SPMC Technical Review EN

Application of modified cellulose nanofibers/resin composites ("STARCEL®") to foamed material

SEIKO PMC CORPORATION
Technology Division Takafumi Sekiguchi
Shuhei Yamada
Daisuke Kuroki
Akihiro Sato

1. Introduction

In recent years, technologies for utilizing renewable, sustainable and biodegradable plant biomass have been actively studied to mitigate global warming. Especially, cellulose nanofibers (CNFs), which is a material composed of cellulose microfibrils with nanometer width, is gaining increasing attention because CNF has unique features such as high strength, high elastic modulus, low linear thermal expansion coefficient, and large specific surface area. There are a lot of researches conducted for use in various applications such as thickeners, gas barrier films (for packaging materials), transparent sheets (for optical materials), emulsifiers, and fiber reinforced plastics.

We have been focusing our efforts on development of CNF as a reinforcing material for resins and rubbers, which are expected to be one of the most promising markets for CNF, and developed chemically modified CNF reinforced thermoplastic resin "STARCEL®". By homogeneous incorporation of hydrophobic- modified CNF into resins, CNF reinforced plastics show not only higher strength but also superior heat resistance (difficulty of deformation at high temperature). In the case of foam materials, CNF gives good foamability and less energy loss during deformation. Therefore, it is expected to be applicable to various industries such as automobiles, home appliances, and building materials.

This paper describes the manufacturing method and characteristics of the chemically modified CNF reinforced resin composites STARCEL®, and its application to foamed materials.

2. History

We started the research & development of CNF in 2006 and participated in the NEDO project led by Professor Hiroyuki Yano of Kyoto University in 2007, in which extensive development of high strength resin reinforced with CNF was actively conducted. With gaining the assistance of the Ministry of Economy, Trade and Industry's Innovation Center Establishment assistance program, we built a demonstration facility (pilot plant) of CNF / resin composites at our Ryugasaki Plant (Ibaraki Prefecture) and we started to provide hydrophobic-modified CNF resin composites in 2014. After experiencing further facility expansion, commercial production of STARCEL® started in January 2018. The annual production capacity is 70 metric tons for modified cellulose and 200 metric tons for CNF composite materials. In June 2018, ASICS Corporation launched the world's first running shoes using CNF, in which STARCEL® was used to reinforce foam cells of midsole, sponge-like material of running shoes.

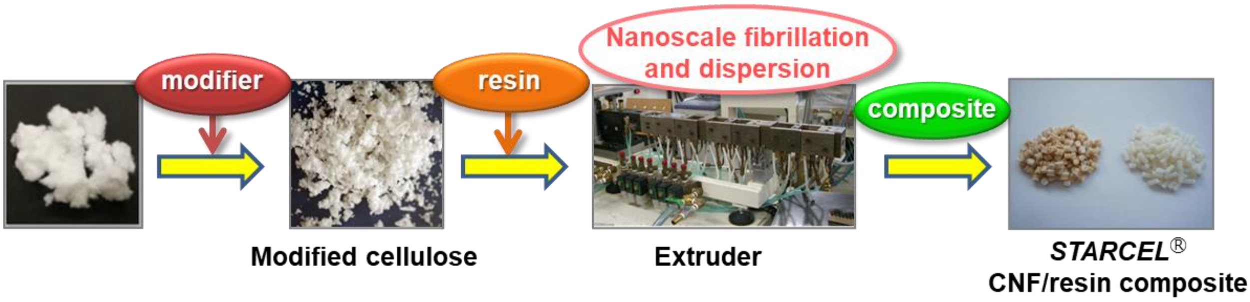


Figure 1. Manufacturing process of modified CNF/resin composite.

3. Manufacturing method

The manufacturing flow of the modified CNF reinforced resin STARCEL® is shown in Figure 1. After hydrophobic-modification of plant fibers such as wood pulp, defibration and nano-dispersion are achieved at the same time by melt-kneading with resin. Most of the currently proposed CNFs are hydrophilic and can be obtained by defibrating and dispersing in water, whereas in our method, hydrophilic plant fibers are preliminarily hydrophobically-modified to impart superior compatibility with hydrophobic resins, thus leading to enhancement of affinity between cellulose fiber and resins. Easy nano-defibration of cellulose and homogeneous dispersion of modified CNF in resins are achieved during kneading process.

When CNF obtained by nano-defibration of cellulose pulp in water is used as a starting material, CNF contains a large amount of water which requires a lot of energy to remove it. On the other hand, direct kneading of hydrophobically-modified pulp with resin is a more efficient and simpler manufacturing process, and it is expected to significantly reduce manufacturing cost of CNF reinforced plastics. Thermoplastic resins having melting point at 200°C. or lower, such as polyethylene (PE) and polypropylene (PP) are mainly employed as matrix resins of STARCEL® to reduce the risk of thermal degradation of cellulose.

4. Characteristics of modified CNF reinforced resin

Scanning Electron Microscope (SEM) observation of residues obtained by removing matrix resin from the modified CNF / resin composites shows that fiber diameter of the modified CNF was about 100 to 500 nm (Figure 2).

Hydrophobically-modified CNF has the following features when it is mixed with thermoplastic resins.

(1) Increase in melt viscosity

(2) Reinforcement of resin molded product

(3) Promotion of crystal orientation

4-1. Increase in melt viscosity

The addition of hydrophobically-modified CNF increases resin viscosity. The results of dynamic viscoelasticity measurements are shown in Figure 3. The hydrophobic-modified CNF/resin composite shows higher complex viscosity compared with base PP at any angular frequency and a large decline of viscosity is observed as shear rate increases, that is shear thinning behavior. The difference between viscosity of CNF containing PP and that of base PP is narrowing as the angular frequency increases. At the shear rate of 1.0×10^3 to 10^6 s^{-1} which is equal to that of resin experiencing at nozzle for injection molding, the viscosities of CNF/PP composite and base PP were almost the same because CNF aligns in the flow direction at higher shear rates.

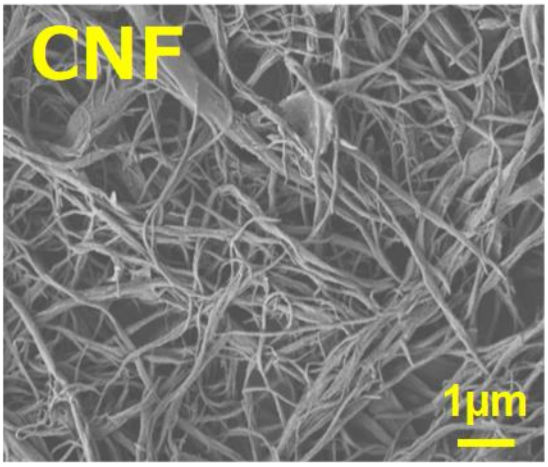


Figure 2. SEM image of CNF in extracted from CNF/resin composite

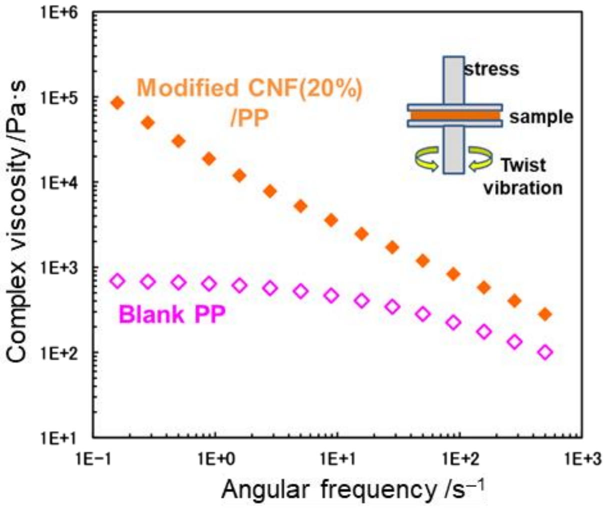


Figure 3. Dynamic viscoelasticity of modified CNF/PP composite

4-2. Reinforcement of resin molded product

Physical characteristics of the injection molded products of hydrophobically-modified CNF reinforced PP are shown in Table 1. As dosage of modified CNF increases, the flexural modulus and flexural strength increase, and the heat deflection under load was improved.

Table1. Physical and mechanical properties of modified CNF/PP composite

	[%]	0	13	25
Density	[g/cm^3]	0.91	0.95	1.00
MFR	[g/10min]	44.7	27.8	12.0
Flexural modulus	[MPa]	1950	2730	3530
Flexural strength	[MPa]	56.4	62.6	67.7
Charpy impact test	[kJ/m^2]	1.9	1.3	1.2
Heat Deflection Temperature	[°C]	116	126	129

4-3. Promotion of crystal orientation

In the case of injection-molded products of high density polyethylene (HDPE) containing hydrophobically-modified CNF, shishi-kebab structure in which stretched chains of PE are oriented in the flow direction as well as CNF and lamellar structure of PE are formed around them[1]. In addition, it is confirmed from retardation values that PE is oriented in the injection direction by adding modified CNF (Figure 4)[2].

5. Characteristics of modified CNF / resin foam

CNF can impart various features to foamed materials. During foaming process, following three key steps were involved.: (1) generation of bubble nuclei, (2) elongation of the bubble wall and expansion of the bubble, (3) retention of the bubble wall structure. Detailed studies of physical foaming using nitrogen gas as a foaming agent [3, 4, 5] were conducted to clarify the roles of CNF. Physical foaming is a method in which a gas (nitrogen, carbon dioxide, butene, etc.) is dissolved in a resin under high pressure, and then pressure is quickly reduced to enhance the bubble nucleation.

5-1. Generation of bubble nuclei

Modified CNF increases the number of bubble nuclei generated in the PP matrix. Flash DSC analysis reveals that modified CNF containing composite shows higher crystallization temperature compared with base PP[3],

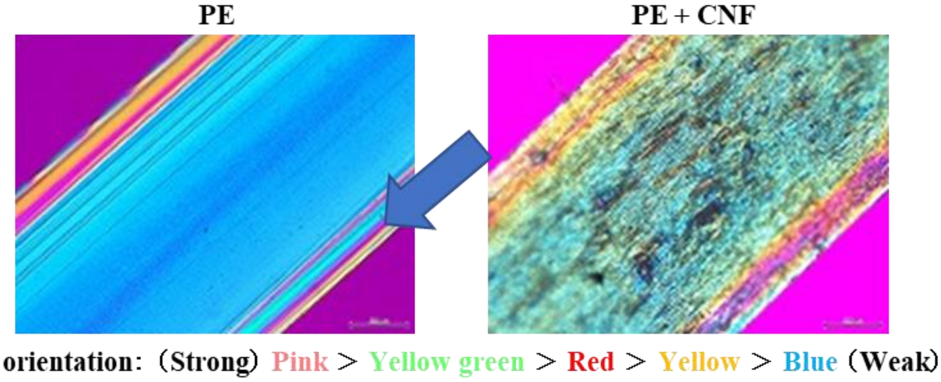


Figure 4. Crystal orientation of PE promoted by modified CNF

which indicates that CNF works as an effective crystal nucleating agent. In physical foaming using nitrogen gas, uniformly and highly dissolved nitrogen gas in PP matrix reached supersaturated at PP - PP crystals interface and PP crystal–CNF interface during cooling process, and generates foams. Therefore, it can be seen that CNF can function not only as crystal nucleating agent but also as a nucleating agent of foams.

5-2. Expansion of bubbles

CNF increases the complex viscosity of the resin shown in Figure 3, thus leading to suppression of bubble coalescence and rupture. 5% of CNF enabled formation of PP foams with 18 times expansion ratio by core-back physical foaming using nitrogen gas.

5-3. Morphology and crystalline microstructure of cell wall

Figure 5 shows that cell walls are highly deformed and oriented along the core-back direction and CNF are uniformly distributed in PP matrix. Close inspection of the interfacial area reveals that regularly aligned lamellae (kebab) are attached to the CNF surface, indicating the formation of hybrid shishi-kebab in cell wall.

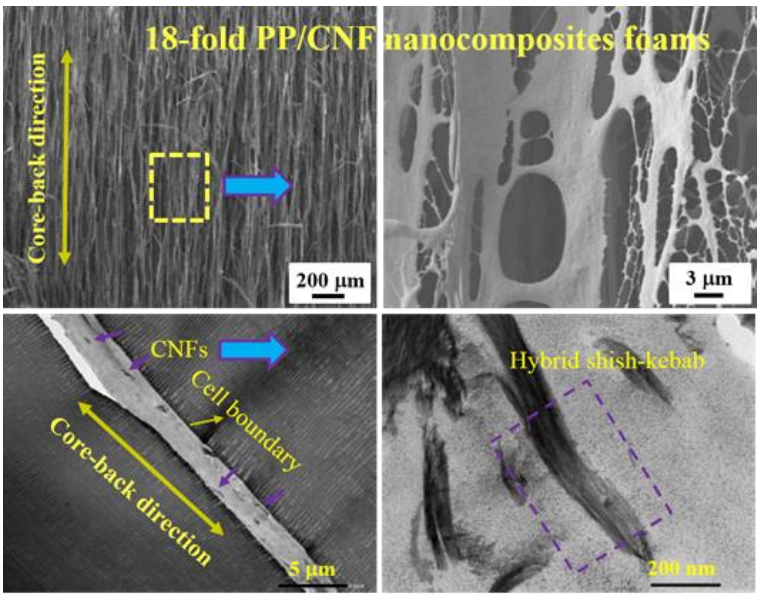


Figure 5. TEM image of PP foam containing modified CNF

6. Characteristics of foam

Physical properties of foam materials of modified CNF / L-LDPE composites obtained by chemical blowing were evaluated. Chemical blowing was carried out as follow. Chemical blowing agent (CBA), blowing aid, and cross-linking agent were mixed with L-LDPE and the mixture was sealed in the mold in molten state above decomposition temperature of CBA until most CBA decomposed. Upon release of pressure to atmospheric pressure, nucleated bubbles grew to their ultimate size.

Foams having different expansion ratios were prepared by adjusting the amount of CBA, foaming aid, and cross-linking agent. The higher expansion ratio means the lower specific density of foam materials. Figure 6 shows that the tensile stress of foam materials having various expansion ratios at 50% of elongation.

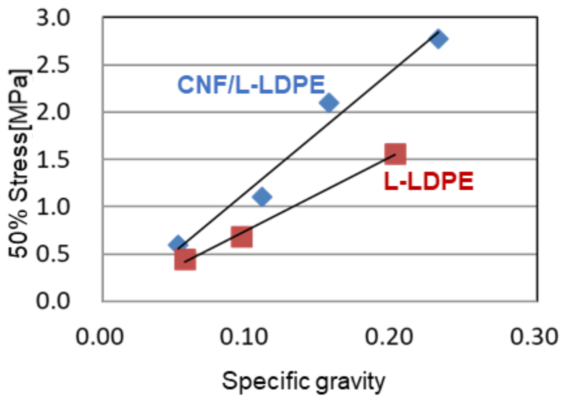
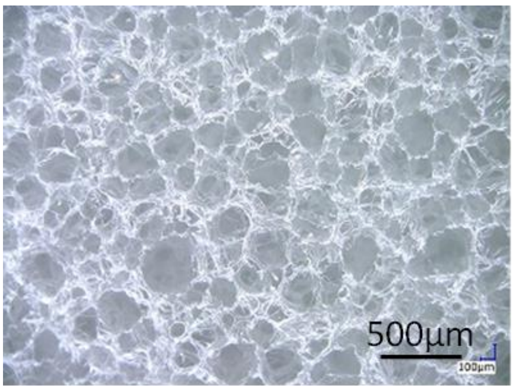


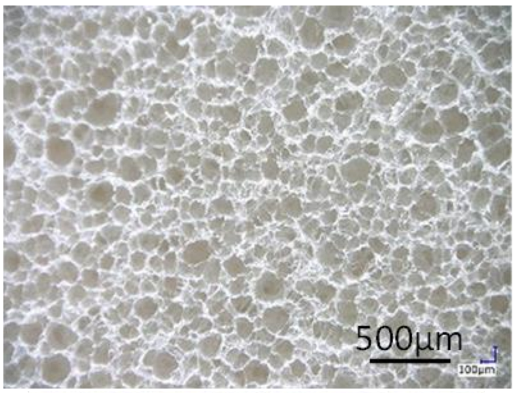
Figure 6. Tensile strength of L-LDPE foams

Comparison of tensile strength of foams at the same specific gravity shows that CNF reinforced composites gives foams with more superior strength than base resin.

Observation of cross sections of foam materials shows that bubble diameters of CNF reinforced foam material are fairly smaller than that of base resin at about the same specific gravity (Figure. 7), which is probably attributed to formation of bubbles with smaller diameters and reinforced wall by CNF. To evaluate cushioning properties of foam materials, we conducted that compression set testing under low load (Figure. 8). The foam was compressed at 0.6 MPa for 24 hours and the recovery was measured after the pressure was just after released and 30 minutes later. The foam containing 6% of modified CNF shows superior recovery compared with base L-LDPE. Figure 9 shows the result of observation of the bubble walls after compression set testing. A rupture is found in the cell wall of base L-LDPE foam, whereas no rupture is detected in the case of CNF containing foam materials. Reinforced cell wall by CNF can improve the durability of the bubbles, thus resulting in highly elastic and highly durable foam.



L-LDPE, specific gravity 0.0096



Modified CNF/L-LPDE, specific gravity 0.110

Figure 7. Sectional view of L-LDPE foams.

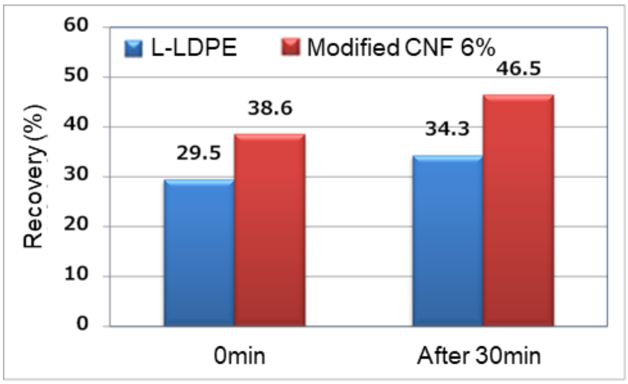


Figure 8. Compression set evaluation result of L-LDPE foam containing modified CNF

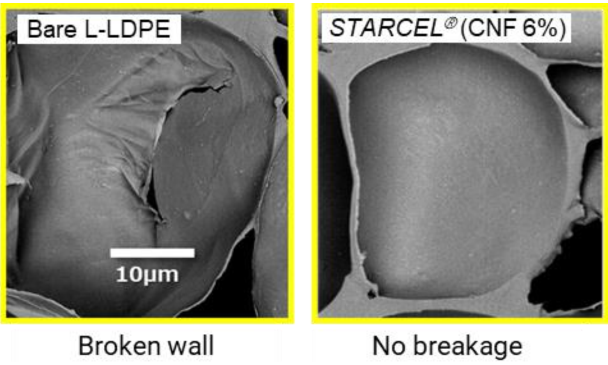


Figure 9. SEM image of cell wall after compression set test

7. Conclusion

The addition of CNF greatly improves cellular structure of PP and L-LDPE, giving smaller cell sizes, higher cell densities, higher strength and superior toughness. These facts reveal that CNF has the following three unique features, encouraging formation of bubble nuclei, suppressing growth of bubbles and reinforcing cell walls. These effects of CNF enable to manufacture light-weighted foam materials with superior strength. Therefore, the hydrophobically-modified CNF/resin composites are considered to be useful and promising as an additive for foaming.

＜References＞

1) A. Sato, H. Sano, H. Yano et al. : *Polymer Preprints, Japan*, **61** (2), 5411 (2012).

2) D. Kuroki, *Journal of the Imaging Society of Japan*, **55**(3), 97 (2016).

3) L. Wang, S. Ishihara, Y. Hikima, M. Ohshima, H. Yano et al.: *Composites Part A: Applied Science and Manufacturing*, **98** (1), 166 (2017).

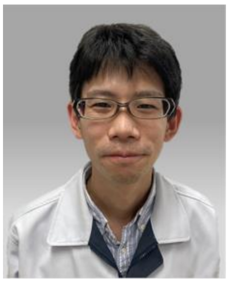
4) L. Wang, S. Ishihara, Y. Hikima, M. Ohshima, H. Yano et al.: *ACS Applied Materials and Interfaces*, **9**(11), 9250 (2017).

5) L. Wang, Y. Hikima, M. Ohshima, H. Yano et al.: *RSC ADVANCES*, **8**(28), 15405 (2018).

Some of the content mentioned in this paper includes the results of the 2009-24 NEDO Green Sustainable Chemical Process (GSC) Basic Technology Development Project. It also includes the results of the JST Strategic Creative Research Promotion Project Advanced Low Carbon Technology Development (ALCA), which has been ongoing since FY2015.

Profile

SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Chief
Takafumi Sekiguchi



SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Shuhei Yamada

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

SEIKO PMC CORPORATION
Technology Division
CNF Business Promotion Department
Director
Akihiro Sato