APPLICATION NOTE

Characterization of Cellulose Nanofiber Using N_2 and H_2O Adsorption Isotherms

Abstract

Cellulose nanofibers are nano-sized fibers that are five times lighter and seven to eight times stronger than steel. In particular, TEMPO cellulose nanofiber (TOCN) has been gaining much attention for its filaments that are unlikely to get entangled, dissimilar to those of fibers produced through mechanical defibration. However, the characteristics of TOCN have not to be fully established, yet. We characterized TOCN (specific surface area, external surface area, primary fiber diameter, and hydrophilicity/hydrophobicity) using N_2 (77 K) and H_2O (298 K) adsorption isotherms of TOCN samples. The samples were obtained by adding 10 mmol of NaClO and a certain percentage (10%, 20%, and 40%) by weight of TBA (tert-butyl alcohol) to an aqueous solution of TOCN and freezing dehydration of the solution.

Measurement Instruments

High precision gas/vapor adsorption isotherm measurement system

BELSORP MAX II

[Measurement principle]
Volumetric gas adsorption + AFSM
[Measurement ranges]
Specific surface area: ≧0.0005 m^2/g
Pore size distribution (diameter):
0.35 to 500 nm

Specific surface area/pore size distribution measurement system

BELSORP MINI X

[Measurement principle]
Volumetric gas adsorption + AFSM
[Measurement ranges]
Specific surface area: ≧0.01 m^2/g
Pore size distribution (diameter):
0.7 to 500 nm

True density measurement system

BELPYCNO

[Measurement principle]
He gas displacement
[Sample cell volume]
10, 3.5, and 1.0 cm^3

Results

Samples: TEMPO cellulose nanofiber

Equipment : BELSORP-miniX

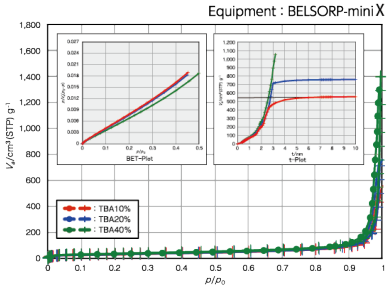

Fig. 1: N_2 (77 K) Adsorption isotherms of TOCN
(left, BET plots used to calculate specific surface areas; right, t-plots used to calculate external surface areas, from standard t-curves of FHH)

Equipment : BELSORP-maxII

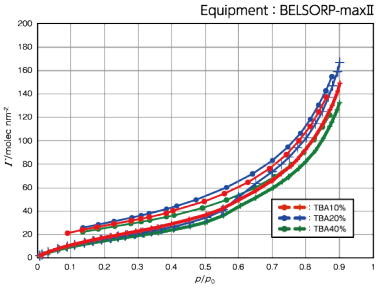

Fig. 2: H_2O (298 K) Adsorption isotherms of TOCN
(vertical axis: the number of H_2O molecules per specific surface area)

Equipment : BELPycno

Sample name	Parameter	TOCN		
	TBA	10%	20%	40%
True density	g/cm^3	2.0284	2.1592	1.9734

Table 1: True density measurements of TOCN

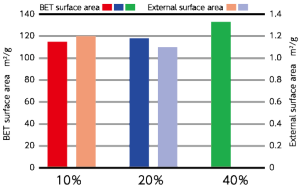

Fig. 3: Comparison of BET surface areas and external surface areas of TOCN

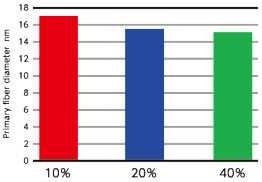

Fig. 4: Evaluation of primary fiber diameters of TOCN

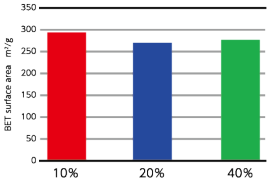

Fig. 5: Comparison of H_2O-based BET surface areas

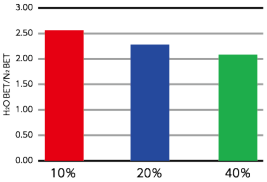

Fig. 6: Evaluation of hydrophilicity/hydrophobicity

Discussion

The lyophilized samples of TOCN were pretreated at 90℃ for 7 hours and at 105℃ for 20 hours in a vacuum, and the adsorption isotherms were measured. The N_2 adsorption isotherms (77 K), in Fig. 1, were type II in terms of shape, which indicates non-porosity. These adsorption isotherms were used to determine the specific surface areas and external surface areas of the TOCN samples from BET plots (left in Fig. 1) and t-plots (right in Fig. 1), respectively, as shown in Fig. 3. The specific surface area increased with increasing TBA content. The external surface area increased with decreasing specific surface area. This is presumably because when the TBA content of the aqueous solution of TOCN fell below a certain limit, the filaments aggregated with no TBA infiltrating the spaces therebetween and were dried in that state. Primary fiber diameters were determined from skeletal volumes of TOCN calculated from the specific surface areas and the inverses of separately measured true densities (Table 1). The primary fiber diameter increased with decreasing TBA content (Fig. 4), supporting the occurrence of aggregation.

As shown in Fig. 5, the specific surface area determined from a water vapor adsorption isotherm (298 K) was substantially constant, seemingly because water molecules are smaller and therefore more likely than N_2 molecules to get adsorbed by penetrating in gaps between aggregates. Plots of water vapor adsorption isotherms based on the number of water molecules per BET specific surface area (Fig. 2) indicate that the TBA 10% sample had the most hydrophilic surfaces at P/P0 up to about 0.5 (50% RH), and the ratios of water-based to N_2-based specific surface areas (Fig. 6) indicate that the 10% TBA sample was the most hydrophilic. The H_2O adsorption/desorption isotherms had hysteresis, as demonstrated by the change in the slope of the water vapor adsorption isotherms at a P/P0 of 0.5. These suggest the presence of a region that performs expansion of the fibers. In this way, precise measurement of N_2 and H_2O adsorption isotherms allows for the characterization of TOCN.

Sample provided by Professor Akira Isogai,
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For further information, please contact us at:

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