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Cellulose Nanofibers and Its Applications for Resin Reinforcements

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Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/55346>

1. Introduction

It is widely recognized that technologies that can convert biomass resources into commercially viable materials are needed. Cellulose is a candidate among biomass due to its abundance in nature. The characteristics of cellulose, which include no thermoplasticity and being insoluble in ordinary solvents, have limited its applications. With the aim of widening its application possibilities, several works have been documented on mechanochemical treatments of cellulose in the dry state and in the wet states.[1-6] Endo et al. [1-4] developed novel cellulose composites by ball milling mixtures of cellulose and poly(ethylene glycol) (PEG). The composites are reported to have formed by insertion of PEG molecules among the cellulose molecular chains. [3,4]

Works of Kondo et al. [5] and ours [7] appeared as patent publications. In the former case, fine cellulose powder (average powder length and width: 28 and 11 μm , respectively) was pulverized in aqueous suspension by counter collision at a pressure of 200 MPa, being done once or repeatedly up to 60 times or more, using an ultra high-pressure homogenizer, Star Burst System HJP-25005(Sugino Machine Ltd.). In our case [7], cellulose micronized powder (KC flock W-400G, average particle size 24 μm) was used in the same way at a pressure of 245 MPa, being done once or repeatedly up to ten times, using a Star Burst System HJP-25080. These patents appeared independently within the period of 13 months. Kondo et al. [5,6] claimed that pulverization by an ultra high counter collision successfully decomposed the interaction within the assembly structures of cellulose molecules without any damage of the molecular structure, and finally liberated the components into various sizes in water to provide a transparent and homogeneous component–water system after repeated treatments (60 times). While having some claims in common with those of Kondo et al., [5] our work [7] concentrated more on utilization of the ultra high-pressure counter collision-treated cellulose.

In fact, our research interests were stimulated by the works of Endo et al., [1-4] and we started to research suitable methods for efficient wet mechanochemical treatment of biomass. Works were performed with the intention of determining pretreatment methods for successive efficient chemical reactions for cellulose in water. The scope of our preliminary works included using a planetary ball mill (Fritch Japan Co.,Ltd.), a bead mill (Ashizawa Finetech Ltd.), a vibration mill (Chuo Kakoki Co.,Ltd.) as well as ultra high-pressure homogenizers. The last of these, the Star Burst System HJP-25080 (Sugino Machine Ltd.) [7], was found to be the most effective and acceptable for successive chemical reaction in water.

It can be said that this counter-collision treatment at ultra high pressure is an extension of the microfibrillation of cellulose done by ITT Rayonier research group, in which dilute slurries of cellulose fibers were subjected to the repeated mechanical actions of “homogenizing” machine (Gaulin) [8,9]. The slurry was pumped at high pressure and fed through a spring-loaded valve assembly [8]. The aqueous cellulose slurry was pumped at 0.5–5 l/min. The operation pressure was 55 MPa, which is 20%–25% of those for the Star Burst System models.

Because cellulose is composed of aggregated micron-sized microfibrils within the cellulose fiber, the above finding suggests that the cellulose fibers were rapidly expanded in the surface area and grew into their substructural microfibrils by mechanical action and heat. Cellulose nanofiber (CNF) formation or its primordials is considered to be attained.

Starting from these fabricating cellulose nanofibers, authors have been conducting trials for developing related biomass composites. This review chapter addresses some of our findings, which are reported in the three following sections, each having their own experimental section and results and discussion section.

2. Fabricating cellulose nanofibers through ultrahigh pressure (245 MPa) counter collision treatments

As described in the above introduction section, Kondo et al. [5] and authors [7] found a method for fabricating cellulose nanofiber through ultrahigh pressure (200 or 245 MPa) counter collision treatments of cellulose powders in an aqueous slurry state. In our case, the morphologic features of the obtained cellulose nanofiber (CNF) were explored by use of freeze-drying technique and SEM observations. Obtained nanofiber are tend to cohere by themselves during the melt-blending with thermoplastic polymers, oligomers or prepolymers. Thus, the blending or fabricating methods have been explored on the one hand, and chemical modification of starting cellulose in order to prevent the agglomeration of the CNF on the other hand. The chemical modification can place restraint on the inducement of self-assembly of CNF by steric hinderance, electrostatic repulsion and so forth. A recent finding was that the species of the cellulose affects a lot for this fabrication of the nanofiber. These obtained features of CNF are discussed first.

2.1. Experimental

2.1.1. Materials

Micronized cellulose powder (KC flock W-400G, average particle size: 24 μm) was supplied by Nippon Paper Chemicals. "Avicel", Crystalline Cellulose was from Asahi Kasei Co. Deionized water was used throughout, including in suspension of sample powders.

2.1.2. Methods

Micropulverization of cellulose powders

Approximately 500 g of cellulose micronized powder was suspended in 20 times weight of deionized water assisted by a powerful stirring device and placed in the feed tank of the Star Burst HJP-25080 (Sugino Machine Ltd.), which was used for slurry jet counter collision. The aqueous cellulose slurry from the feed tank was divided into two flow channels, which were then pressurized to 245 MPa and are instantaneously injected from small nozzles at high speed. This allowed each fluid stream to collide in the chamber where they combined. The machine automatically permits repeated ultra high-pressure counter-collision treatments and our samples received one to ten collisions (passes).

Characterization

Scanning electron microscopy

Morphologies of the untreated cellulose as well as the freeze-dried cellulose, before and after the counter-collision treatment, were observed using a JSM-T330A (JEOL) scanning electron microscope. The samples were mounted on brass stubs and were coated with a thin layer of gold using an ion sputter coater. The freeze-drying treatment was applied for the aqueous cellulose suspensions as well as those obtained through solvent exchange described hereafter. Four freeze-drying methods were performed.

Regular freeze drying 1. Aqueous slurry of the cellulosic sample was placed in a glass bottle and placed in a conventional freeze drier (EYELA FD-550; Tokyo Rikakikai), cooled at -30°C and subjected to freeze drying.

Regular freeze drying 2. Aqueous slurry of the cellulosic sample was placed in a glass bottle and was frozen by immersing the bottle in liquid nitrogen. The sample was then subjected to conventional freeze drying.

Solvent exchange freeze drying. Imbibed water of cellulose aqueous slurry was exchanged to methanol and then to benzene or *t*-butyl alcohol, with several changes of each solvent. The gel containing benzene or *t*-butyl alcohol was subjected to regular freeze drying 2 as described above.

Rapid freeze drying. Imbibed water of cellulose aqueous slurry was exchanged to methanol and then to *t*-butyl alcohol, with several changes of each solvent. Several drops of the *t*-butyl alcohol-containing gel were put directly into liquid nitrogen stored within a dewar vessel and then subjected to the conventional freeze drying as above.

2.2. Results and discussion

At first, a planetary ball mill, a bead mill, and an ultra high-pressure homogenizer were all tried to be used to convert cellulose suspension into an appropriate nanopulverized state. The ultra high-pressure homogenizer was found to be the most suitable, because it can offer increased efficiency and flexibility over the others. In particular, the ultra high-pressure homogenizer offered the most straightforward means and ease of handling in separating the sample from the treating medium (balls, beads). The problems due to contamination of the treated sample with impurities derived from the medium can be avoided, and treatment of larger amounts of samples is possible within a shorter period of time. In this study, Star-Burst HJP-25080 was used as the ultra-high pressure homogenizer.

The additional feature of this ultra high-pressure homogenizer treatment is that the treated cellulose fiber can be homogeneously dispersed in water for a prolonged period. [5, 7] It is considered that cellulose fibers can be pulverized heavily to enlarge its specific surface area to give a much more highly hydrated state than that achieved with untreated cellulosic fiber. To visualize micropulverized states of the counter collision-pretreated cellulose, the morphological structure was studied by SEM as a function of drying method.

Figure 1 shows a SEM photograph of the counter-collision treated cellulose dried by the regular freeze drying 1 method in comparison with that of untreated cellulose. The Star Burst treated cellulose (Fig. 1b) is observed to have surface morphological features different from the untreated cellulose (Fig. 1a). The former has a fibrous surface when compared with the latter, but much of the surface area is severely coagulated to form aggregate structures. It is widely accepted that the relatively slow freezing process causes the formation of ice crystals and squeezes out cellulose microfibrils to form the aggregate structure. The growth of ice crystal on freezing is considered to be prevented by rapid cooling [10]. To confirm the descriptive validity, an SEM photograph was taken of the counter collision-treated cellulose dried by regular freeze drying 2 method (Fig.2).

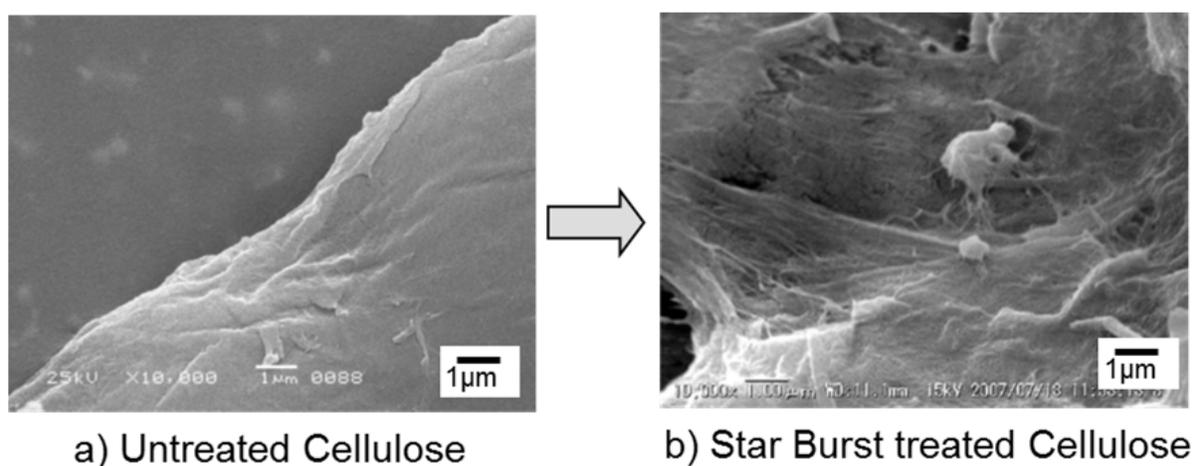


Figure 1. a, b. Scanning electron microscopy (SEM) photographs of cellulose fibers before (a) and after (b) Star Burst treatment (10 passes) followed by the regular freeze drying 1. KC flock W-400G was used as the cellulose sample.

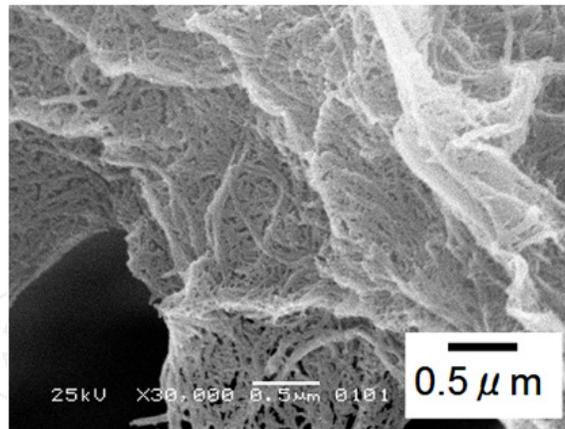


Figure 2. SEM photograph of cellulose fibers after the Star Burst treatment (10 passes) followed by the regular freeze drying 2. KC flock W-400G was used as the cellulose sample.

From Fig. 2, the Star Burst treated cellulose is observed to have surface morphological features more significantly different from that for the untreated cellulose (Fig. 1a). It loses the severe aggregate structure of Fig. 1b, but the whole surface is still regularly coagulated to form a laminate layer of thin leaves. Each thin leaf appears to be lamellae composed of cellulose microfibrils.

It is also known that preservation of cellulose fibrillar morphology is better achieved by solvent-exchange freeze drying using methanol and benzene or *t*-butyl alcohol [10]. Thus, it was planned that an additional solvent-exchange experiment was conducted. And, in addition to it, in order to accelerate the freezing process and to hinder ice crystal formation, rapid freeze drying was employed. To this end, drops of the exchanged slurry were directly put into liquid nitrogen stored in a dewar vessel after the solvent exchanges of water–methanol–*t*-butyl alcohol, and then subjected to the rapid freeze drying.

The resultant SEM photograph is shown in Figs. 3 and 4. When compared with the image in Fig. 2, it is clear that each thin leaf of cellulose fibrillar lamellae exists separately from others in these figures, noting that thin lamellae (leaves) are stuck to each other and produce laminated materials in the image in Fig. 2. This ease of coalescence among the thin leaves is caused by the easy formation of hydrogen bonding among the hydroxyl groups present on the different surfaces. That is, the thin leaves of cellulose fibrils have high density of –OH groups on the surface, which have a tendency to form hydrogen bonds between hydroxyl groups of adjacent molecules belonging to another thin leaf of cellulose fibrils.

Although the most desirable freeze-drying conditions for this experiment were employed, fibrous microfibrillated cellulose could not be directly obtained. As the ways of dealing with this problem, authors experimented with three investigations.

The first investigation was charging additional agitations for converting the thin leaves of cellulose fibrils into nanofibers. It was started from magnetic stirring during the solvent-exchange process before the freeze-drying. That is, cellulose slurry was pulverized by counter collision at a pressure of 245 MPa, after which the pulverized product was solvent-exchanged followed by freeze-drying. In the experiment, benzene was used as the final

solvent of the solvent-exchange process and mechanical agitation was used during the solvent-exchange process. The SEM photograph of the corresponding freeze-dried product is shown in Fig. 5.

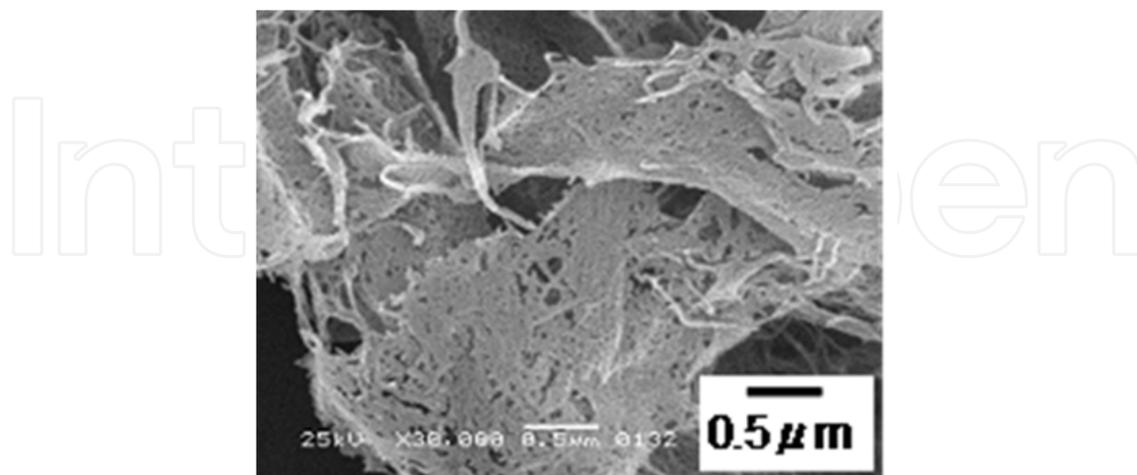
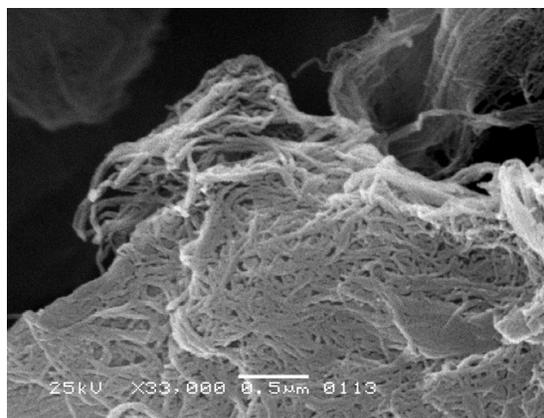


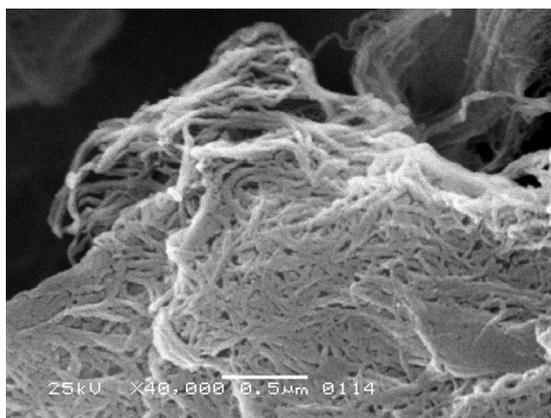
Figure 3. SEM photograph of cellulose fibers after Star Burst treatment (10 passes) followed by solvent exchange and rapid freeze drying.



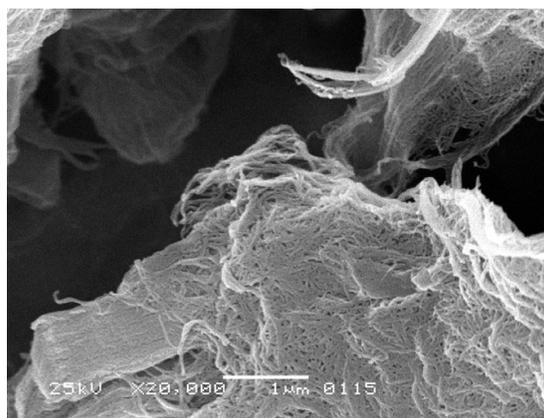
No. 112, ×40,000



No. 113 ×33,000



No. 114, ×40,000



No. 115 ×20,000

Figure 4. Other examples of SEM photographs of cellulose fibers after Star Burst treatment (10 passes) followed by solvent exchange and rapid freeze drying.

Figure 5 shows that a large number of cellulose fibers are yielded on or near the surface but lamellae-like structures are observed behind. The cellulose fibers can be recognized as a nanofiber when taking the thickness (ca. 38nm) of the gold coating into consideration. Thus, it may be argued that although the untreated cellulose fibers with diameters of 8–20 μm were pulverized to diameters of several nanometers, the formation of nanofibers was limited and incomplete (Fig. 5). This is despite the fact that the cellulose received the ultra high-pressure homogenizing treatment and stirrer agitation during the solvent-exchange process. When comparing the results of Figs. 2 and 5, however, it can be said that the magnetic-stirrer agitation having continued two days resulted in an insufficient formation of cellulose nanofiber.

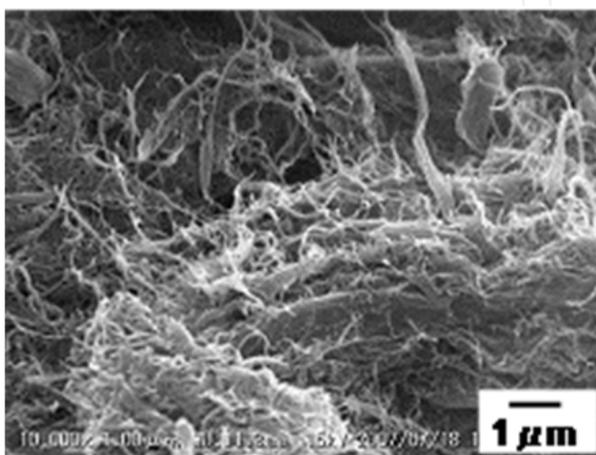


Figure 5. SEM photograph of cellulose fibers after Star Burst treatment (10 passes) followed by solvent-exchange and regular freeze drying 2.

Then, the degree of mechanical stimulations used for post-processing of the counter-collision were tried to be strengthened by use of T. K. ROBOMIX® (PRIMIX Co.), or by an ultrasonic processor (Sharp Co.; UT-205HS). An aggressive stirring with the rate of 15,000 rpm for 60 min was used by the former, and a treatment for 60 min at 40 kHz was taken for the latter.

After these treatments, both aqueous slurries were rapidly freeze dried and SEM photograph were taken. As shown in Fig. 6, developments of CNF were clearly advanced, but even after these post-treatments, thin leaf structures of cellulose lamellae are still partially remaining. Effect of the treatment with T. K. ROBOMIX became larger compared with that with the ultrasonic processor [11].

It is considered that strong agitation followed by adept kneading with twin-screw extruder, would break the thin leaf structure of cellulose fibrillar lamellae, yielding nanofibrous microfibrillated cellulose. To examine this point, several experiments were performed and results are shown in the third section of this article.

The second investigation was to use half-esterified cellulose of dibasic acid anhydride (e.g. maleic anhydride) for the ultra high-pressure homogenizer treatment. By introducing small

amounts (1~5wt%) of the half- esters on the amorphous region and microfibril surface of cellulose, followed by the counter collosion treatment, electrostatic repulsion and steric hinderance effects rose up and a rather well formation of nano-fibers was caused as shown in Fig. 7. It is understandable from this figure that the degree of conversion to nano-fiber is advanced.

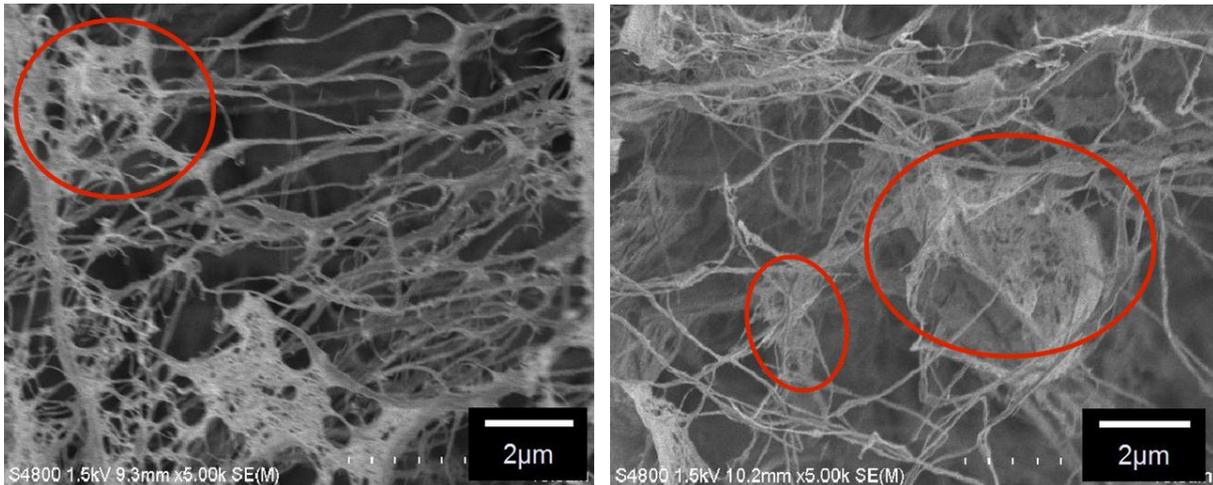


Figure 6. SEM photograph of KC flock W-400G after Star Burst treatment (10 passes) followed by an aggressive stirring with the rate of 15,000 rpm for 60 min (left), or by ultrasonic processor treatment (40 kHz) (right), and further followed by rapid freeze drying.



Figure 7. SEM photograph of half- esterified cellulose fibers after Star Burst treatment (10 passes) followed by rapid freeze drying.

The third investigation was to choose the species of cellulose. There are big differences in the nanofiber formation behavior between KC flock W-400G micronized cellulose powder and "Avicel", crystalline cellulose. Conversion to nano-fiber is easier for the latter when compared with the former. Even in non-treated state there are obvious differences between them as shown in Fig. 8. In Avicel's case, fibers are clearly observable and in KC flock W-400G's case, fibers are buried much more within the matrix binders.

On the other hand, however, when Avicel was used, nano-fiber formation was accomplished through 5 min of an aggressive post stirring with the rate of 15,000 rpm after the Star Burst treatment gave the tremendous effect in this cellulose species (Fig. 9). The results shown in Figs. 8 and 9, and also 6 reveals the big difference caused by selection of cellulose species.

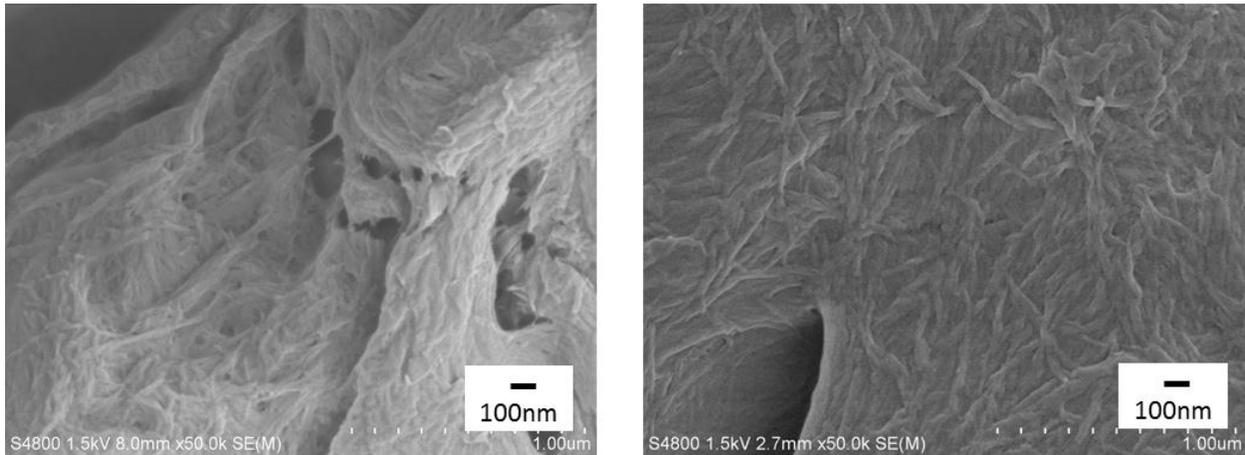


Figure 8. SEM photographs of the surfaces of untreated KC flock W-400G (right) and "Avicel"(left) powders.

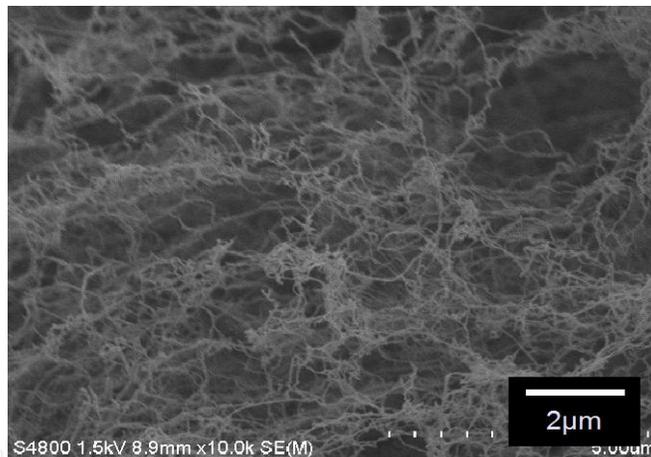


Figure 9. SEM photograph of Avicel after Star Burst treatment (10 passes) followed by an aggressive stirring with T. K. ROBOMIX (stirring rate of 15,000 rpm for 5 min) and by rapid freeze drying.

Percentage amounts of nano-cellulose fiber composited to matrix resins have been an another problem. In general, investigators and scientists are tried to employ the values of 10% or more. At first, they used higher CNF concentration of 50~90 % in the corresponding composites.

On the other hand, there are arguments claiming that the smaller the particle, the smaller the clearance of the particle in particle/matrix resin composites, when the particle concentration is constant [12]. Nano-particles are those having near the smallest in dimension which cause their particle clearances the smallest. Being influenced by these arguments, authors have made choice of the concentration of CNF small, that is, less than 1

wt%. In this regard, 0.05 % Avicel nano-fiber aqueous slurry was prepared and its SEM images were taken after the rapid freeze drying (Fig. 10). The nano-fiber preparation was as follows: an aqueous mixture of Avicel fine powders having Avicel concentration of 0.05% was prepared, treated with Star Burst at 245 MPa counter collision (10 passes), followed by an aggressive stirring with T. K. ROBOMIX (stirring rate of 15,000 rpm for 5 min) and by rapid freeze drying. It is known from this figure that, though the slurry concentration is as low as 0.05 % , nano-fibers are indicating a closely-arranged morphology responsible for network structures [11]. That is, a crowded three dimensional network structure is shown.

It is known that CNF formation is much more attained when compared with Figs. 6, 7 and 10. This means again that choice of Avicel instead of KC flock W-400G makes the nano-fiber formation much easier.

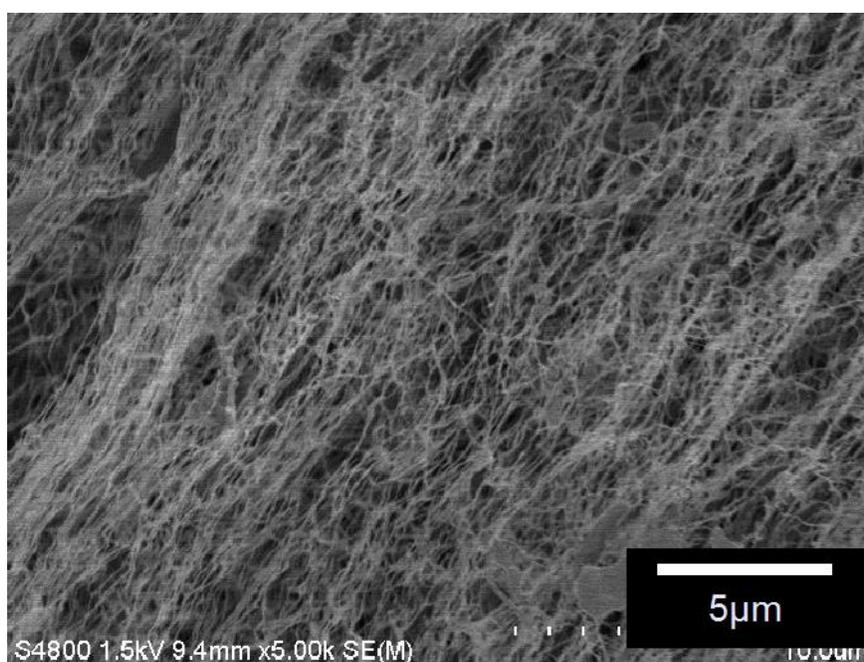


Figure 10. SEM photograph of the rapid freeze dried 0.05% Avicel nano-fiber aqueous slurry. The sample was made from 0.05 wt % Avicel aqueous mixture after Star Burst treatment (10 passes) followed by an aggressive stirring with T. K. ROBOMIX (stirring rate of 15,000 rpm for 5 min) and by rapid freeze drying.

3. Usage of pulverized cellulose prepared by ultra high-pressure water jet treatment in polymer nanocomposites

Using the resultant micropulverized cellulose emulsion prepared from KC flock W-400G, we attempted compositing with vinyl polymers through kneading and evaluated the effects of the counter-collision treatment. Use of KC flock W-400G has been known to result in less than perfect formation of CNF, however, adept kneading with twin-screw extruder was expected to break the thin leaf structure of cellulose fibrillar lamellae, yielding CNF, in the previous chapter. This point will be discussed in this chapter. This newly developed approach offers new opportunities for creating innovative products derived from biomass.

3.1. Experimental

3.1.1. Materials

Micronized cellulose powder (KC flock W-400G, average particle size: 24 μm) was supplied by Nippon Paper Chemicals. Deionized water was used throughout, including in suspension of sample powders. Agri-wood pellets, rice-type (BIOPOLY JOETSU Co.,Ltd.) including, Agri-wood(R)_1, Agri-wood(R)_2 (advanced second-generation) and Agri-wood(R)_3 (advanced third-generation), as well as their inflation-molded sheets were used. Both of Agri-wood(R)_2 and 3 are composed of old stockpiled rice (rice stored for almost 10 years since harvest), Wintec polyolefin WSX02 (polypropylene random copolymer; Japan Polypropylene), ultra high-pressure counter collision-pretreated cellulose aqueous slurry, and additives, in which the cellulose nanofiber concentration is around 0.05% (w/w). In the cases of Agri-wood(R)_2 and Agri-wood(R)_3 pellets, the ultra high-pressure counter collision-pretreated cellulosic slurry at around 0.05% nanofiber concentration was kneaded with Wintec polyolefin WSX02 (polypropylene random copolymer; Japan Polypropylene) and above mentioned old stockpiled rice in the presence of small amounts of additives, using a super high-torque twin-screw extruder (Supertex 77 α , The Japan Steel Works), under a controlled moisture vapor release. In the case of Agri-wood(R)_1, the aqueous cellulose nanofiber slurry was not combined. Inflation-molded bags have been produced commercially from Agri-wood(R)_2 and 3 and widely used as municipal government-approved garbage bags. For our work, these garbage bag sheets were taken as test pieces. Recycled polyethylene (PE) was supplied by Ecos Factory.

3.1.2. Methods

Micropulverization of cellulose powders

The method for micropulverization of cellulose powders is the same that taken in the previous chapter.

Preparation of test pieces from inflation-molded bags of Agri-wood(R) pellets for tensile testing

Inflation molded bags were prepared using a blown film machine (Placo) from Agri-wood(R)_2 and Agri-wood(R)_3 pellets as well as first-generation Agri-wood(R)_1 pellets (not combined with cellulose nanofiber) as a control. Sample strips measuring 100 \times 5 \times 0.4 mm were cut from the molded sheets.

Preparation of test pieces of Agri-wood(R) pellets for tensile testing

Agri-wood(R)_1~(R)_3 pellets were molded into sheets at a prescribed temperature by hot pressing using a Toyo-Seiki 10 tons bench hot press. Each sample (approximately 3 g) was placed between polyethylene terephthalate (PET) sheets with a 0.4 mm-thick spacer. For molding, a gauge pressure ranging from 0 to 5 MPa was applied slowly over 3–5 min to allow air bubbles to dissipate. The pressure was subsequently raised to 15 MPa quickly and maintained there for 30 s. The samples were cooled for 10–15 min to room temperature by cold pressing under the same pressure. Sample strips measuring 80 \times 5 \times 0.4mm were cut from

the molded sheets. Agri-wood(R)_1~(R)_3 pellets were directly subjected to the measurement of melt index (MI) [melt-flow rate (MFR)].

Compounding micropulverized cellulose with recycled PE

The ultra high-pressure counter collision-pretreated cellulosic slurry was kneaded with recycled PE at around 0.05 % nanofiber concentration using a super high-torque twin-screw extruder (TEX77 α , The Japan Steel Works), under a controlled moisture vapor release. Compounded pellets were obtained from which films were prepared with a blown-film machine (Placo). Recycled PE with or without kneading by the Supertex 77 α were used as the controls in the form of films.

Preparation of test pieces of micropulverized cellulose – recycled PE composites for tensile testing

The test pieces for tensile testing were prepared as described above. The compounded pellets of cellulosic slurry and recycled PE and their control were molded into specimens for the Charpy impact test by use of an Elject NEX110-12E (Nissei Plastic) high-performance injection molding machine.

Characterization

Scanning electron microscopy

The method for obtaining SEM photograph is the same that taken in the previous chapter. Fracture cross sections obtained by tensile elongation testing of the inflation-molded sheets prepared from Agri-wood(R)_2 and 3 were visualized by SEM.

Mesurements of mechanical properties of the Agri-wood(R), and recycled PE composite

An IM-401 Charpy-type Impact Tester (Tester Sangyo) was used for Charpy impact test, while a Universal Testing Machine AG10kNIS (Shimadzu) was used for tensile testing. Melt flow rate was measured by a Melt Flow Indexer IMC-1540 (Imoto Machinery).

Dynamic viscoelastic measurements were performed for the strips using a Rheogel-E4000 (UBM) under tension mode (frequency 10Hz, rate of temperature increase 3°C/min).

3.2. Results and discussion

Composite processing

Inflation films molded from pellets of Agri-wood(R)_2 and 3 were prepared, their tensile properties were measured, and fracture cross sections obtained were visualized by SEM. Figure 11 shows the SEM photographs for the fracture cross section of Agri-wood(R)_2 film. It is apparent from the figure that there is a scattering of fine starch of a few μm in diameter. The starch particles are almost completely exposed on the destroyed surface. This means that surface adhesion between the starch particle and the matrix resin, percolated by the microfibrillated cellulose fibers is poor. At the time of kneading, cellulose was added as Star Burst treated cellulose slurry (0.5% w/w) to give a concentration of ca. 0.05% in the pellet.

This kneading technique to prepare Agri-wood(R)_2 pellets was further advanced recently by modifying kneading conditions. Major improvement efforts have been focused on

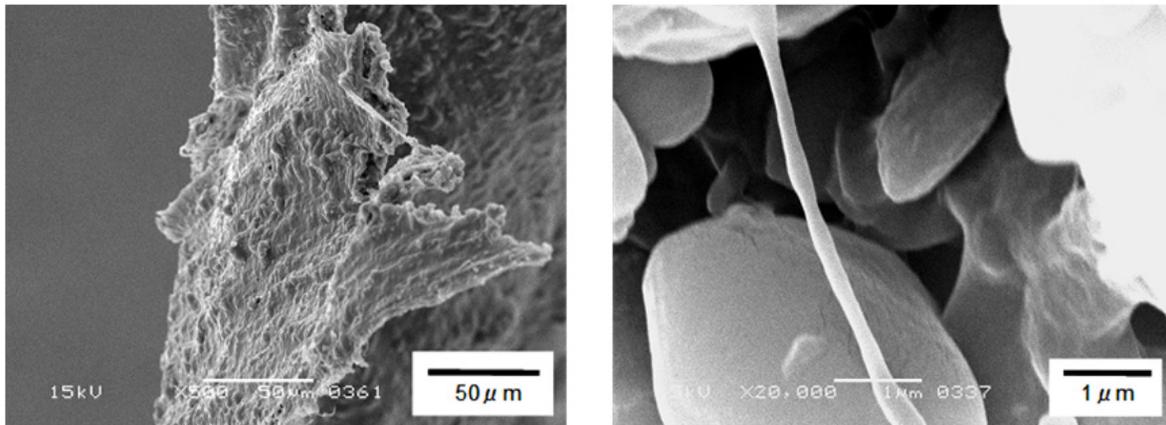


Figure 11. SEM photographs of fracture cross section of inflation film molded from Agri-wood(R)_2 [second-generation Agri-wood(R)] pellets obtained by tensile elongation test.

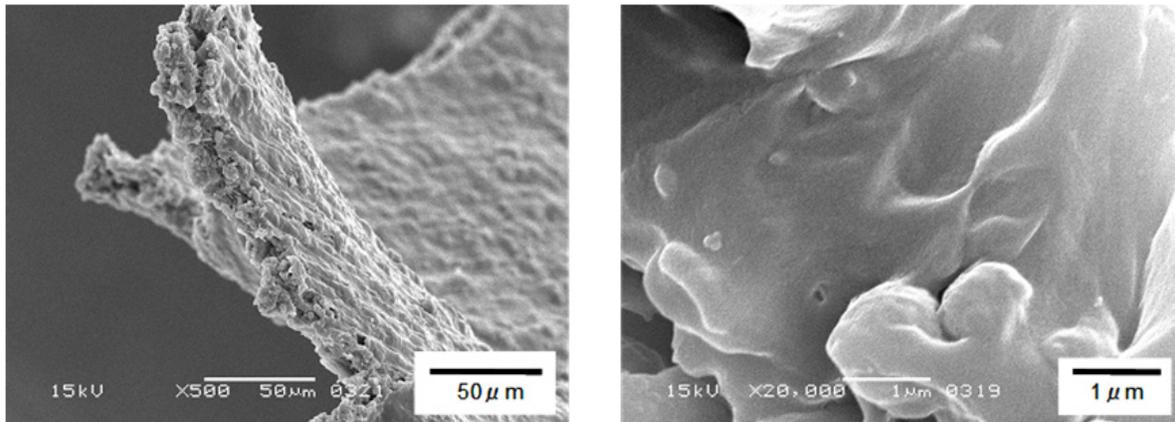


Figure 12. SEM photographs of fracture cross section of inflation film molded from Agri-wood(R)_3 [third-generation Agri-wood(R)] pellets obtained by tensile elongation test.

techniques of programmed evacuation of water vapor from the vents at pressurized, normal, and reduced pressures, as well as adopting appropriate paddle constructions [13, 14]. Such advancements were actually reflected on the SEM photographs of the fracture cross section of the film molded from Agri-wood(R)_3 pellets (Fig. 12). The starch particles are almost completely covered by the matrix resin, showing that surface adhesion between the starch particle and the matrix resin, percolated by the microfibrillated cellulose fibers is enhanced and morphological characteristics among these three components became more intimately unified. That is, cellulose nanofibers and starch particles (smaller size than those in Fig. 11) are homogeneously dispersed and combined with the matrix resin. Four photographs corresponding to and confirming Fig. 12 are shown in Fig. 13. The starch particles are also almost completely covered by the matrix resin, and penetrations of microfibrillated cellulose fibers through starch grains as well as matrix resin can be observed. That is, the mechanical interlocking caused by cellulose nanofibers are occurring, though the amounts are quite small. This argument is at least supported by the MFR values

shown in Table 1. When comparing the MFR value for sample No. 2 with that for sample No. 3, the latter value is smaller than the former. The melt flowability of the matrix resin, Wintec polyolefin WSX02, is obviously much higher than that of rice starch and the microfibrillated cellulose fibers. It is thus considered that sample No. 2 composite is less blended than the advanced type and contains partly polyolefin rich portions in the composite due to the nonadvanced kneading technique. Therefore, the part of free polyolefin that is not well compatibilized with the rice starch and the microfibrillated cellulose fibers preferably passes through the melt flow indexer die head providing a higher MFR value.

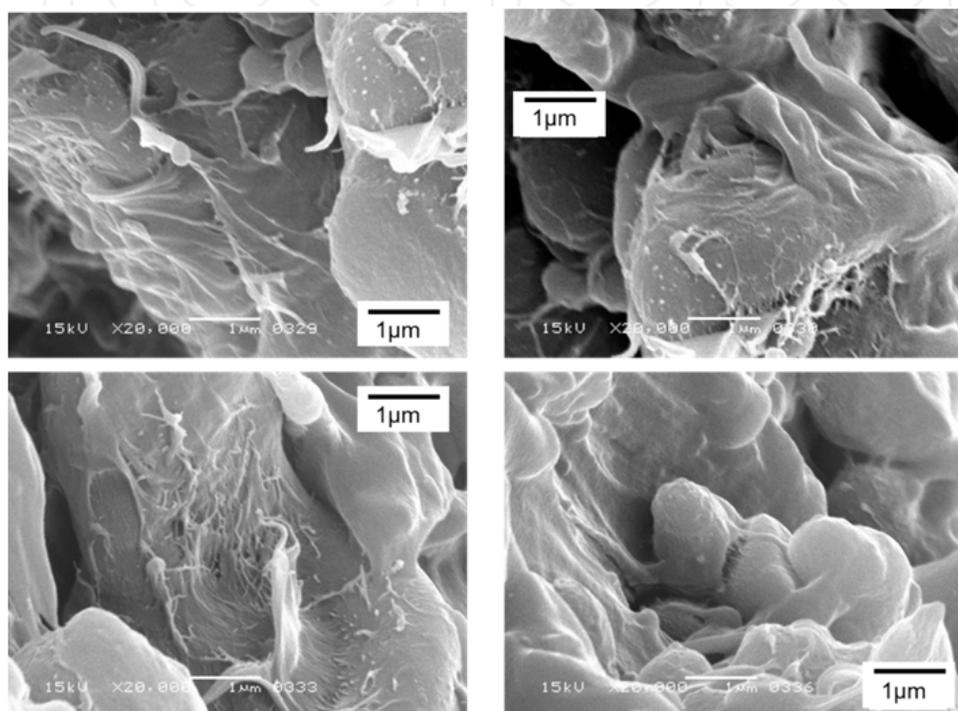


Figure 13. SEM photographs of fracture cross section of inflation film molded from Agri-wood(R)_3 [third-generation Agri-wood(R)] pellets obtained by tensile elongation test as the other examples for Fig. 12.

These observations strongly indicated that cellulose can exist more dispersedly within the nanocomposite after enhanced twin-screw kneading, in which 35%–70% amounts of rice was kneaded with 30%–65% of Wintec polyolefin WSX02 in the presence of small amount of Star Burst treated cellulose slurry. This argument is further enhanced by the results obtained from measuring the solid state properties of the molded test pieces. As shown in Table 1, all the tensile properties were enhanced in the order of the extent of nanofiber reinforcement. Especially, the value of tensile elongation at breakage can reflect the enhancement of compatibilization of the composite components of starch grain, matrix polyolefin, and microfibrillated cellulose fibers.

Concerning these findings, followings are found in the literatures. It can be stated as the first place, that cellulose nanofibers have a high density of hydroxyl groups, facilitating their agglomeration, and reducing interaction with surrounding matrix. Agglomeration is the

formation of groups of cellulose fiber due to the hydrogen bonds between each of them. Overcoming strong hydrogen bond requires high energy. The high pressure and high energy in the presence of added water, afforded by the action of a twin-screw extruder were imparted to the cellulose fibers to defibrillate fibrils intensively in achieving acceptable dispersion levels [15].

No.	Sample	Tensile strength (MPa)	Young's modulus (GPa)	Tensile elongation at break (%)	MFR ^a (g/10min)
1	Agri-wood(R)_1 ^b (Control)	27.3	1.88	2.60	10.5
2	Agri-wood(R)_2 ^c	30.6	2.04	3.14	9.96
3	Agri-wood(R)_3 ^d	31.1	2.23	6.94	7.23

^a 190°C, 10.58 kg

^b First generation Agri-wood(R); no added cellulose nanofiber; polyolefin / rice = 30 / 70 (w/w)

^c Second generation Agri-wood(R); polyolefin / rice / cellulose nanofiber = 30 / 70 / 0.05 (w/w)

^d Third generation Agri-wood(R); polyolefin / rice / cellulose nanofiber = 30 / 70 / 0.05 (w/w)

Table 1. Mechanical properties of a series of Agri-wood(R) samples

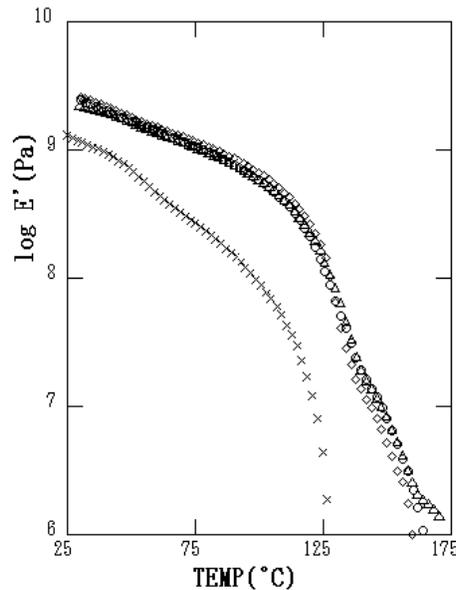
The inherent polar and hydrophilic nature of the nanofiber and the non-polar characteristic of most thermoplastics result in difficulties in compounding the filler and the matrix. In view of these, there is a possibility that the presence of starch in the kneading system play a prominent role in achieving acceptable dispersion levels. It is possible that the starch molecule interacts with cellulose nanofibers, covers them and by that improves the dispersion of the cellulose nanofiber. Actually, Oksman *et.al.*, studied a manufacturing process of cellulose whisker / polylactic acid (PLA) nanocomposites and found by TEM observation that dispersed composite structures could be obtained when water-soluble polyethylene glycol (PVA) was included as an additive [16].

Figure 14 shows the storage modulus as a function of temperature for neat polyorefine (Wintec WSX02)(x), the first generation Agri-wood without cellulose nanofiber and the two kinds of Agri-wood/Cellulose nanofiber composites. The latter three are corresponding to Agri-wood(R)_1~3 in Table 1.

The curve corresponding to the pure matrix (x) shows typical of thermoplastic behavior. The neat polyorefine (Wintec WSX02) is a random copolymer of PP (with small amounts of PE) having a melting temperature of 125 °C. Thus, the starting temperature (room temperature) for the measurement is very close to Tg of the polymer, from which a rapid decrease in the elastic tensile modulus is occurring. Then, a rapid decrease in the elastic tensile modulus, by more than 3 decades, is observed, corresponding to the glass-rubber transition, after which it seems to go directly into flow region but the experimental setup fails to measure it.

The storage modulus in Fig. 14 shows that the three of the Agri-woods have higher moduli on the entire temperature ranges compared to that of the neat polyorefine (Wintec WSX02),

which is caused by the starch filler effect. The corresponding data have shown large effect of starch fillers, which is further reinforced by the small coexistence of cellulose nanofibers, in order to obtain composites with good mechanical properties and increased stability at higher temperatures. The contents of cellulose nanofiber are remarkably small (ca.0.05%), its role can hardly be seen in the figure (Fig. 14).



◇ Agri-wood (R) 1st Generation (Control) (no added cellulose nanofiber; polyolefin/rice=30/70(w/w)); △: Agri-wood (R) 2nd Generation (polyolefin/rice/cellulose nanofiber=30/70/0.05(w/w)); ○ Agri-wood (R) 3rd Generation (polyolefin/rice/cellulose nanofiber=30/70/0.05(w/w))

Figure 14. Temperature dependencies of storage modulus (E') of neat polyolefine (Wintec WSX02) (×) and the Agri-wood/Cellulose nanofiber composites.

The influence of nanofiber existence for enhancing physical properties can be observed in the case of physical blending of microfibrillated cellulose fibers with thermoplastic polymer. An example is shown in Table 2. In this case, recycled PE was used instead of Wintec polyolefine WSX02 and kneaded with a small amount of Star Burst treated cellulose slurry. The resulting physical properties of the molded specimen were significantly improved when compared with the corresponding control, especially for impact strength and tensile elongation at breakage. This showed that nanofibrous microfibrillated cellulose was well dispersed within the molded specimen.

No.	Sample	Charpy impact strength / kJm^{-2}	Tensile strength / MPa	Tensile elongation at break / %	MFR ¹⁾ / (g/10min)
1	Control 1 (Untreated recycled PE)	29	17	72	17
2	Control 2 (Kneaded recycled PE)	28	14	64	11
3	Cellulose nanofiber composite ²⁾	46	15	300	10

1) 190°C, 10.58 kg

2) Recycled PE / Cellulose nanofiber = 100 / 0.05 (w/w)

Table 2. Mechanical properties of the recycled PE / cellulose nanofiber composite

4. Usage of pulverized cellulose prepared by ultra high-pressure water jet treatment in development of separator sheets equipped within the lithium ion battery (A feasibility study)

As shown in Table 1 in the previous chapter, the tensile properties were enhanced in the order of the additional or advantageous effect of nanofiber reinforcement. And also in Table 2, it was shown that when recycled PE was kneaded with a small amount of aqueous Star Burst treated cellulose slurry, the resulting molded specimens indicated improved physical properties when compared with the corresponding control. It is known, at the same time, that the presence of small amounts of cellulose nanofiber effects an enhancement of the heat resistance of the matrix resin [14]. These data encouraged us to apply these CNF reinforced HDPE to separator sheets equipped within the lithium ion battery.

An utilization of CNF reinforced polyolefin for the separator sheets equipped within the lithium ion battery [17] has been experimenting as a feasibility study. By use of the CNF from KC flock W-400G, half-esterified KC flock W-400G and half-esterified Avicel, the heat resistance and strength properties of the modified polyolefin sheets have been enhanced, which enables the sheets to be used for this purpose. Concerning data obtained up to now will be shown and discussed.

4.1. Experimental

4.1.1. Materials

Micronized cellulose powder (KC flock W-400G, average particle size: 24 μm) was supplied by Nippon Paper Chemicals. "Avicel", Crystalline Cellulose was from Asahi Kasei Co. Deionized water was used throughout, including in suspension of sample powders. Succinic anhydride was from nacalai tesque high-density polyethylene (HDPE)("HI-ZEH(HDPE)7000F") was from Mitui Hi-Zex Co. Ltd.

4.1.2. Methods

Half esterification of cellulose with succinic anhydride

Half esterification of cellulose powders (KC flock W-400G and Avicel) with succinic anhydride was conducted by use of 500 mL Dispersion Mixer (MS Moriyama Co.). 100 weight parts of cellulose fine powders were mixed and reacted with 5 weight parts of succinic anhydride without solvent at 140°C for 40 min.

Micropulverization of the half esterified cellulose powders

0.5 and 5% aqueous slurries of cellulose or the prepared succinic anhydride half esterified cellulose fine powders were converted to nano-fiber by use of Star Burst mini (Sugino Machine Ltd.). The method for micropulverization of cellulose powders is the same that token in the previous chapter.

Compounding micropulverized cellulose (CNF) with high-density polyethylene (HDPE) (“HI-ZEH (HDPE) 7000F”)

The ultra high-pressure counter collision-pretreated cellulosic or half-esterified cellulosic slurry(5% and 0.5%) was kneaded with high-density polyethylene (HDPE (“HI-ZEH (HDPE) 7000F”) at around 0.5 or 0.05 % nanofiber concentration with or without maleic anhydride modified PP (3%) and lubricant (BYK-P4101(1%)), using a super high-torque twin-screw extruder (Intermeshed co-rotation twin screw extruder (screw diameter= 48 mm, L/D=60), Technovel.Co.), under a controlled moisture vapor release. The compounding was done in the plant of Shiraishi Biomass Co. Ltd., located in Kyoto prefecture. Compounded pellets were obtained as shown in Table 3, from which films were prepared as described later.

Pellet No.	Composition	Cellulose	Additive	CNFcomposition amount	Slurry input amount	Slurry concentration	Star Burst treating frequency
①	HDPE			0	0		
②	HDPE			0	10phr	Water only	
③	HDPE+half-esterified CNF	KC flock W400G		0.1phr*	20phr	0.5wt%	10 passes
④	HDPE+half-esterified CNF+ maleic anhydride modified PP	KC flock W400G	Maleic anhydride modified PP 3%	0.1phr	20phr	0.5wt%	↑
⑤	HDPE+half-esterified CNF	KC flock W400G		0.5phr	10phr	5wt%	↑
⑥	HDPE+half-esterified CNF	Avicel		0.1phr	20phr	0.5wt%	↑
⑦	HDPE+half-esterified CNF+ lubricant	KC flock W400G	BYK-P4101 1%	0.1phr	20phr	0.5wt%	↑
⑧	HDPE+half-esterified CNF+ lubricant	KC flock W400G	BYK-P4101 1%	0.5phr	10phr	5wt%	↑

*phr : per hundred resin

Table 3. CNF composited HDPE pellets

Preparation of biaxially-drawn porous film made by a phase separation method

Each compounded pellets of micropulverized non-treated or half-esterified cellulose with HDPE (“HI-ZEH (HDPE) 7000F”) (Table 3) was mixed with liquid paraffin at a weight rate of 6:4, first in a beaker for the swelling of the pellets with liquid paraffin for 30 min, and then by use of a small size mixer at 180°C for 30 min, as shown in Figs. 15 and 16.

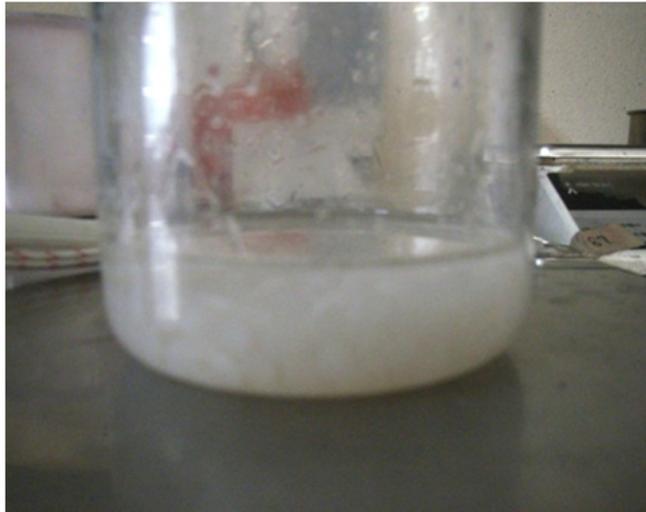


Figure 15. Swelling of the CNF compounded HDPE pellets with liquid paraffin.



Figure 16. The small size mixer used for kneading the pellets with liquid paraffin.

The kneaded products were molded with a metal mold (100mm Φ x 1mm thickness) at 180°C under the pressure of 20 MPa. From obtained sheets, square shape sheets with a dimension of 80mm x 80mm were punched out, which were biaxially-stretched simultaneously in 5 x 5 multiples through the use of a table tenter (Fig.17). The stretching temperature was 110°C and the rate of stretching was 8000 mm/min.

Then, from the prepared biaxially-drawn sheets, liquid paraffin was extracted with methylene chloride, obtaining biaxially-drawn porous films. These operations were done in the plant of The Japan steel works, Ltd., located in Hiroshima prefecture. Then, from the

SEM observations and the measurements of air permeability on the biaxially-drawn porous films, the potentiality of the obtained sheets for the application to the separator sheets equipped within the lithium ion battery was discussed.

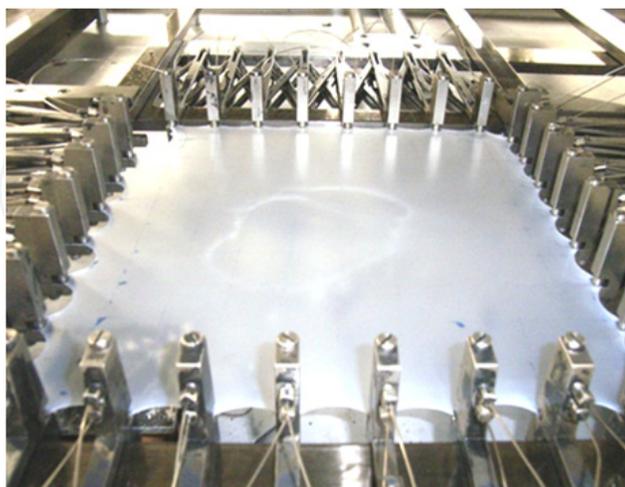


Figure 17. The table tenter used for biaxially-stretching the sheets.

Characterization

Scanning electron microscopy

SEM observations were done after extracting liquid paraffin through methylene chloride, trying to obtain biaxially-drawn porous films. SEM photographs 18 and 19 were obtained by FE-SEM (Thermal field emission scanning electron microscope, JSM-7000F) (JEOL), after platinum deposition of ca. 3 nm thickness through the ion sputtering device, Super Fine Coater : ESC-101 (ELIONIX). The FE-SEM photographs were shown at the magnification ratio of 20,000.

Mesurement of air permeability

Air permeability measured by the Gurley densometer IM38-03-00 (air permeability measuring device; Testing Machines Inc.).

4.2. Results and discussion

Composite processing

As described in the experimental section, six kinds of CNF/higher molecular weight HDPE pellets have been prepared (Table 3). Also, as described in the experimental section, an array of biaxially-drawn porous films were finally prepared.

SEM observations of prepared biaxially-drawn porous films

The characterful SEM images obtained for biaxially-drawn porous films are shown in Figs. 18 and 19, those film of which are prepared from pellet ④ and ⑥ in Table 3, respectively. Fibrous substances in several μm length are dispersed and unlevel pore like patterns are

existing. The latter are presumed to be derived from shrinkage of the pores, caused by residual stress, arising from biaxially-stretching or liquid paraffin extraction. In this experiment, the second biaxially-stretching at certain temperature was not performed after the liquid paraffin extraction, which is usually conducted in the correspondent industrial plant. Thus, the shrinkage of the pores, caused by residual stress, would rise up and pore would be obstructed partly. From these observations, it can be said that the samples ④ and ⑥ have evidences of coming with good to excellent pores and are pointed out the possibility of expressing characteristics as separator sheets.

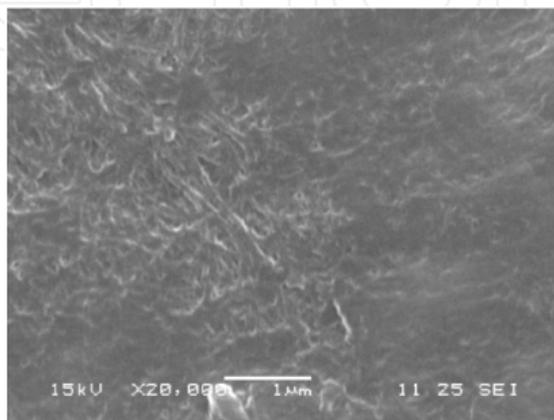


Figure 18. SEM photographs of the surfaces of biaxially-drawn porous films prepared from pellet ④ in Table 3. (20,000 magnifications)

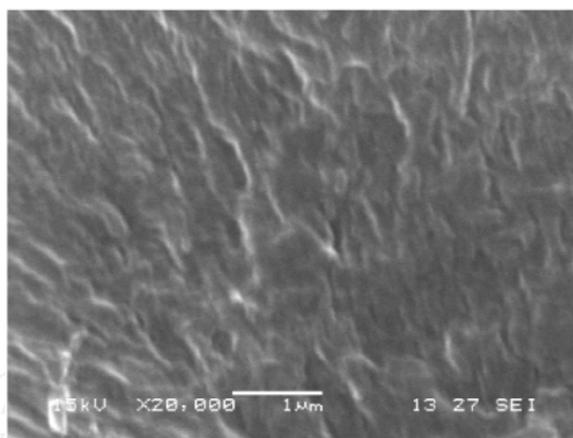


Figure 19. SEM photographs of the surfaces of biaxially-drawn porous films prepared from pellet ⑥ in Table 3. (20,000 magnifications)

Air permeability of prepared biaxially-drawn porous films

Pore volumes and air permeabilities of the biaxially-drawn porous films prepared from raw material pellets ③~⑧ are shown in Table 4. Pore volumes were derived from thickness and weight of 50 mm square sample sheets. As the density of samples, the density of used HDPE (HI-ZEH (HDPE) 7000F), that is, 0.95g/cm^3 , was adopted.

Air permeabilities were calculated from the obtained Gurley values, using the formulas shown in the footnote of Table 4.

Sheets prepared from raw material pellets ③ and ④ reveal Gurley values (times required 100ml air passing through the sheet) less than 1000, however, others have the values more than 3000, reflecting the small pore existence rate. Especially, the sheet prepared from raw material pellet ④ exhibits the air permeability value almost equal to that obtained for the standard sample, showing the existence of pass-through pores. The previous SEM observation also pointed out that the sheet prepared from raw material pellet ④ gave the result showing the existence of pass-through pores.

From these data, it can be said that the second biaxially-stretching at certain temperature should be performed after the liquid paraffin extraction. In addition, there is an argument in our research group that as the matrix resin, more appropriate high molecular weight HDPE should be adopted. Under these considerations and others, the related developing studies are continuing.

Pellet No.	Average thickness (μm)	Pore volume (%)	Gurley value (s/100cc)	Air permeability ¹⁾ ($\mu\text{m}/(\text{Pa}\cdot\text{s})$)	Remarks
③	25	21.4	356	0.38	
④	13	33.8	1000	0.14	Accuracy of thickness : good
⑤	27	9.34	>3000	0.05>	
⑥	44	27.2	> 3000	0.05>	Unevenness of thickness : large (high heat stability) ²⁾
⑦	18	18.1	>3000	0.05>	
⑧	24	11.39	>3000	0.05>	(high heat stability) ²⁾
Standard sample	—	—	280	0.34	

1) Air permeability : $p=135.3/t$ (time to 100ml permeable), t: Gurley value(s/100cc)

2) Heat stability: Stability during SEM observation.

Table 4. Pore volumes and air permeabilities of prepared biaxially-drawn porous films

5. Conclusions

Cellulose fine powders were found to be effectively pulverized and emulsified by an ultra high-pressure counter collision treatment in an aqueous suspension state. The emulsion was visually stable and did not show any phase separation even after a few years of storage. The fiber diameter of cellulose was reduced from an average of 24 μm to several nanometers by the described treatment. The different effects of different freeze-drying methods were visualized by SEM observations. The coalescence of microfibrillar structures was observed easily when the freeze-drying conditions were inadequate. While the degrees of the microfibrillation done by use of homogenizers including the Star-burst were unsatisfactory for use as fillers for the preparation of polymer nanocomposites, the situation was found to become acceptable one by subsequent after treatment such as using proper kneading techniques. Presence of rice starch or hydrophilic polymers in the CNF and polyolefin kneading system has a big role in improving the dispersion of the CNF in the composite. It

is possible that the starch molecule interacts with CNF, covers them and by that improves the dispersion of the CNF. To use half-esterified cellulose of dibasic acid anhydride (e.g. maleic anhydride) enhanced the formation of CNF. By introducing small amounts (1~5wt%) of the half- esters on the microfibril surface of cellulose, followed by the counter collosion treatment, electrostatic repulsion and steric hinderance effects rose up and a rather well formation of nano-fibers was caused. To choose the species of cellulose is one of the factors obtaining a high quality CNF. There are big differences in KC flock W-400G micronized cellulose powder and "Avicel", crystalline cellulose, for example. Conversion to nano-fiber is easier for Avicel when compared with KC flock W-400G. Percentage amounts of nano-cellulose fiber combined to matrix resins have been an another key factor. Usually, the values of 10% or more are preferably employed. However, there are arguments claiming that the smaller the particle, the smaller the clearance of the particle in particle/matrix resin composites, when the particle concentration is constant. Nano-particles are those having near the smallest in dimension which cause their particle clearances the smallest. Being influenced by these arguments, authors have made choice of the concentration of CNF less than 1 wt%. It is known that the physical properties were enhanced by this nanofiber reinforcement and that the presence of small amounts of CNF effects an enhancement of the heat resistance of the matrix resin. As an application study of these CNF reinforced HDPE, preparations of separator sheets for lithium ion battery have been proceeded. From SEM observations, it is known that fibrous substances in several μm length were found to dispers and pores for lithium ion transference could be formed in the biaxially-drawn films prepared from CNF/HDPE pellets. Further studies are required for this application. Especially, the second biaxially-stretching trials for the separator sheets after the liquid paraffin extraction are required, and HDPE with more adequately high molecular weight should be used. Under these situations and considerations, the developing studies are continuing.

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