile strength was estimated to be 1.7 GPa [11]. Because the mechanical performance of CNF is comparable to that of glass fiber, many research has been focused on the examination of its possibilities and limitations as nanoscale reinforcement in green composite system [12].

Yano and Nakahara fabricated starch/microfibrillated pulp composites by a press forming technique, and evaluated their flexural properties as a function of water retention, which is thought to be one of the most effective indices for the degree of microfibrillation [13]. They also described that the mechanical properties depended strongly on the degree of fiber microfibrillation; namely the reinforcing fibers’ fineness.

Nakagaito and Yano applied paper-making technique to fabricate high strength CNF composites [14]. They made paper-like sheets by filtration of CNF aqueous suspensions, and then impregnated with phenolic resin and compression molded. Takagi and Asano also made chemically modified starch-based resin/CNF green composites by hot-pressing method, and examined the effect of processing conditions on the flexural properties of resultant green composites [6]. They pointed out the importance of uniform dispersion of nanofibers in the resin matrix.

In this study, a green composite material of polyvinyl alcohol (PVA) reinforced by CNF was developed and the strength properties were evaluated. Pre-molding sheets (i.e. preform sheets) were obtained by drying a mixture of aqueous suspensions of CNF and PVA. CNF-reinforced PVA-based green composites were fabricated using a hot press by laminating a number of sheets inside a mold. However, the surface of the dry pre-molding sheets would contain many tiny bubbles. It was considered that the presence of the air bubbles on the surfaces of the sheets is responsible for the reduction in the mechanical performance of the resulting composites. Therefore we investigated the mechanical properties of CNF-reinforced PVA and evaluated the effects of the presence of bubbles generated during the fabrication process on the composites’ mechanical properties. The effects of different parameters such as filler load on the mechanical properties were also discussed.

2 Experimental methods

2.1 Materials
Thin slurry containing 90wt% water and 10wt% CNF (Celish® KY-100G, Daicel Cooperation, Japan) (Fig. 1) was used as the reinforcing material of PVA (RS-2117, Kuraray Co. Ltd., Japan). Figure 2 shows a SEM photomicrograph of the CNF used in this study. Average length of the CNF is 350 μm and width ranges from 10 nm to 100 nm according to the product’s catalogue [15].

Before preparing the PVA-CNF suspension mixture with a predetermined CNF loading, a dilute suspension of CNF in water (CNF suspension) and a solution of PVA in water (PVA solution) were made using the following sequences.

**2.1.1 Preparation of CNF suspension**
For the preparation of CNF Suspension, 20.0 g of CNF and 450 ml of water were stirred in a beaker using a magnetic stirrer at 600 rpm for 24 hours at room temperature. During this mixing process, the beaker was covered with a sheet of thin plastic film to prevent water evaporation.

**2.1.2 Preparation of PVA solution**
For PVA solution, 500 ml of water in a beaker was heated to 90°C using a mantle heater. When the water temperature reached 90°C, PVA powder was gradually added in the hot water, and was dissolved while stirring with a glass rod. The final PVA concentration of the CNF suspension was calculated by the ratio of the weights of PVA powder added and resultant CNF suspension.

**2.2 Fabrication of pre-molding sheets**
First, CNF suspension and PVA solution were mixed and stirred at 500 rpm for 10 minutes with a magnetic stirrer. The liquid mixture was poured into a heat-resistant 300 mm by 240 mm plastic tray. Then, the tray containing the liquid mixture was dried by using a convection-type oven at 70°C for 24 hours and finally pre-molding sheets were peeled off from the plastic tray.

**2.3 Vacuum stirrer treatment**
During the stirrer mixing treatment described in the section 2.2 many small bubbles could be seen in the solution, and therefore the bubbles were also formed on the surface of the resultant pre-molding sheets after drying. To avoid these small bubbles, a vacuum stirrer treatment was applied to the CNF-PVA mixture (Fig. 3). The process chart is shown in Fig. 4.

**2.4 Green composites fabrication**
The dried pre-molding sheets were cut into strips sized 100 mm by 10 mm. These strips were then laminated and set into a metallic mold. Next the laminated sheets were hot-pressed at 210°C, under 10 MPa, for 10 minutes, and cooled down before specimens were removed from the metallic mold. Then, small burrs at the specimen edges were removed with sandpaper, and finally paper tabs of 35 mm by 10 mm were attached with an adhesive on both extremities of the specimens.
2.5 Mechanical characterization
Quasi-static tensile tests were performed with an Instron universal testing machine (Model 5567, Instron Corporation, USA) at a cross-head speed of 1.0 mm/min with a gauge length of 30.0 mm at room temperature (Fig. 5).

2.6 Surface characterization
The fracture morphology of composites and fibers was examined by an optical microscope (SZH-10, Olympus, Japan) and scanning electron microscope (SEM: S-4700, Hitachi, Japan). All samples were sputter-coated with gold/platinum prior to the SEM observation.

3 Results and Discussion
3.1 Effect of vacuum stirrer treatment
If the pre-molding sheets were produced without the vacuum stirrer treatment, small bubbles were observed on the surface of the entire sheet as shown in Fig. 6. However when the vacuum stirrer treatment (vacuum defoaming) was performed, bubbles were not visible at all on the surface of the pre-molding sheets (Fig. 7).

3.2 Mechanical properties
The pre-molding sheets obtained by vacuum stirrer treatment resulted in composites with higher mechanical properties as shown by the stress-strain curves in Fig. 8. Thus we can see that the presence of air bubbles generated during stirring and drying processes was one factor that reduced the tensile strength of CNF green composites. If the pre-molding sheets contain air bubbles, the surface has
irregularities causing adhesion failure when laminated to make the composites.

In addition, the tensile strength of the CNF composites fabricated from vacuum-stirrer-treated pre-molding sheets was also affected when the CNF content was varied from 30 to 70wt%. According to Fig. 9, the tensile strength is highest at 50wt% CNF content, but further increases in CNF content does not lead to higher strength. Similar dependence was also reported in the CNF-starch green composite system [16].

3.3 Fracture behaviors
The fracture surface of the composite with 50wt% CNF without defoaming treatment is presented in Fig. 10, showing a laminate cracking. This cracking might lead to reduction both in tensile strength and fracture strain. In addition, there are many small holes on the fracture surface as shown in Fig. 11. These holes seem to be formed by agglomeration of much smaller air bubbles dispersed in the PVA solution before drying. The fracture surface of the composites with vacuum stirrer treatment is
presented in Fig. 12, there is no cracking on the fracture surface.

Fig. 10 SEM photograph of the fracture surface of composite (50wt.%CNF, without vacuum-stirred).

Fig. 11 SEM photograph of the fracture surface of composite (50wt.%CNF, without vacuum-stirred).

Fig. 12 SEM photograph of the fracture surface of composite (50wt.%CNF, with vacuum-stirred).

4 Conclusions

We successfully fabricated CNF-reinforced PVA-based green composites, and evaluated the mechanical properties of the CNF-PVA green composites, and then examined the effects of the presence of bubbles generated during the fabrication process on their mechanical properties. The experimental results showed that the vacuum stirrer defoaming process is effective to obtain the CNF reinforced green composites with better mechanical performance.

References


