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DEVELOPMENTS OF MANUFACTURING TECHNIQUES AND APPLICATIONS OF CELLULOSE NANOFIBRE

Haruo Konno[1], Takeshi Fujii[1], Kazuhiko Ishizuka[2] and Masayuki Kawasaki[1]

[1] Cellulose Nanofiber Research Laboratory, Nippon Paper Industries, Co., Ltd.
[2] NPI Research Laboratory, Nippon Paper Industries, Co., Ltd.

1 INTRODUCTION

Nippon Paper industries has been developing Cellulose Nanofibre (CNF) products prepared by the fibrillation of chemically modified pulp since 2007.

In November 2013 we started to operate a pre-commercial plant in order to provide CNF for the collaborators, potential users and internal use, after 5 years of fundamental research together with our collaborators with the aim of commercialization of products using CNF. In our pre-commercial plant, mainly TEMPO oxidized CNF is produced, a process developed by the research group of Prof. A. Isogai at The University of Tokyo [1], [2], [3]. In addition to TEMPO oxidation, other chemical modifications such as carboxymethylation are carried out in our plant as well. Thus collaborators can choose the type of CNF samples, depending on their target applications.

In 2016, NPI announced the plan to install a CNF full-scale production facilities at the Ishinomaki Mill and the Gotsu Mill in Japan. At the Ishinomaki Mill, CNF prepared by TEMPO oxidation will be produced, and at the Gotsu Mill, CNF prepared by carboxymethylation will be produced.

In this brief paper we will present our developments of manufacturing techniques and applications of chemically modified CNF.

2 EXPERIMENTAL SECTION

2.1 Materials

Softwood bleached kraft pulps produced at six different Nippon Paper Industries (NPI) mills were used as raw material for CNF with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) oxidation as pre-treatment. TEMPO, NaBr, 12%NaClO solution and other chemicals used for TEMPO oxidation were of reagent grade and used without further purification.

2.2 TEMPO oxidation and nanofibrillation

The addition amount of the chemicals to pulp was similar to what has been described in the literature [1]. 500 g of pulp was suspended in 50L of ion exchanged water together with TEMPO and NaBr. The TEMPO oxidation reaction was started by adding 12% NaClO solution to the pulp suspension. During the reaction, 3M NaOH solution was added to the pulp suspension to maintain pH 10.5 in the suspension. The TEMPO oxidation reaction was completed after 3 hours, followed by repeated washing of the oxidized pulp with ion exchanged water several times to remove TEMPO and other salts such as NaCl. As the next step, the TEMPO oxidized pulp was suspended in ion exchanged water resulting in a suspension of 1 wt% concentration. This suspension of TEMPO oxidized pulp was defibrillated mechanically to CNF, where the mechanical defibrillation was conducted under the same condition for all the experiments.

2.3 Analysis

The carboxyl group contents (mmol/g) of original pulps and TEMPO oxidized pulps were determined by electric conductivity titration [1]. Fibre lengths of the different pulps were measured using the Fiber Tester (Lorentzen & Wettre). Transmittances of the CNF aqueous slurries (at 1 wt%) were measured using a UV-Vis spectrometer (UV-1800, Shimazu) at the wavelength of 600 nm. The transmittance of a CNF aqueous slurry is used as a measure of the degree of nanofibrillation. A higher transmittance value is thus considered to correlate to a higher degree of nanofibrillation.

Furthermore, the viscosity of the CNF aqueous slurries were measured using a Brookfield viscometer (DV-I Prime, Brookfield). The viscosity of a CNF aqueous slurry depends on its degree of nanofibrillation and fibre length, where increased viscosity is interpreted as a higher degree of nanofibrillation and longer fibre length in general. Finally, fibre lengths of the CNF were estimated from images obtained using an Atomic Force Microscope (AFM; Nanocute, SII). For each sample 50 fibres were measured.

2.4 CNF coated paper

CNF aqueous slurries was used to coat on uncoated paper, having a basis weight of 45 g/m^2. The coating was carried out with a laboratory bar coater equipped with a Meyer rod. The coating weights were in the range of 0.01 to 0.3 g/m^2 by adjusting the concentrations of CNF. Poly vinyl alcohol (PVA; Poval-117, Kuraray) and Hydroxyethyl Starch (HES; Ethylex 2035, Tate & Lyle, Inc) were used as reference coating materials. After coating, the CNF coated paper was dried on cylinder dryer under unrestrained condition. Finally, air resistance (Oken method) and the oil drop absorbency of the coated paper samples were measured.

3 RESULTS AND DISCUSSION

3.1 Effect of raw material pulps on the properties of TEMPO oxidized pulp

Figure 1 shows the carboxyl group contents of original pulps and the TEMPO oxidized pulps. The carboxyl group contents in the original pulps were in the range of 0.08 to 0.14 mmol/g, and after TEMPO oxidation, the carboxyl group

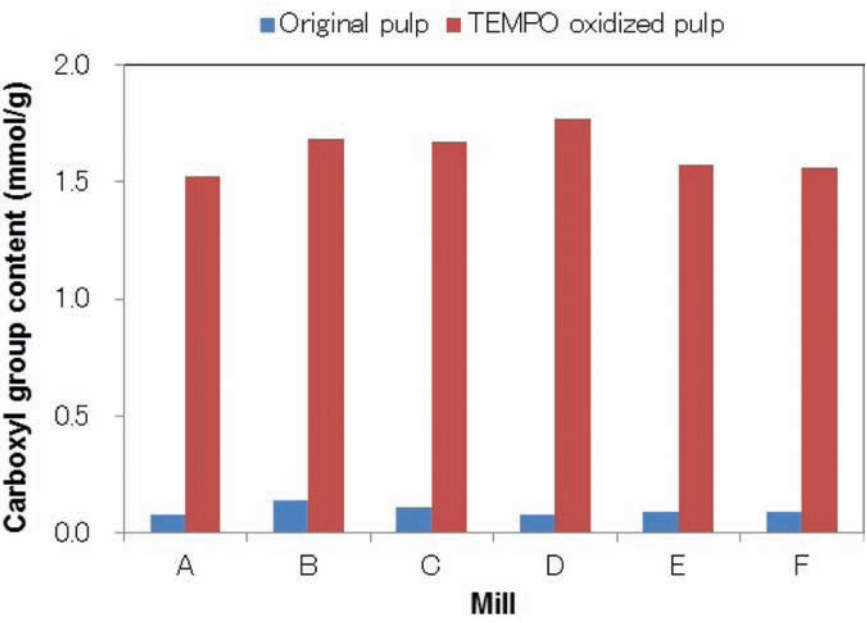

Figure 1. Carboxyl content of original pulp and TEMPO oxidized pulp.

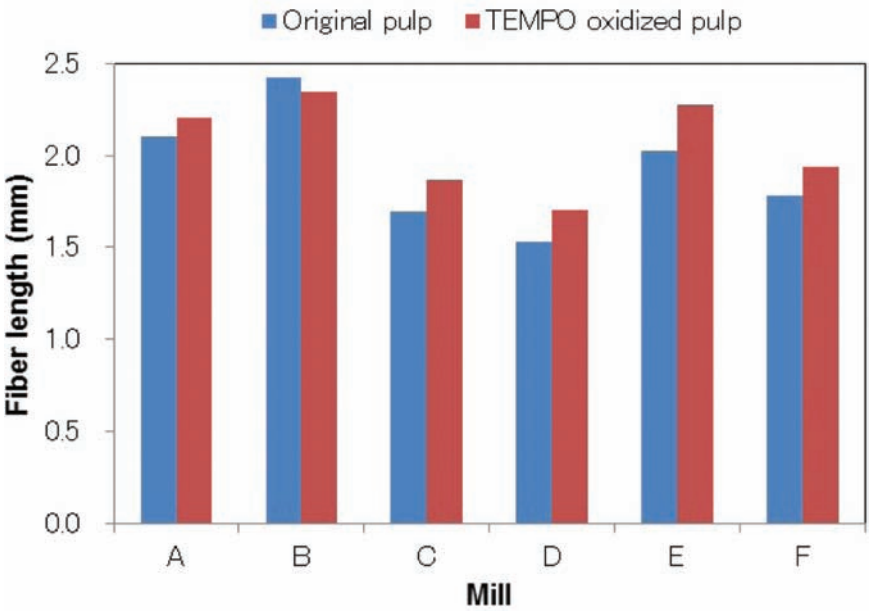

Figure 2. Fibre lengths of original pulp and TEMPO oxidized pulp.

contents in the pulps increased to being in the range of 1.52 to 1.77 mmol/g. The result shows that under similar reaction conditions, the carboxyl group contents of the oxidized pulps did not differ significantly. The average fibre lengths of the TEMPO oxidized pulps were around 2 mm, almost the same as the lengths of the original pulps, which can be seen in Figure 2. Given these results the conclusion is that the degree of TEMPO oxidation used in these experiments does not affect the fibre lengths of oxidized pulps significantly.

3.2 Effect raw material pulps on the properties of CNF

Figure 3 shows the transmittances of the obtained CNF aqueous slurries. The transmittances of the five CNF aqueous slurries were around 90%. Only the pulp produced at mill C shows a reduced transmittance. There was no large difference in the sugar compositions of the original pulps. Although the reason for the difference in the transmittances is not obvious, we hypothesize that the crystallinity and the micro-structure of a pulp affects the efficiency of the pre-treatment and defibrillation process.

With respect to CNF suspension rheology, the Brookfield viscosities of the CNF slurries varied significantly as shown in Figure 4. In this figure, the fibre lengths of CNFs are also plotted, and there seems to be a strong correlation

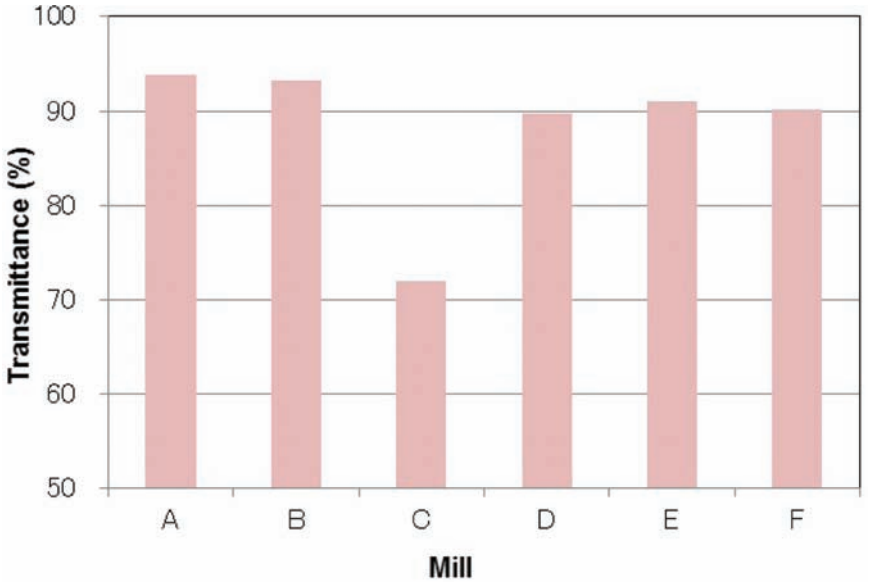

Figure 3. Transmittance of TEMPO oxidized CNF aqueous slurries.

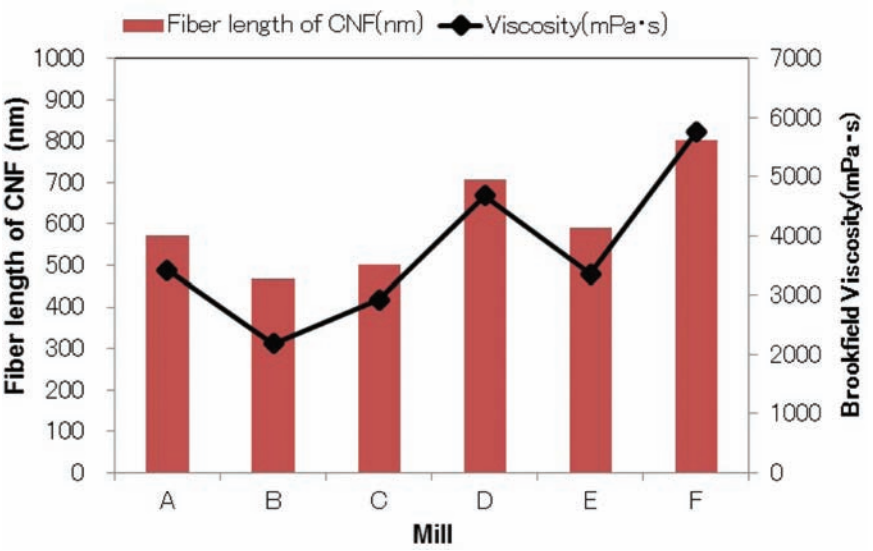

Figure 4. Fibre length of TEMPO oxidized CNF and the viscosity of corresponding CNF slurries.

between the CNF fibre length and the viscosities of the slurries. From our experiments, it is clear that we can obtain CNF slurries with different viscosities at a given concentration by choosing appropriate raw material pulps.

3.3 TEMPO oxidized CNF coated paper

There are many prospective applications of CNF. In this presentation, the application for paper will be pursued. A CNF aqueous slurry can be coated on paper substrates by appropriate dilution using various coating methods such as RMSP, air-knife coating, and spray coating. The reason why the CNF slurry can be coated on paper is attributed to its shear-thinning [4], which means that fluids show high viscosity at low shear rate and low viscosity at high shear rate. A CNF aqueous slurry can thus be coated onto the paper with a suitable coating applicator, since the viscosity of the CNF aqueous slurry is low under the high shear rate conditions during coating. Immediately after coating, the CNF remains on the surface of the paper and does not penetrate into the paper, since the viscosity of the CNF becomes very high at low shear rate.

Figure 5 shows the value of air resistance of CNF coated paper samples against the coating weight. In the very low coating weight region, CNF increased the air

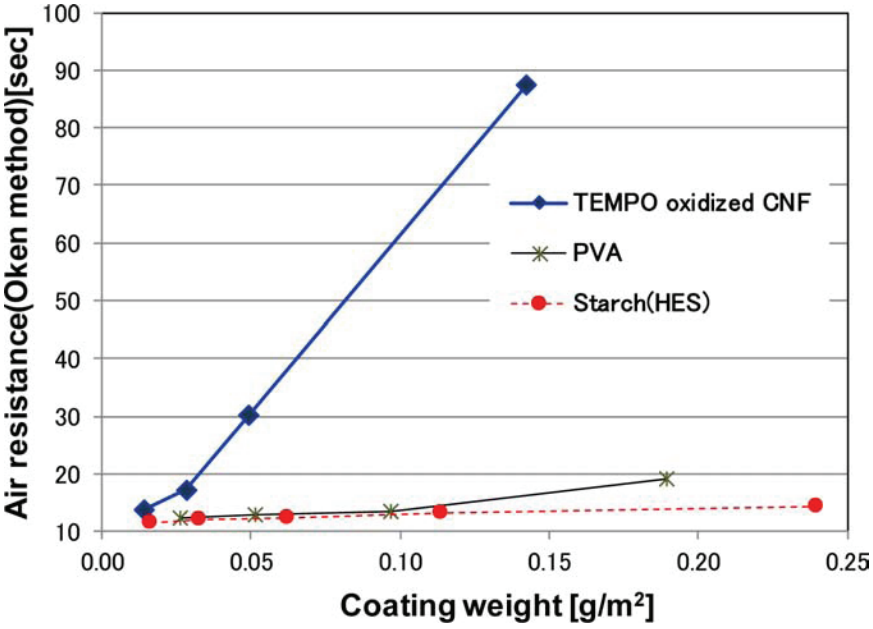

Figure 5. Plot of air resistance of coated paper against coating weight.

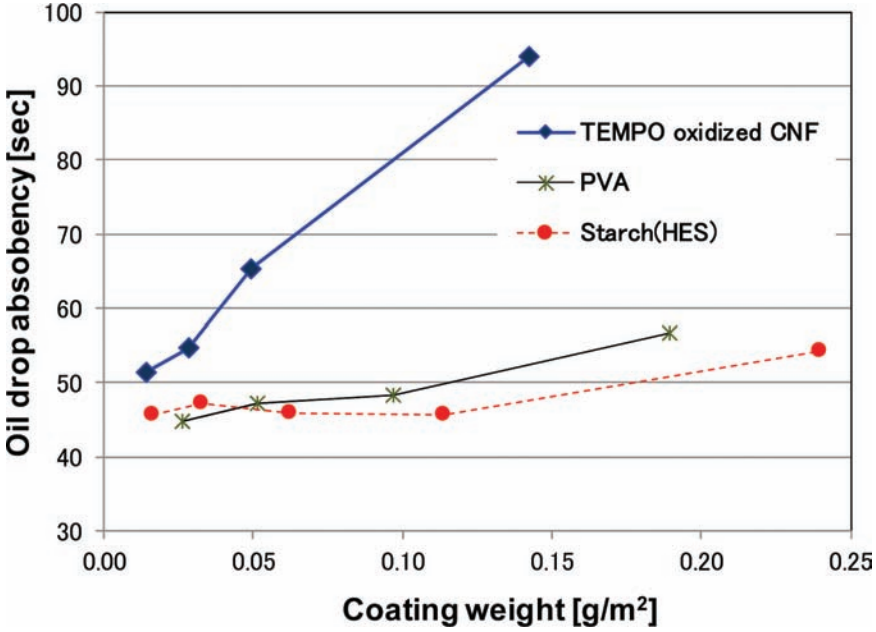

Figure 6. Plot of the oil drop absorbency of coated paper against coating weight.

resistance of the paper significantly compared to PVA and HES, which are conventional paper chemicals. Furthermore, CNF has hydrophilic properties such that the CNF coated paper samples show high oil drop absorbency, which means low oil absorbency. In Figure 6, the oil drop absorbency against the coating weight is also shown. The results show that oil drop absorbency increased significantly compared with PVA and HES at a given coating weight of the coated paper samples. Thus, we have shown that CNF has unique properties with respect to air and oil barrier, specifically in the low coating weight region.

4. CONCLUSIONS

- From our experiments, viscosities of CNF slurries were strongly correlated to the fibre lengths of CNF.
- We have shown that CNF slurries with different viscosities at the same concentration can be obtained by choosing appropriate raw material pulps.
- We have found that CNF had unique properties of air and oil barrier especially in the low coating weight region and we anticipate that good air and oil barrier paper with CNF will be achieved.

5. LITERATURE

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Transcription of Discussion

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Wolfgang Bauer Graz University of Technology

Is your TEMPO-oxidated CNF FDA approved for food contact?

Haruo Konno Nippon Paper Industries, Co., Ltd.

No, not yet.

Wolfgang Bauer

Do you think that tempo-oxidated CNF will be approved in the future?

Haruo Konno

In the future. I think the applications for food will be for dietary fibre.

Jean-Claude Roux Grenoble Institute of Technology

You have chemical pretreatment of the pulp, but you have not said very much on the transformation between TEMPO-oxidized pulp and TEMPO-oxidized CNF. Can you comment on it please?

Discussion

Haruo Konno

So, you mean the differences over the chemical treatment?

Jean-Claude Roux

No, I mean you have given details of chemical treatment to get TEMPO-oxidized pulp, but later you have said it was a mechanical device in order to get TEMPO-oxidized CNF. Can you comment on the mechanical treatment?

Haruo Konno

Actually, we cannot disclose it.

Jean-Claude Roux

Thank you very much for your answer.

Haruo Konno

The process is very confidential.

Gil Garnier Monash University

Good presentation. What is the effect of lignin on the process, if any?

Haruo Konno

We used fully bleached kraft pulp. The primary hydroxyl group in lignin is oxidized by TEMPO, so we don't want to use TEMPO on the unbleached pulp.

Gil Garnier

So, processwise, do the optimum pulping conditions to get good fibres for paper making produce the optimum pulp to produce nanofibers?

Haruo Konno

Yes.

Gil Garnier

So, you use the same process and pulp; you don't modify the pulping process?

Haruo Konno

Yes.

Gil Garnier

But is it the best? Or is it optimized for nanocellulose?

Haruo Konno

In the mill, we have produced quite a lot of pulp. The only way to get the pulp is for papers at this moment.

Gil Garnier

Unless the value of your nanocellulose is higher than the value of your paper, which you can achieve with your diapers.

Haruo Konno

At this moment we use pulp for papers, but we can produce cellulose nanofibres. This might change in the future.

Gil Garnier

So, in this case, why is the pulp for Mill C worse in terms of transmittance?

Haruo Konno

I don't know, but it doesn't matter. We have five other fibres we can use.

Harshad Pande Domtar Inc

Do you think we can use the size press to apply the nanofibrils?

Haruo Konno

Yes. We can apply nanofibres at the size press.

Harshad Pande

For this one you use the size press?

Discussion

Haruo Konno

In this experiment, we did not. In other experiments, we use the size press. It can be used because of thixotropy.

Harshad Pande

And you coated one side?

Haruo Konno

Yes.