SPMC Technical Review

Application of Cellulose Resin Composite (“STARCEL®”) to Structural Material

SEIKO PMC CORPORATION
Technology Division Yuya Terao
Tomoaki Yoshimura
Daisuke Kuroki

1. Introduction

In recent years, interest in a sustainable society has been surging around the world. The plastic material industry has faced to global issues such as shortage of raw materials due to the depletion of fossil resources and environmental pollution caused by plastic waste and marine plastic litter. “Plastics Material Cycle Strategy” formulated in 2019 in Japan calls for the effective use of biomass materials and the promotion of recycling.

Cellulose fiber is renewable material derived from inedible botanical resource. Therefore, its utilization contributes to producing carbon neutral plastic materials. Cellulose nanofibers (CNF), which are defibrated cellulose fiber in nanoscale, are being studied for various applications because of their characteristics such as high fiber strength and elastic modulus, low coefficient of linear thermal expansion, large aspect ratio due to the nanometer-order width of the fiber shape, and large specific surface area. By making cellulose fiber surface hydrophobic, we have enabled cellulose fiber to disperse into thermoplastic resins (e.g., PP and PE) that are usually not compatible with cellulose. For now, we are developing CNF mainly for use in reinforcement of resin, resin foam, and rubber.[1),] There is large market of structural materials such as automobile interiors and exteriors, home appliance housings and construction materials. If CNF resin composite can improve the strength and weight reduction, it is expected that metal and resin materials used in these fields can be replaced with CNF resin composite.

On the other hand, CNF resin composite has not yet been used widely because of the high production cost and low impact resistance. Thus, we have working to solve these problems. This paper introduces the features of our cellulose resin composite as structural materials, the STARCEL® NC series (CNF resin composite) and the STARCEL® HC series (cellulose microfiber resin composite) which shows high impact resistance, and then refers our approach toward the cost reduction.

2. Manufacturing method

In general, there are two ways of producing CNF. One is by suspending cellulose fibers in water and treating them by machines. Another is by introducing ionic groups to cellulose fibers by chemical pretreatment, followed by mechanical treatment to break them down into thin fibers (defibrillation in water)[2), 3)]. On the other hand, we are manufacturing CNF by kneading hydrophobically modified cellulose fibers with melted thermoplastic resin. During kneading process, cellulose fibers defibrate into nanoscale and disperse into resin. This process is called “Kyoto Process” (Figure 1). In the Kyoto process, cellulose fibers with tens of microns in width unravel from the outside and become CNF with less than several hundred nm in width. Therefore, in this process, CNF is obtained as dispersion in thermoplastic resins such as polyethylene (PE) and polypropylene (PP). Comparing to defibrating cellulose fibers in water, the Kyoto process is more energy-efficient because the energy loss of water removal is smaller. Moreover, hydrophobically modified cellulose, one of our distinctive technologies, shows high reinforcement effect because it can disperse into various hydrophobic resins such as thermoplastic resins (PE and PP) and rubber without agglomeration.

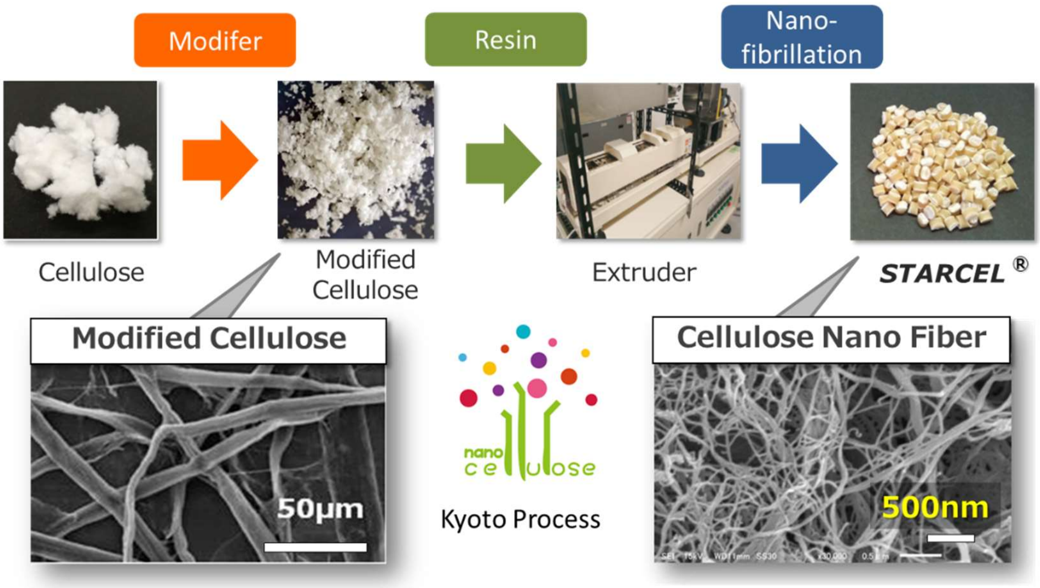

Figure 1. Manufacturing method of STARCEL®(Kyoto Process).

3. Features of STARCEL® as structural materials

CNF has various excellent properties such as light weight, high strength, high elastic modulus, and low linear thermal expansion. CNF resin composite does not only contribute to increase biomass content of resin, but also have various unique physical characteristics due to above properties. Here we introduce (1)weight reduction by increasing strength, (2)recyclability, and (3)mold shrinkage suppression.

3-1. Weight reduction by increasing strength

Figure 2 shows the strength properties of injection-molded PP with CNF (NC series) as structural material applications. The flexural modulus and flexural strength become higher with increasing CNF content. Since CNF has lower density than other reinforcing fibers, it is shown that weight reduction is possible by reducing the use of resin.

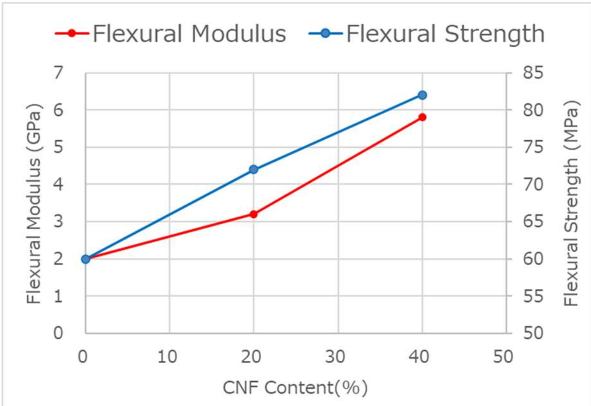

Figure 2. Flexural modulus and flexural strength of NC Series.

3-2. Recyclability

Figure 3 shows the deterioration of flexural modulus and flexural strength of NC series and PP with 20% Glass Fiber(GF) after repeated molding. The flexural modulus and strength of PP with GF decreased due to

GF breaking during the recycling process, and after four times recycling, the strength decreased by 30%. On the other hand, NC series (CNF blended PP) showed a very small deterioration in physical properties after repeated recycling. This makes it possible to recycle runners, sprues, and trash generated during injection molding and cutting processes, as well as mechanical recycling of products. Furthermore, CNF blended PP has the advantage of generating thermal energy when incinerated. (energy recycling)

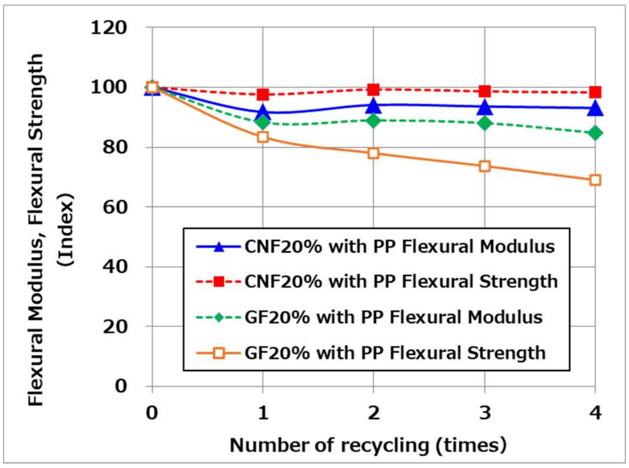

Figure 3. Number of recycling versus flexural properties (index with pre-recycling as 100).

3-3. Mold shrinkage suppression

When molding thermoplastic resins, the melted resin is cooled and solidified accompanied by volume reduction. The ratio of volume after cooling to volume of mold design is called shrinkage rate. Crystalline resins such as PP and PE have particularly high shrinkage rate, resulting in molded products that differ from the targeted shapes. For this reason, in injection molding, the shape of the mold is designed by taking the shrinkage rate into account.

Incidentally, a major problem with FDM (Fused Deposition Modeling) 3D printers, which have become increasingly popular for home use in recent years, is that they produce warped models due to resin shrinkage. Since CNF reinforces the resin and suppresses shrinkage, we applied CNF blended resin to improve moldability in FDM 3D printers. Figure 4 shows the shrinkage rate of moldings made by CNF blended polylactic acid (PLA), which is commonly used in FDM 3D printers. PLA originally has a low shrinkage rate, but as the amount of CNF content increased, the shrinkage rate further decreased. Therefore CNF makes it possible to obtain more precise moldings. Figure 5 shows a sample of CNF blended PLA modeled by HOTTY POLYMER inc. using a 3D printer. No warping was observed, and the modeled product has a woody appearance.

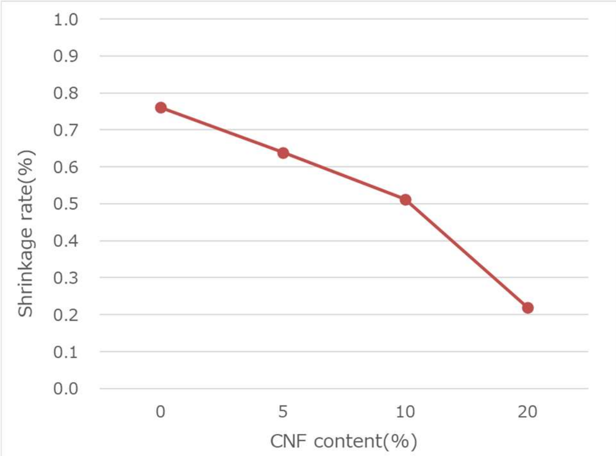

Figure 4. Shrinkage rate of CNF blended PP.

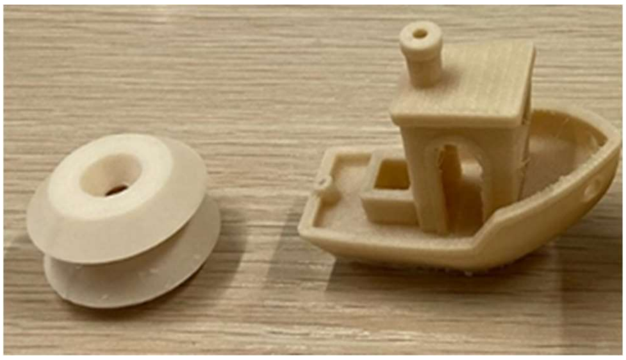

Figure 5. 3D printer modeling of CNF blended PP (provided by HOTTY POLYMER inc.).

4. STARCEL® HC series with high heat resistance and high impact resistance

The NC series has been evaluated by customers in applications requiring rigidity and heat resistance. As the cellulose content is increased, the elastic modulus, strength, and heat deflection temperature (HDT) of the NC series increase. However, impact strength is decreased and the design is restricted by discoloring during the molding process. Therefore, there are many requests for higher impact strength and whiteness. Therefore, we developed the HC series, which has slightly inferior flexural and tensile properties, but significantly improved impact strength, HDT, and whiteness. The HC series is made from non-wood pulp, and its heat resistance and impact resistance have been successfully improved by changing the hydrophobization method of cellulose fibers and adjusting the degree of cellulose fiber defibration. Table 1 and Figure 6 show the evaluation results of flexural tensile properties, impact properties, and HDT obtained by injection molding the NC series and the developed HC series as an example.

Table 1. Comparison of physical properties of STARCEL® as structural materials.

	Measurement Method		Unit	PP	NC Series		HC Series	
CNF Content			%	0	20	40	20	40
Specific Gravity	JIS K7112			0.91	1.00	1.12	0.99	1.11
MFR	JIS K7210 230 ℃	2.16 kgf	g/10 min	45	12	-	14	-
		10 kgf	g/10 min	-	-	25	-	16
Flexural Modulus	JIS K7171		GPa	2.0	3.2	5.8	2.9	5.0
Flexural Strength			MPa	60	72	82	70	94
Tensile Modulus	JIS K7161		GPa	1.9	2.8	4.5	2.6	4.0
Tensile Strength			MPa	39	44	52	45	63
Izod Impact Strength	JIS K7110	notched	kJ/m^2	2	2	2	4	4
		unnotched	kJ/m^2	31	22	15	31	32
HDT	JIS K7191-1	0.45 MPa	℃	117	127	136	137	149

(Values in the table are representative values.)

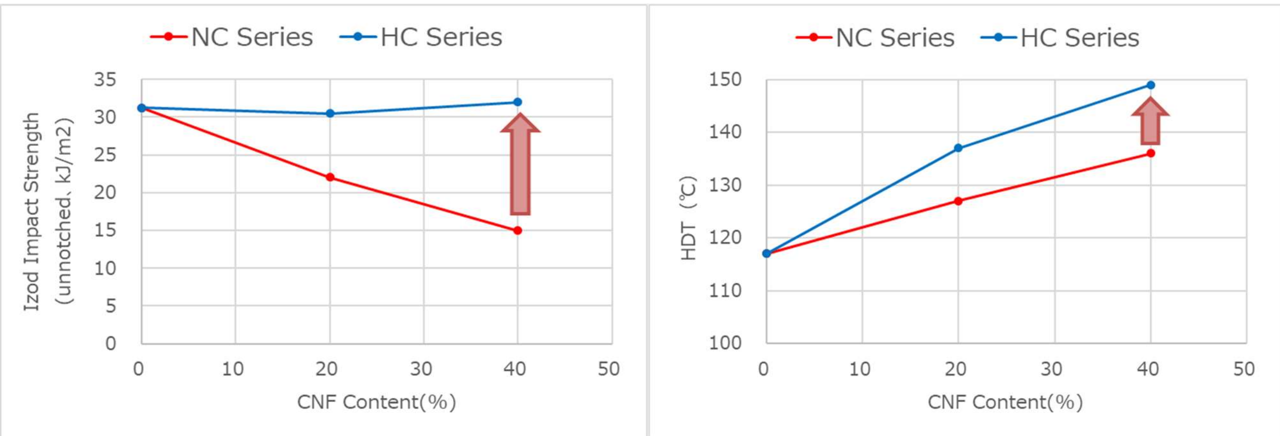

Figure 6. Impact strength and HDT of STARCEL® as structural materials.

Figure 7. shows a scanning electron microscope (SEM) image of a cellulose fiber in the HC series. Nano-sized fibers exist on the surface of micro-sized fibers. We assume that the nano-sized fibers contribute to the performance of CNF, and the micro-sized fibers contribute to high impact resistance. Figure 8 shows the pellet appearance of the NC series and HC series at 40% cellulose content. The HC series is whiter than the NC series and can be molded into wider variety of shapes. Figure 9 shows the thermogravimetric analysis (TGA) results of the modified cellulose in the HC and NC series. The modified cellulose used in the HC series does not easily decompose and lose weight during melt-kneading, thereby suppressing discoloration caused by decomposition products (hydroxymethylfurfural, levoglucosan, tar, etc.). The HC series is expected to be available in October.

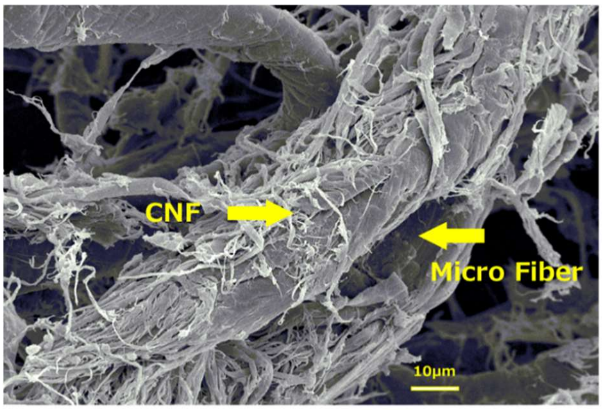

Figure 7. SEM image of cellulose fibers in the STARCEL® HC series.

Figure 8. Appearance of NC series and HC series (40% cellulose content).

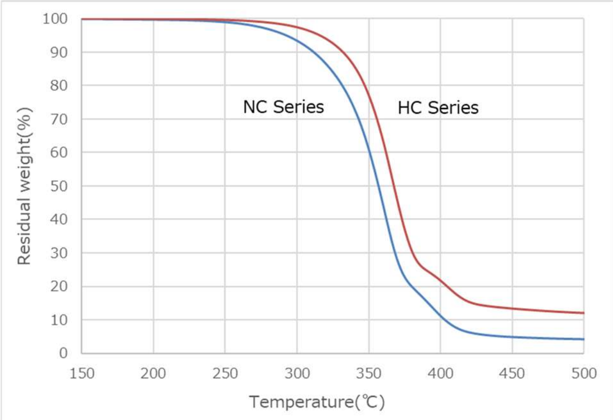

Figure 9. TGA curve of modified cellulose used in HC and NC series.

5. Efforts to establish high-productivity processes

Because of the excellent properties of CNF, its practical applications are underway in such fields as food, cosmetics, and leisure and sporting goods. On the other hand, there has been little progress in practical application as structural material, which is in great demand. In order to promote CNF in the field of structural materials, it is also necessary to further reduce production costs and improve material properties. Therefore, since 2020, we have been developing a manufacturing process for CNF resin composite under a project subsidized by the New Energy and Industrial Technology Development Organization (NEDO), aiming to improve the physical properties and reduce manufacturing costs. More specifically, we are studying improvements in the production process for CNF resin composite and its intermediate, modified cellulose.

The Kyoto process, described in section 2, is used to manufacture the CNF resin composite. In this process cellulose fibers are defibrated into nano scale. When productivity is increased by raising the kneading speed, the time that the melted resin stays in the biaxial kneading machine becomes shorter, making it difficult for cellulose fibers to become nano-sized, and the physical properties of the composite will decrease accordingly. Therefore, we improved the kneading conditions of the Extruder. Figure 10 shows a photograph of a heat-pressed film of the kneaded product obtained under high discharge conditions. The material obtained by the conventional process has some undispersed cellulose (white dots in the photo), but the material obtained by the improved process has no undispersed cellulose, indicating that the cellulose fibers were well defibrated. Figure 11 shows the relationship between production rate and flexural modulus of CNF resin composite. The improved process has the potential to increase productivity by more than three times while maintaining physical properties, because cellulose is well dispersed even when residence time is shortened. In addition, the yield rate of good products during kneading was improved. We evaluate the basic physical properties and the practical properties of the material as an automotive component. We continue improving physical properties while maintaining high productivity.

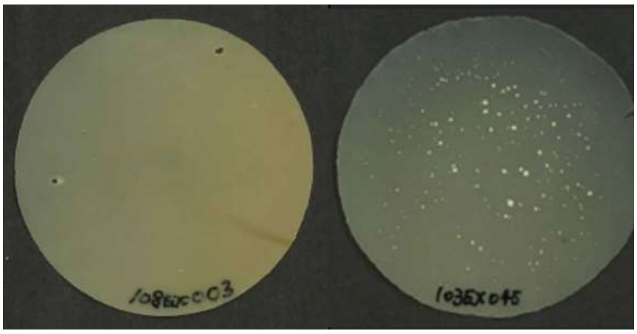

Figure 10. Press films of compound (high discharge condition, left: improved process, right: conventional process).

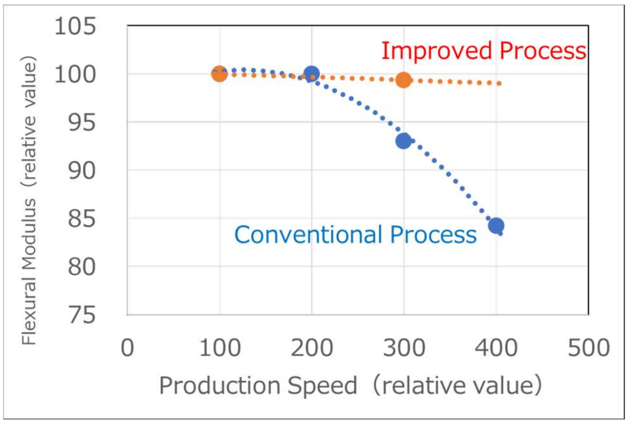

Figure 11. Productivity and flexural property of CNF resin composite (NEDO project results).

6. Conclusion

We have developed the HC series, cellulose microfiber resin composite as structural materials, with improved impact resistance, heat resistance and whiteness. In addition, significant cost reductions can be expected by improving the process. Although CNF has great potential, it has yet to realize its full potential. The cost issue is very significant for the widespread use of this material as an industrial material. We will accelerate development in collaboration with our customers and other related parties and continue to work toward solving issues to contribute to the improvement of environmental and social sustainability through the spread of CNF.

＜References＞

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3) T. Endo, *Japanese journal of paper technology*, **6**, 21-25 (2021).

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Profile

SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Yuya Terao

SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Chief
Tomoaki Yoshimura

SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Manager
Daisuke Kuroki