Application News

No. T155

Thermal Analysis

Thermogravimetry (TG) of Cellulose Nanofibers

Because cellulose nanofibers (CNF) are a type of plant-derived carbon-neutral material, CNF has attracted considerable interest for carbon dioxide (CO_2) reduction as a global warming countermeasure, and research and development are progressing. CNF is a fibrous material which is extracted from cellulose, a principal component of plants, and has numerous advantages, including light weight, high strength, and a high elastic modulus. Application to automotive components is expected, as CNF weighs only 1/5 as much as steel and is 5 times stronger. However, thermal stability is one issue for the development of applications for CNF. In this article, the thermal stability of CNF was studied by thermogravimetry (TG).

A. Naganishi

Samples

Six types of samples were used in the measurements, as follows:

(1) Pulp-derived cellulose nanofibers

Three types of BiNFi-s™ (Sugino Machine Limited) with different fiber lengths (standard, extra-long, extra-short)

(2) Non-pulp-derived cellulose nanofibers

Nano-fibrillated bacterial cellulose (NFBC)

Carboxymethylcellulose (CMC)

TEMPO-oxidized CNF

Sample Preparation

CNF samples dispersed in water were dried by heat-treatment at 80 °C for 8 h. Discoloration due to drying was observed in the TEMPO-oxidized CNF and NFBC (Fig. 1).

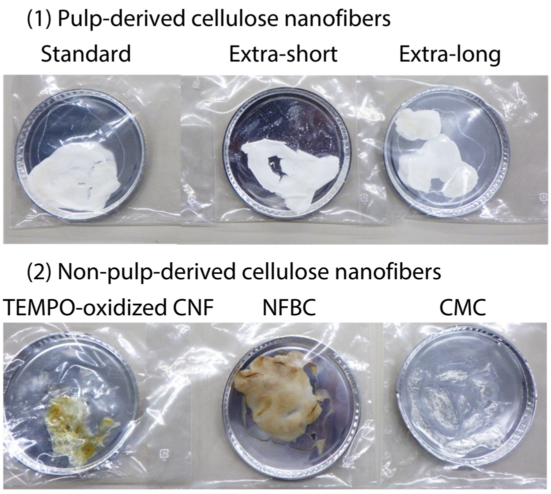

Fig. 1 Samples After Drying at 80 °C × 8 h

(1)-1 TG of Pulp-Derived CNF

Thermogravimetry (TG) of the three types of pulp-derived CNF with different fiber lengths was conducted (Fig. 2). Although the samples were heated in a macrocell with a height of 5 mm, which is deeper than the normal cell (1.5 mm), they overflowed from the cells due to expansion. Therefore, a cover in which holes were made to secure gas ventilation was used as a drop lid. The samples were still not completely dried after heat treatment at 80 °C for 8 h, and a weight reduction that was regarded as evaporation of water continued until around 200 °C, after which decomposition of the CNF began from around 250 °C.

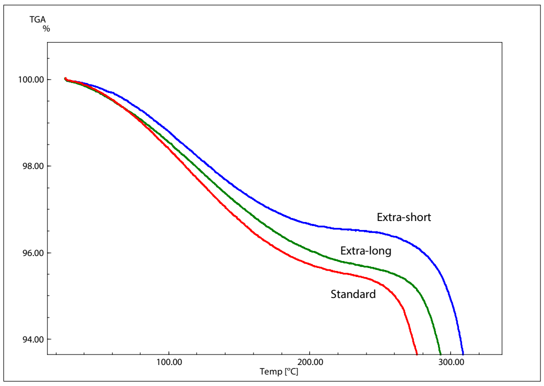

Fig. 2 TG Curves of Pulp-Derived CNF Dried at 80 °C × 8 h

Next, after additional drying at 80 °C for 2 h for water removal, TG was conducted (Fig. 3). Even after water removal, weight reduction occurred in two stages, suggesting that volatile substances exist or decomposition occurs at low temperature. The temperature for achieving a 5% weight reduction from the weight at 100 °C was 285 °C with the standard CNF, 304 °C with the extra-long CNF, and 312 °C with the extra-short CNF. Thus, a difference in the decomposition temperature depending on the fiber length was observed. The decomposition temperature increased, indicating higher thermal stability, in the order of standard -> extra-long -> extra-short.

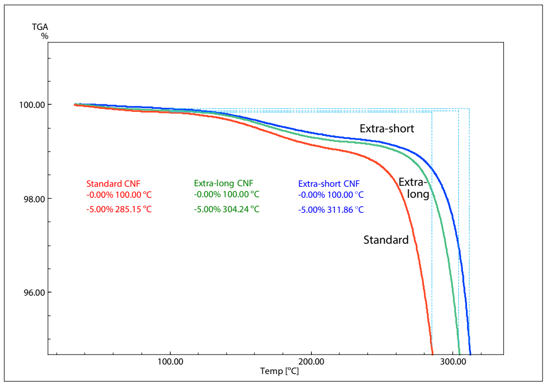

Fig. 3 TG Curves of Pulp-Derived CNF with Additional Drying

(1)-2 Comparison of Pulp-Derived CNF and 97% Pure Cellulose Powder

The TG curves of the pulp-derived extra-long CNF in Fig. 3 and cellulose powder with purity of 97% or higher were compared (Fig. 4). Weight reduction of the extra-long CNF occurred in two stages, from around 140 °C and around 260 °C. The temperature for weight reduction (decomposition) in the second stage seen on the high temperature side was substantially identical with the temperature for weight reduction (decomposition) of the cellulose powder, suggesting that the first-stage weight reduction was caused by a substance other than cellulose.

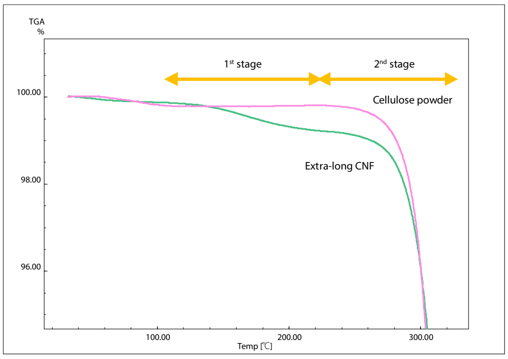

Fig. 4 TG Curves of Pulp-Derived CNF (Extra-Long) with Additional Drying and Cellulose Powder

(2) TG of Non-Pulp-Derived CNF

As could be seen in Fig. 1, discoloration of the TEMPO-oxidized CNF and NFBC occurred when the samples were dried after heat treatment at 80 °C for 8 h, indicating the possibility that thermal degradation had already occurred. When TG was conducted, residual water was vaporized during heating, and decomposition of the CNF began before weight reduction was substantially completed (Fig. 5).

In addition, differences in the temperature and decomposition behavior could also be seen, depending on the three sample types.

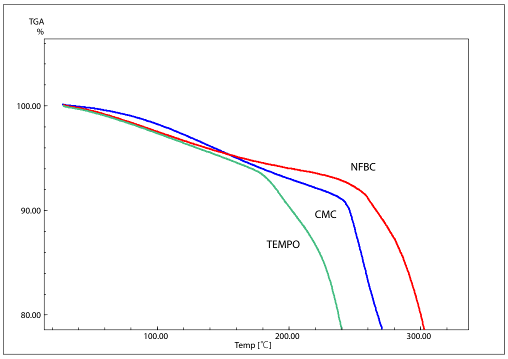

Fig. 5 TG Curves of Non-Pulp-Derived CNF Dried at 80 °C × 8 h

Since discoloration was observed in the TEMPO-oxidized CNF sample, a non-discolored sample was prepared by vacuum-drying followed by additional drying at 80 °C for 50 min to evaporate the water. The TG curves of this vacuum-dried TEMPO-oxidized CNF and the TEMPO-oxidized CNF dried at 80 °C for 8 h were compared (Fig. 6). Comparing the decomposition start temperatures by the tangent intersection temperatures, the decomposition start temperatures were 222 °C for the vacuum-dried CNF and 182 °C for the CNF dried at 80 °C for 8 h. Because decomposition of the CNF dried at 80 °C for 8 h, in which discoloration was observed, began from a lower temperature, it was suggested that degradation proceeded as a result of extended heat treatment.

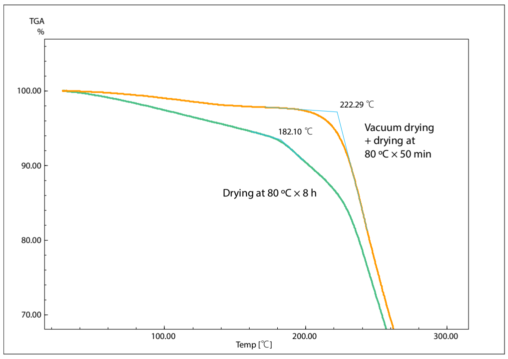

Fig. 6 TG Curves of Vacuum-Dried Sample and Sample Dried at 80 °C for 8 h of TEMPO-Oxidized CNF

A CMC sample that had been heat-treated at 80 °C for 8 h was subjected to additional drying at 80 °C for 2 h in order to eliminate the influence of water. Weight reduction in two stages could be confirmed even after water removal (Fig. 7). Comparing the temperatures for 5% weight reduction, the results were 243 °C for the CMC with additional drying and 303 °C for the cellulose powder. Therefore, it was found that the decomposition temperature of the CMC was lower.

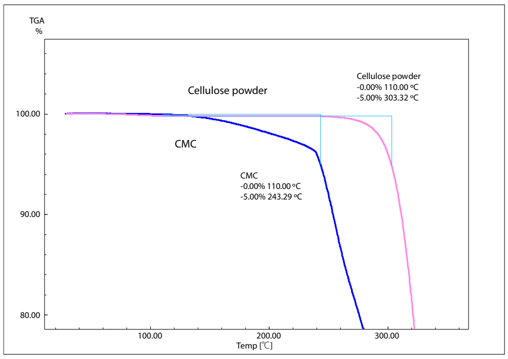

Fig. 7 TG Curves of CMC with Additional Drying and Cellulose Powder

Conclusion

Although one issue for practical application of CNF is thermal stability, analysis of the decomposition temperature and decomposition behavior by thermogravimetry (TG), as demonstrated in this experiment, is considered to be an effective technique for evaluating thermal stability.

Related Materials:

- Application News No. S30: Observation of Cellulose Nanofibers and Measurement of Fiber Length/Width, Shimadzu Corporation
- Application News No. Q121: Characterization of Fiber Length and Dispersibility of Cellulose Nanofibers, Shimadzu Corporation

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