

ORIGINAL ARTICLE

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## Fabrication of pulverized cellulose by ultra high-pressure water jet treatment and usage in polymer nanocomposites and graft copolymerization

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**Abstract** Cellulose powders were pulverized by an ultra high-pressure counter-collision treatment in an aqueous suspension state, and then used in composites with vinyl polymers and graft copolymerized with methyl methacrylate using ceric ion initiator. The influence of freeze-drying methods after microfibrillation of cellulose was visualized by scanning electron microscopy (SEM). The coalescence of microfibrillar structures was observed to increase easily reflecting the freeze-drying conditions. While the degree of microfibrillation was unsatisfactory for use as fillers in preparing polymer–nanocellulose composites, the situation was found to be rectified with the use of a proper kneading technique. The roles of microfibrillated cellulose in processes producing bio-nano-composites suitable for practical uses were studied through SEM observations and measurements of physical properties. The characteristics of the successive graft copolymerization were studied through examining the monomer conversion and the grafting efficiency. The significant improvement in the grafting became apparent in response to the counter-collision pretreatment. Dynamic viscoelastic properties of the molded sheets of the grafted products were studied to measure the effects of the graft copolymerization compared with the corresponding physically blended material and neat poly(methyl methacrylate). The grafting reaction resulted in composites with much higher heat-resisting properties than those obtained for the latter two.

**Key words** Ultra high-pressure water jet treatment · Cellulose · Microfibrillation of cellulose · Nanocomposite · Graft copolymerization

### Introduction

It is widely recognized that technologies that can economically convert biomass resources into commercially viable materials are needed. Cellulose is a candidate among biomass resources 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 state.<sup>1–6</sup> Endo et al.<sup>1–4</sup> 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.<sup>3,4</sup>

The work of Kondo et al.<sup>5</sup> and ours<sup>7</sup> recently appeared in 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). In our case, 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 10 times, using a Star Burst System HJP-25080. These patents appeared independently within a period of 13 months. Kondo et al.<sup>5,6</sup> claimed that pulverization by an ultra high counter collision successfully decomposed the interaction within the self-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).

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While having some claims in common with those of Kondo et al.,<sup>5</sup> our work 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.,<sup>1-4</sup> 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), a bead mill (Ashizawa Finetech), a vibration mill (Chuo Kakoki), and ultra high-pressure homogenizers. The last of these means, in particular the Star Burst System<sup>7</sup> HJP-25080 (Sugino Machine), 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 performed by the ITT Rayonier research group, in which dilute slurries of cellulose fibers were subjected to the repeated mechanical actions of a "homogenizing" machine (Gaulin).<sup>8,9</sup> The slurry was pumped at high pressure and fed through a spring-loaded valve assembly.<sup>8</sup> The aqueous cellulose slurry was pumped through the machine 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.

In this study, the degree of the microfibrillation of cellulose achieved by ultra high-pressure counter-collision treatment was studied by scanning electron microscopy (SEM). Using the resultant micropulverized cellulose emulsion, we attempted compositing with vinyl polymers through kneading as well as graft copolymerization of methyl methacrylate (MMA) onto the activated cellulose by using ceric ammonium nitrate (CAN) as initiator, and evaluated the effects of the counter-collision treatment. This newly developed approach offers new opportunities for creating innovative products derived from biomass.

## Experimental

### 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; Agri-wood(R); Agri Future Joetsu] prepared in December 2007 [1-year-old sample; second-generation Agri-wood(R); Agri-wood(R)\_2], and recently prepared [July 2008, advanced sample; third-generation Agri-wood(R); Agri-wood(R)\_3], as well as their inflation-molded sheets were used. Both Agri-wood(R)\_2 and 3 are

composed of 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). 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, the garbage bag sheet prepared ca. 1 year ago and that prepared recently were taken as test pieces. Recycled polyethylene (PE) was supplied by Ecos Factory.

MMA, CAN, and other chemicals were obtained from Wako. MMA monomer was purified by conventional methods, but others were used as received.

### 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, 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 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).

### 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 × 5 × 0.4 mm were cut from the molded sheets.

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

Agri-wood(R) 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 MPa 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 at the same pressure. Sample strips measuring 80 × 5 × 0.4 mm were cut from the molded sheets. Agri-wood(R) pellets were directly subjected to the measurement of melt index (MI) [melt flow rate (MFR)].

## Compounding of 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 (Supertex 77 $\alpha$ , 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 $\alpha$  extruder 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.

### Grafting of MMA onto micropulverized cellulose samples initiated by ceric ammonium nitrate

A counter collision-pretreated cellulosic slurry containing 10 g of cellulose was diluted with deionized water to a liquid ratio of 40. The resultant slurry and its control, composed of 10 g of untreated sample and 400 g of deionized water, were individually placed in a three-necked 500-ml separating flask and mixed well with stirring. In the first part of the experiment, 30 g of MMA and then a given amount of CAN (in 1 N HNO<sub>3</sub> solution) were added with stirring at 60°C to initiate grafting. After the reaction, the resultant reaction liquid was poured into a large excess of deionized water, allowed to agitate overnight, and the mixture was filtered on a sintered glass crucible. The refined solid residue was washed with water, dried in a vacuum oven at 70°C, and weighed to determine the monomer conversion and weight increase. Then the dried reaction product was Soxhlet-extracted with acetone for 40 h, dried in a vacuum oven at 70°C, and weighed to calculate grafting rate and grafting efficiency.

### Preparation of test pieces of graft copolymerized products and related blended products for dynamic viscoelastic measurements

Graft copolymerized products and related blends were molded into sheets by hot pressing using the conditions described above. Sample strips measuring 40 × 5 × 0.4 mm were also cut from the molded sheets for dynamic viscoelastic measurements.

## Characterization

### Scanning electron microscopy

Morphologies of untreated cellulose as well as the freeze-dried cellulose, before and after counter-collision treatment, were observed using a JSM-T330A (JEOL) scanning electron microscope. Fracture cross sections obtained by tensile elongation testing of the inflation-molded sheets prepared from Agri-wood(R)\_2 and 3 were also visualized by SEM. 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 conventional freeze drying as above.

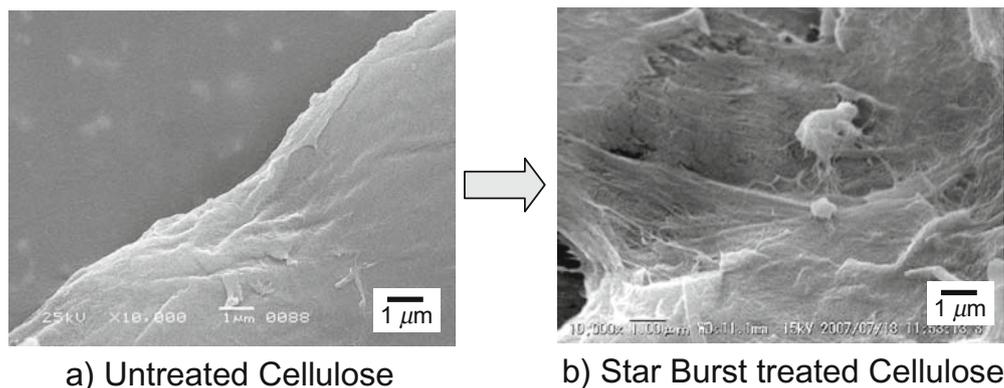
### Negative-staining transmission electron microscopy

The rapid freeze-dried cellulose treated with ultra high-pressure counter collision was dispersed in distilled water with a liquid ratio of 1000, followed by agitation with a magnetic stirrer, and was studied by transmission electron microscopy (TEM) with the aid of negative staining. One drop of the mixture was placed on a Formvar coated copper grid for 1 min and then drained off with filter paper. Subsequently, the specimen was negatively stained with 2% uranyl acetate. The grid was then placed in the TEM instrument (JEM-1220, JEOL Japan) and examined.

### Mesurements of mechanical properties of Agri-wood(R), recycled PE composite, and grafted products

An IM-401 Charpy-type Impact Tester (Tester Sangyo) was used for the Charpy impact test, while a Universal Testing

**Fig. 1a, b.** Scanning electron microscopy (SEM) photographs of cellulose fibers before (a) and after (b) Star Burst treatment (ten passes) followed by regular freeze drying 1



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).

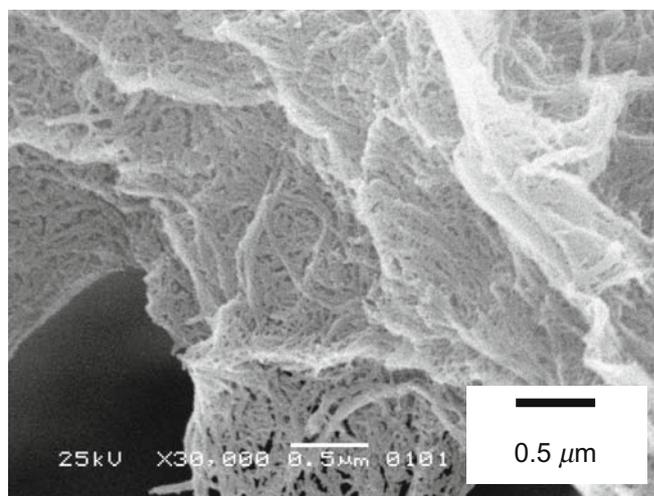
## Results and discussion

Wet mechanochemical treatment of cellulose as pretreatment for efficient graft copolymerization of vinyl monomer in water

A planetary ball mill, a bead mill, and an ultra high-pressure homogenizer were all used to convert cellulose suspension into an appropriate nanopulverized state for the successive grafting reaction. 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). For example, the problems due to contamination of the treated sample with impurities derived from the medium can be avoided, and treatment of larger samples is possible within a shorter period of time.

The additional feature of ultra high-pressure homogenizing treatment is that the treated cellulose fiber can be homogeneously dispersed in water for a prolonged period.<sup>5,6</sup> It is considered that cellulose fibers can be pulverized heavily to enlarge the specific surface area to give a much more highly hydrated state than that achieved with untreated cellulosic fiber. To visualize the 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 comparison of SEM photographs of the counter-collision treated cellulose dried by the regular freeze-drying 1 method and untreated cellulose. The Star Burst treated cellulose (Fig. 1b) is observed to have surface morphological features significantly different from the untreated cellulose (Fig. 1a). The former has a fibrous

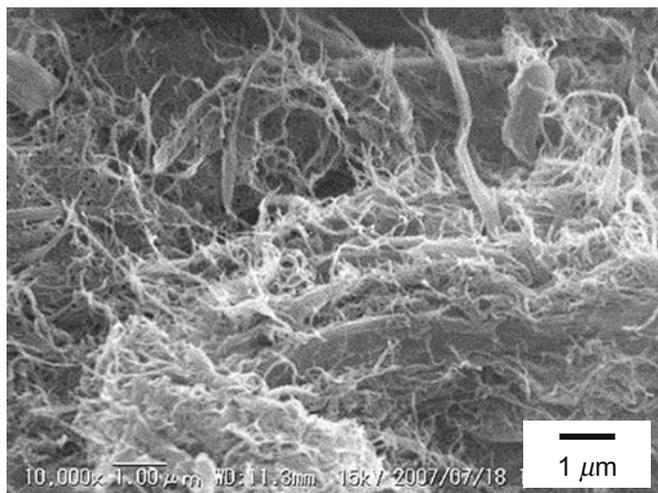


**Fig. 2.** SEM photograph of cellulose fibers after Star Burst treatment (ten passes) followed by regular freeze drying 2

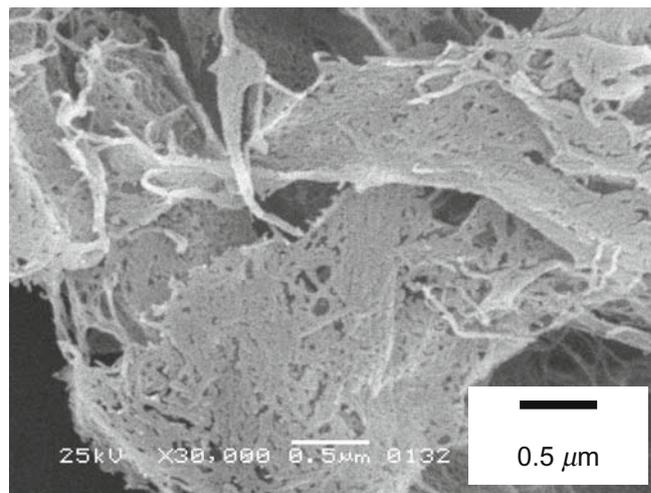
surface when compared with the latter, but much of the surface area is severely coagulated to form subaggregate structures. It is widely accepted that the relatively slow freezing process causes the formation of ice crystals and squeezes out cellulose microfibrils to form the subaggregate structure. Accordingly, the growth of ice crystals on freezing can be prevented by rapid cooling.<sup>10</sup> To confirm, an SEM photograph was taken of the counter collision-treated cellulose dried by regular freeze drying 2 method (Fig. 2).

From Fig. 2, the Star Burst treated cellulose is observed to have surface morphological features significantly different from the untreated cellulose (Fig. 1a). It loses the subaggregate 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 the cellulose fibrillar morphology is better achieved by solvent-exchange freeze drying using methanol and benzene or *t*-butyl alcohol.<sup>10</sup> With this perspective, cellulose slurry was pulverized by counter collision at a pressure of 245 MPa, after which the pulverized product was freeze-dried by the solvent-exchange method. In our experiment, benzene was used as the final solvent of the solvent-exchange process and mechanical



**Fig. 3.** SEM photograph of cellulose fibers after Star Burst treatment (ten passes) followed by solvent exchange and regular freeze drying 2



**Fig. 4.** SEM photograph of cellulose fibers after Star Burst treatment (ten passes) followed by solvent exchange and rapid freeze drying

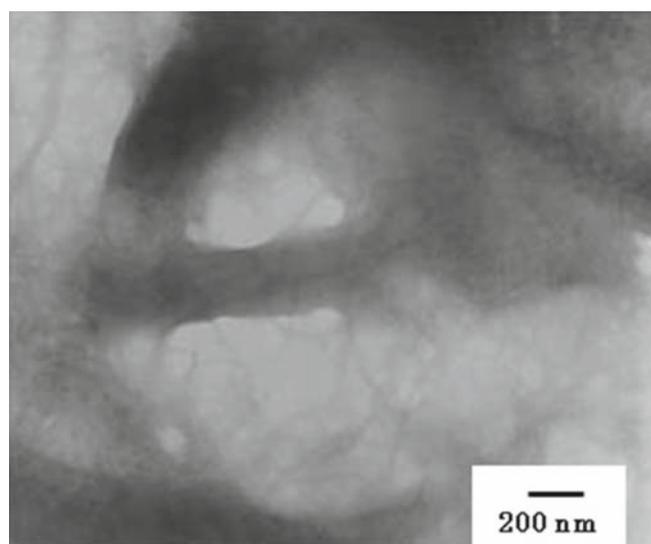
agitation was used during the solvent-exchange process. The SEM photograph of the corresponding dried product is shown in Fig. 3.

Figure 3 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. 38 nm) 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. 3). This is despite the fact that the cellulose received ultra high-pressure homogenizing treatment and stirrer agitation during the solvent-exchange process.

From the above results, it was decided that an additional solvent-exchange experiment should be conducted without agitation to understand its role. In addition, 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 regular freeze drying.

The resultant SEM photograph is shown in Fig. 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 the sample in Fig. 4, noting that thin 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 between the hydroxyl groups present on the different surfaces.

Although the most desirable freeze-drying conditions for this experiment were employed, fibrous microfibrillated cellulose could not be directly obtained. However, the result shown in Fig. 3 suggested that strong agitation followed by adept kneading with a twin-screw extruder would break the thin leaf structure of cellulose fibrillar lamellae, yielding



**Fig. 5.** Transmission electron microscopy (TEM) photograph of microfibrillated percolated cellulose

nanofibrous microfibrillated cellulose. To test this point, several experiments were performed.

First, the possible effects of stirrer agitation for loosening the thin leaf structure of cellulose lamellae in considerably dilute aqueous slurry were studied. The freeze-dried sample of Fig. 4 was again dispersed in 1000 times weight of distilled water, and agitated heavily with a magnetic stirrer, after which one drop of the slurry was placed on a copper grid, dried, and examined by TEM. As shown in Fig. 5, the result clearly reveals the formation of nanofiber networks, showing that magnetic stirring of significantly diluted aqueous slurry broke the thin leaf structure of cellulose lamellae of Fig. 4.

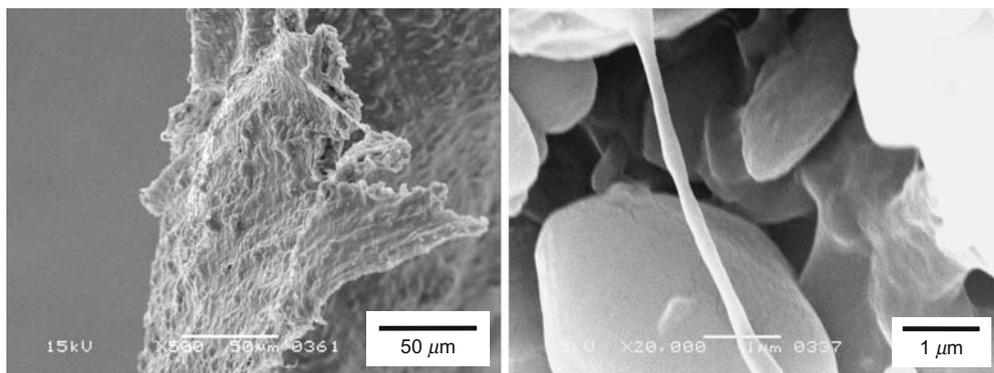
Second, inflation films molded from pellets of Agri-wood(R)\_2 and 3 were prepared, their tensile properties were measured, and fracture cross sections obtained were

visualized by SEM. Figure 6 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 particles of around 1  $\mu\text{m}$  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.

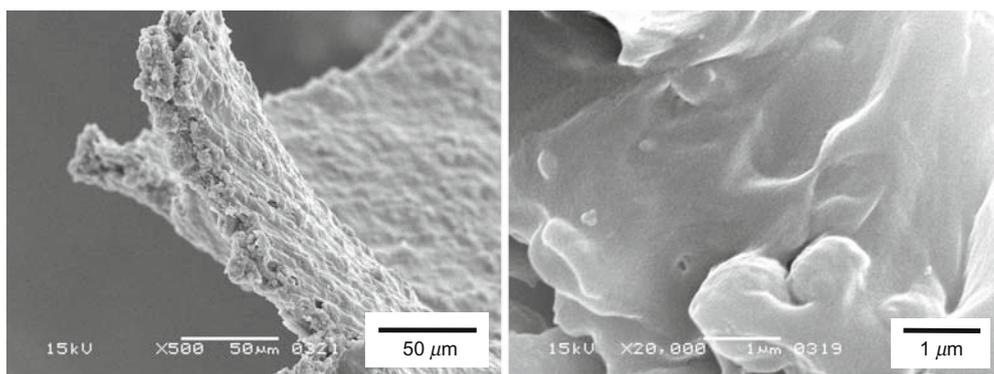
This kneading technique to prepare Agri-wood(R)\_2 pellets was further advanced recently. Major improvement efforts have been focused on techniques of programmed evacuation of water vapor from the vents at pressurized, normal, and reduced pressures,<sup>11</sup> as well as adopting appropriate paddle constructions. 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. 7). 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. 6) are homogeneously dispersed and combined with the matrix resin. 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 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.

**Fig. 6.** SEM photographs of fracture cross section of inflation film molded from Agri-wood(R)\_2 [second-generation Agri-wood(R), prepared in December 2007] pellets obtained by tensile elongation test



**Fig. 7.** SEM photographs of fracture cross section of inflation film molded from Agri-wood(R)\_3 [third-generation Agri-wood(R), prepared in July 2008] pellets obtained by tensile elongation test



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

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

MFR, Melt flow rate

<sup>a</sup> 190°C, 10.58 kg

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

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

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

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.

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 polyolefin 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.

Graft copolymerization of poly(methyl methacrylate) onto cellulose with or without pretreatment by Star Burst counter collision in water

Table 3 shows data concerning the effects of counter-collision pretreatment by Star Burst (ten passes) as well as the catalyst amounts and reaction period upon poly(methyl methacrylate) (PMMA) graft copolymerization. In all cases, the obtained monomer conversion values are very high.

Even in the case of addition of a very small amount of catalyst and a short reaction time, 0.75 g addition and 15 min, respectively, the conversion value is still ca. 92% not only for nanopulverized cellulosic slurry but also for untreated cellulose blank. However, this value decreased gradually with decline in the catalyst amount. This result demonstrates that this redox polymerization can proceed quickly and completely when the conditions shown in Table 3 are adopted.

On the other hand, Table 3 shows that there are meaningful differences in the efficiency of the grafting between the reactions with or without Star Burst pretreatment. For the cases with Star Burst treatment, the graft efficiency values were 14%–20% higher than the corresponding values without pretreatment. These results can be explained in terms of an increase in the specific surface area of cellulose fiber, caused by the wet atomization at ultra high pressure.

Because the values of monomer conversion were quite high, even in the case of the shortest reaction time, there was almost no difference between the results with and without Star Burst treatment. Consequently, experiments employing reduced catalyst amounts were also performed. When the catalyst amount was reduced to half of the lowest value shown in Table 3 (0.375 g), a considerable effect on the polymerization rate of monomer was apparent, and the influence of Star Burst treatment became evident as demonstrated in Table 4. The treatment made monomer conversion values 10–15 times larger than the case for nontreatment. This result also suggests the increase of accessibility of cellulose fiber given by Star Burst treatment.

Dynamic mechanical properties of cellulose fiber graft copolymerized with PMMA

Films of the PMMA-grafted cellulose were analyzed by dynamic mechanical analysis (DMA) in comparison to

**Table 2.** Mechanical properties of the recycled polyethylene (PE)–cellulose nanofiber composite

No.	Sample	Charpy impact strength (kJ m <sup>-2</sup> )	Tensile strength (MPa)	Tensile elongation at break (%)	MFR <sup>a</sup> (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 <sup>b</sup>	46	15	300	10

<sup>a</sup>190°C, 10.58 kg

<sup>b</sup>Recycled PE–cellulose nanofiber = 100 / 0.05 (w/w)

**Table 3.** Effects of Star Burst treatment on graft copolymerization for cellulose fiber

No.	Star Burst treatment	Catalyst <sup>a</sup> (g)	Reaction time <sup>b</sup> (min)	Monomer conversion (%)	Grafting efficiency (%)
1	No	3.00	90	98.7	40.3
2	Yes	3.00	90	98.6	60.8
3	No	2.25	45	97.6	63.0
4	Yes	2.25	45	100	70.4
5	No	1.50	30	96.8	42.0
6	Yes	1.50	30	98.2	61.5
7	No	0.75	15	92.3	56.3
8	Yes	0.75	15	92.8	70.3

<sup>a</sup>Catalyst composition: ceric ammonium nitrate / 1 N HNO<sub>3</sub> = 3/5 (w/v). See “Experimental”

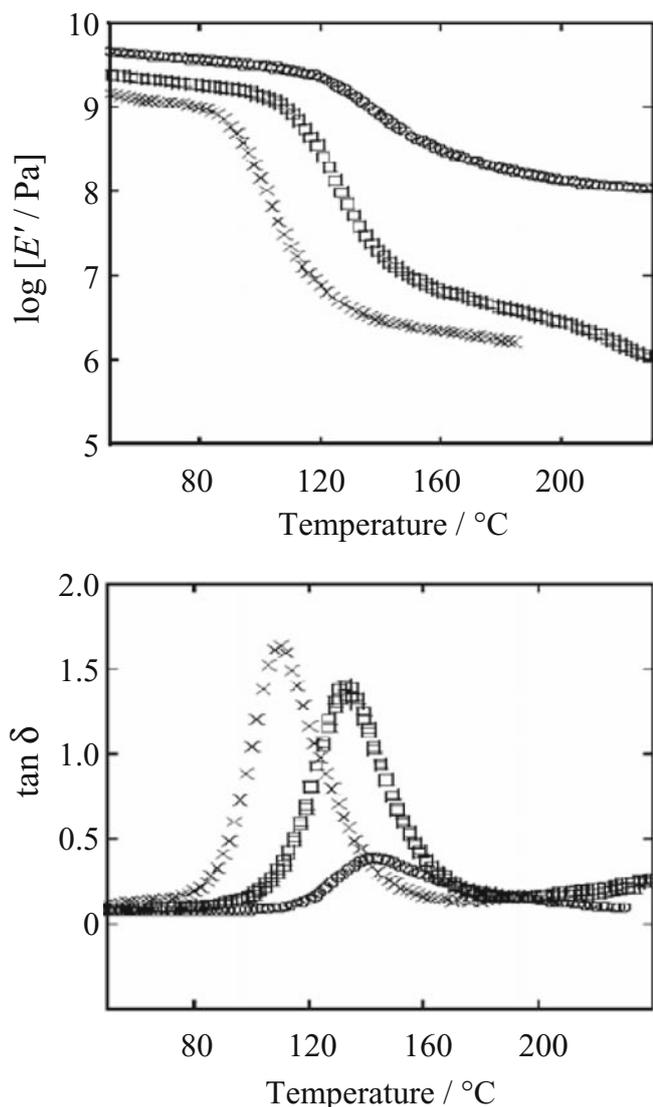
<sup>b</sup>Reaction temperature: 60°C

**Table 4.** Effects of Star Burst treatment on graft copolymerization for cellulose fiber

No.	Star Burst treatment	Catalyst <sup>a</sup> (g)	Reaction time <sup>b</sup> (min)	Monomer conversion (%)
9	No	0.375	30	1.40
10	Yes	0.375	30	14.5
11	No	0.375	15	0.90
12	Yes	0.375	15	13.8

<sup>a</sup> Catalyst composition: ceric ammonium nitrate / 1 N HNO<sub>3</sub> = 0.375 (g)/0.625 (ml)

<sup>b</sup> Reaction temperature: 60°C



**Fig. 8.** Temperature dependencies of  $E'$  and  $\tan \delta$  of cellulose–poly(methyl methacrylate) (PMMA) composite. *Circles*, cellulose grafted with PMMA; *squares*, cellulose blended with PMMA; *crosses*, neat PMMA

those for the corresponding cellulose–PMMA blend and neat PMMA. Figure 8 demonstrates the temperature dependencies of the storage modulus ( $E'$ ) and the loss tangent ( $\tan \delta$ ) of these three materials. In the upper part of Fig. 8, neat PMMA displayed the typical behavior of an amorphous polymer. For temperatures below the glass transition temperature ( $T_g$ ), the polymer was in the glassy state and

the modulus decreased only moderately with increasing temperature. The onset of a significant drop in the modulus, corresponding to the glass–rubber transition, was then observed. The drop proceeded in the same way up to the rubbery region, supposedly the result of amorphous relaxation.

The upper part of Fig. 8 also displays the temperature dependence of the storage moduli of the PMMA–cellulose blend and its corresponding grafted product. The amounts of PMMA in the graft sample and in the blend sample are the same and large (73.8%). The presence of cellulose in the blend and the grafted product are considered as physical and chemical cross links, respectively, and these enabled the materials to obtain enhanced moduli. Thus, below  $T_g$  the modulus of the blend became larger than that for neat PMMA and that for the grafted product became the largest among the three materials. In these connections, it can be pointed out that the cross linking occurring within the blend composite is mainly caused by the interaction among carbonyl carbons in PMMA molecules and hydrogens of hydroxyl groups in cellulose molecules, while that occurring within the grafted product is caused by chemical bonds at the graft copolymerized sites.

Above the apparent  $T_g$ , almost the same amorphous relaxation behavior was observed for the blend product as obtained for neat PMMA, with higher starting temperature of the glass–rubber transition. On the other hand, the drop in modulus was significantly restrained for the grafted product revealing that grafted PMMA is fairly different from neat PMMA. This difference may well be attributable to the chemical bonding to cellulose powders and the molecular weight of the grafted PMMA branches being much lower than that of neat PMMA. It is noted that the starting temperature of the glass–rubber transition was markedly higher in this case.

These differences among the three materials are well reflected in the  $\tan \delta$  data. The apparent  $T_g$  obtained for the blend composite was ca. 22°C higher than that for the neat PMMA as shown in the lower part of Fig. 8. This result shows that a physical blending of cellulose powders can improve the thermal characteristics of PMMA. The interaction among carbonyl carbons in PMMA molecules and hydrogens of hydroxyl groups in cellulose molecules hinders the micro-Brownian motion of PMMA. It is also known that the grafting method, which makes a composite of cellulose and PMMA, through chemical binding, can improve these characteristics more markedly than the case of physical blending. The apparent  $T_g$  of grafted product shifted to about 10°C higher than the latter case, and especially the

decrease in the  $E'$  value at elevated temperature was inhibited. These observations demonstrate that cellulose fiber can work as a pseudo-cross-linking point in the PMMA matrix to inhibit thermal flow of PMMA. Thus, a strong argument can be made that composites with heat-resisting properties, not obtainable through physical blending, can be obtained by grafting.

## Conclusions

Cellulose fine powders were found to be effectively pulverized and emulsified by an ultra high-pressure counter-collision treatment in an aqueous suspension. The emulsion was visually stable and did not show any phase separation even after a few years of storage. The cellulose fiber diameter was reduced from an average of 24  $\mu\text{m}$  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 to increase easily when the freeze-drying conditions were inadequate. While the degree of the microfibrillation was found to be unsatisfactory for use as fillers in preparing polymer nanocomposites, the situation was found to be acceptable by subsequently applying a proper kneading technique. Graft copolymerization of MMA monomer onto cellulose nanofiber obtained through the treatment was successful using the combination of the Star Burst treated aqueous emulsion and a ceric ion redox system. The monomer conversion and the grafting efficiency of the reactions involving cellulose nanofiber were markedly greater than those of untreated cellulose fiber, because the specific surface area of cellulose nanofiber is much larger than that of untreated cellulose fiber. The results of dynamic viscoelastic measurements for the products demonstrated a significant improvement in heat resistance characteristics attributable to grafting, when compared with

physical blends of cellulose and PMMA. Thus, it is asserted that the cellulose nanofiber reinforced the grafting of PMMA because it became a kind of cross-linking site in the products.

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