Abstract

Cellulose nanofibers (CNFs) are generally produced in the form of aqueous dispersion at low concentrations, and it would lead to issues including the high cost of transportation and the high risk of decomposition by bacterial contamination. Therefore, manufacturing dried CNFs is essential for expanding the market of CNFs. In the process of drying, CNFs strongly aggregate and the formed hydrogen bonding inhibits re-dispersion of CNFs in water. Consequently, reduced are resulting characteristics of CNFs, such as high transparency and high viscosity. The prevention of the aggregation in a drying process is the key to the preparation of dried CNFs.

In this paper, we report a preparation of dried CNFs that can be easily re-dispersed in water. The key to the preparation of dried CNFs was the selection of chemically modified CNFs and water-soluble polymers for CNF suspensions. The dried CNFs were easily dispersed in water and their transparency and viscosities were not deteriorated even through the drying process. These CNF materials will be provided in powder form with good handling.

Keywords: CNF, drying process, re-dispersion
prevention of the aggregation in the drying process is the key preparing dried CNF materials. In this paper, we report the preparation of dried CNF materials that can be easily re-dispersed in water. The key to prepare dried CNF materials was the selection of chemically modified CNFs and water-soluble polymers for CNF dispersions. The dried CNF materials were easily dispersed in water and their transparency and viscosities did not deteriorate even through drying process. These CNF materials will be provided in powder form with good handling.

2. Experiment

2.1 Production of carboxymethylated pulp

Softwood bleached kraft pulp (NBKP) for papermaking that was supplied by Nippon Paper Industries, Co., Ltd. was carboxymethylated in alkali condition with the addition of sodium monochloro-acetate. Degree of substitution (DS) of carboxymethylated pulp (CM-pulp) was adjusted at 0.3 so that it does not dissolve in water.

2.2 Production of carboxymethylated cellulose nanofiber

Carboxymethylated pulp obtained by the method described in the 2.1 section was dispersed in water approximately at 1% consistency and disintegrated by passing 5 times through the high-pressure disperser under the pressure of 150 MPa to manufacture the suspension of carboxymethylated cellulose nanofiber.

2.3 Measurement of physical properties

(1) Transparency

Transmittance of CNF suspension (1%) was measured by spectrophotometer (UV 1800, SHIMADZU) at the wavelength of 660 nm. CNF particles that are typically 3-4 nm wide and at least several microns in length are too small to scatter much light of such wavelength. When the particles are of the order of several hundred nm units in diameter, the light beam is scattered or diffracted. Thus perfectly dispersed CNF in nano-scale is expected to show a high transmittance ratio of the incident light while agglomerated CNF shows a low transmittance ratio. As such when more CNF disperses in nano-scale, the transmittance of the CNF suspension increases. Thus the transmittance of the CNF dispersion was used as an index of the content of nano-materials.

(2) Measurement of zeta potential

0.1% consistency carboxymethylated CNF dispersion in water was titrated with 0.05 N sodium hydroxide solution to control pH in the range of 6.5-12. Zeta potential was measured using a commercially available instrument “Malvern ZetaSizer, NanoZS”.

(3) Addition of water-soluble polymer

Carboxymethylated CNF was dispersed in water with the addition of carboxymethylated cellulose (CMC) of different molecular weight and degree of substitution (DS). CMC was supplied by Nippon Paper Industries Co., Ltd.

2.4 Drying of carboxymethylated CNF

Carboxymethylated CNF water dispersion was spread out uniformly in a teflon vat and dried with 105℃ hot air blowing from a ventilator until the weight becomes constant. Dried film was fined down with a pulverizer to produce powdery carboxymethylated CNF.

2.5 Re-dispersing of once-dried carboxymethylated CNF

Powdery carboxymethylated CNF was diluted with water to 1% consistency and re-dispersed using Homodisperser (2.5 type, PRIMIX Corporation) at 1,500 rpm for 30 minutes to prepare re-dispersed carboxymethylated CNF after drying.

2.6 Characterization of re-dispersed carboxymethylated CNF after drying

(1) Transmittance recovery ratio

Transmittance was measured in accordance with the same method described in the section 2.3 and the transmittance of the carboxymethylated CNF water dispersion was compared between once-dried and never-dried samples.

The ratio of \[
\left(\frac{\text{transmittance of once-dried}}{\text{transmittance of never-dried}}\right) \times 100
\]

which indicated effects of drying, was defined as transmittance recovery ratio.

(2) Microscopic observation

Carboxymethylated CNF water dispersion was added
with a few drops of India ink and stirred by VORTEX Mixer (Scientific Industries Inc.) prior to the microscopic observation. A sample was placed on a slide glass, covered with a cover glass and observed with a microscope (KH-8700, HIROX).

3. Results and Discussion

3.1 Dispersability and dispersion stability of carboxymethylated pulp

Mechanical processes, such as high-pressure homogenizers and grinders, have generally been used to extract cellulose fibrils from pulps, resulting in CNF\(^1\). To facilitate the separation of cellulose microfibrils into thinner CNF, chemical pretreatment steps can be applied that effectively weaken the interfibrillar hydrogen bonds. Imparting a charge to the microfibril surface of materials improves the interfibrillar electrostatic repulsive forces. This can be achieved either through oxidation (usually employing TEMPO-mediated oxidation) or adsorption of charged polyelectrolytes (e.g. carboxymethyl cellulose treatment or esterification)\(^2\). Carboxymethylated pulp that was used as a raw material to produce carboxymethylated CNF had a higher zeta potential than untreated pulp, and dispersed uniformly in water without forming large flocs. This was due to the effective disintegration of cellulose microfibers into nano-cellulose fibers (Fig. 2).

3.2 Dispersability and dispersion stability of once-dried carboxymethylated CNF

Fig. 3 compares the transparency between the dispersions of never-dried and once-dried carboxymethylated CNF. The recovery ratio of transmittance was high at 93%, which indicated that drying did not significantly affect re-dispersing capability of once-dried carboxymethylated CNF. Dispersability and dispersion stability of once-dried carboxymethylated CNF was attributed to the strong anionic charge of carboxymethyl groups introduced onto the surface which prevented agglomeration by weakened hydrogen bonding and van der Waals force. Water penetration into carboxymethylated CNF was improved by increased hydrophilicity of carboxymethyl functional groups. India ink that was added to enhance the microscopic observation confirmed the uniform dispersability of never-dried carboxymethylated CNF as shown in the left hand side image in Fig. 4. The right hand side image shows black and white patches by mottled effects. White patches were estimated to be small-size agglomerates of once-dried carboxymethylated CNF, into which small water molecule (in the order of Angstrom) penetrated but large carbon black particles in India ink (average diameter 220 nm) did not. These flocs were not observed in the left hand side image of never-dried carboxymethylated CNF.

3.3 Effect of pH changes

Zeta potential of carboxymethylated CNF water dispersion was dependent on pH and was maximized at pH 9, where the electrostatic repulsive forces became the largest (Fig. 5). Dispersability of dried carboxymethylated CNF at pH 9 was better than that at pH 6.5.
amount of aggregates decreased and the recovery ratio of transmittance improved from 93% to 98% (Fig. 6).

3.4 Effect of CMC addition

For applying more anionic charge to the surface of carboxymethylated CNF to enhance repulsive forces and make uniform water dispersion, various CMCs of different molecular weight and DS were added prior to the drying process. Anionic charge of never-dried carboxymethylated CNF water dispersion increased to about −70 mV with the increasing molecular weight and DS of CMC. In general, when aqueous dispersions of CNFs are directly dried, CNFs are tightly aggregated to one another during water evaporation, forming numerous hydrogen bonding. CMC molecules are expected to prevent hydrogen bonding by its steric hindrance, increase repulsive forces by applying anionic surface charge and accelerate water penetration into CNF powders by CMC’s hydrophilic nature. Fig. 8 shows microscopic observations of carboxymethylated CNF water dispersion with the addition of CMC and India ink. Once-dried CNF dispersed in water without aggregates so uniformly that transmittance recovery ratio was 100%. It exhibited the same functions as never-dried CNF such as thixotropic nature and successfully stabilized the calcium carbonate.
suspension (Fig. 9).

4. Conclusion

To prevent CNF aggregation during water evaporation, we found several methods that were effective to uniformly disperse powdery CNF in water including chemical modification of raw-material pulp, pH control and addition of CMC with optimum molecular weight and DS. The produced CNF materials will be provided in powder form with good handling, water penetration capability and excellent dispersability. Transmittance and viscosity measurements of CNF dispersions were not good enough to evaluate the uniformity of once-dried CNF water dispersion. Our methods using India ink were able to more accurately characterize once-dried CNF. I hope that the new production technology we have developed to manufacture powdery carboxymethylated CNF expand applications and accelerate commercialization.

References