NANO-FIBRILLATION OF WOOD PULP FOR THE UTILIZATION IN OPTICALY TRANSPARENT NANOCOMPOSITES

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Cellulose is a linear polymer consisting of D-anhydroglucose units joined together by β-1,4-glycosidic linkages. All plants and some kinds of animals, fungi, and algae produce cellulose, as far as we know. In the wood cell wall, cellulose molecular chains form fibrous structures called microfibrils that are 3 to 4 nm wide. Due to the stable structure of their crystalline regions, microfibrils show high mechanical properties along the longitudinal direction, such as a Young's modulus close to 138 GPa [1] and an estimated strength of at least 2 GPa, based on experimental results for kraft pulp. Furthermore, measurement of the coefficient of thermal expansion (CTE) of all cellulose composites indicates that the CTE of microfibrils is as small as that of quartz, at 0.1 x 10^{-6} $°C^{-1}$ [2]. These singular features make cellulose microfibrils and related nanofibers prospective candidates for reinforcement in nanomaterials.

Mechanical reinforcement of optically functional materials is of significant interest to various industries. Nanocomposite materials with less than one-tenth of a wavelength in size are free from light scattering, making cellulose nanofibers a promising candidate for reinforcement of transparent materials. Yano *et al.* [3] demonstrated that bacterial cellulose (BC) nanofibers sized 50 x 10 nm in cross-section can reinforce acrylic and/or epoxy resin without losing their transparency at a fiber content of 60 %. Furthermore, they showed that the nanocomposites exhibit a low CTE of 6 x 10^{-6} $°C^{-1}$ (as good as of glass), high strength of 325 MPa, comparable to that of soft steel, and ease of bending similar to that of plastics. Optically transparent nanocomposites are highly suitable for use in electronic devices such as flexible display substrates. However, utilization of BC is limited compared to plant based-nanofibers because of their low productivity. Therefore, the reinforcement of optically transparent plastics by plant based-nanofibers, the most abundant resources on Earth, is highly desirable.

The objective of this study is the development of optically transparent composites using wood pulp nanofibers as reinforcement. Wood pulp is several tens micro-meter wide fiber, consisted of aggregates of 3 to 4 nm wide cellulose microfibrils comprising a multi–layered structure with hemicellulose and lignin as a matrix between the microfibrils. Therefore, the utilization of the pulp as reinforcements of optically transparent composites requires the nano-fibrillation of the pulp into microfibrils or their bundles with several tens nano-meter width. Nano-fibrillation procedures using a high-pressure homogenizer and a grinder were investigated. Then, to optimize the nano-fibrillation treatment, the effect of the treatment conditions on the mechanical and thermal properties of the optically transparent composites was investigated. Finally, to improve the process of nano-fibrillation for the production of optically transparent nanocomposites with high mechanical properties and low thermal expansion, the effects of hemicellulose content on pulp were investigated in terms of the aggregation of microfibrils.

The fibrillation procedures of wood kraft pulp into nano-sized wide fibers were compared using a high-pressure homogenizer and a grinder [4]. The high-pressure homogenizer treatment was not sufficient to achieve uniform nano-fibrillation. On the other hand, repetition of the grinder treatment after the high-pressure homogenizer treatment did fibrillate pulp into uniform nanofibers. To optimize the grinder treatment for the processing of optically transparent composites, the effects of the fibrillation conditions on the physical properties of the composites were investigated [5]. The dissolved pulp was subjected to various passes through the grinder. The fibrillated pulp gradually turned into uniform 20 to 50 nm wide fibers after up to 5 passes through the grinder. The light transmittance at 600 nm wavelength of the fibrillated pulp composites reached 80 %. However, further passes did not change the size of the fibrillated pulp and the light transmittance of the composites. In addition, as the number of passes through the grinder increased, the fibrillated pulp was subjected to degradation, which can be explained by the decrease in the degree of crystallinity and the degree of polymerization of the cellulose. The degradation of the fibrillated pulp led to a decrease in the mechanical properties and an increase in the thermal expansion of the sheets and composites. Thus, it was concluded that the production of high-performance optically transparent nanocomposites requires a reduction in the number of passes in nano-fibrillation using a grinder.

To reduce the number of passes, the effects of hemicellulose content on pulp were investigated in terms of the aggregation of microfibrils [6]. Four types of pulps: never and once-dried holocellulose

pulp with and without alkali treatment were prepared. The mild alkali treatment removed hemicelluloses from holocellulose pulp. Regardless of the presence of hemicelluloses, irreversible hydrogen bonding against rewetting occurred due to drying in the pulps. With the single-pass grinder treatment of the pulps, the never and once-dried holocellulose and never-dried alkali-treated pulps were fibrillated into 10 to 20 nm-wide fibers, while the once-dried alkali-treated pulp did not achieve nano-fibrillation, indicating that hemicelluloses serve as inhibitors of the coalescence of microfibrils, contributing to the ease of nano-fibrillation.

In addition, the coefficient of thermal expansion (CTE) values of the fibrillated never and once-dried holocellulose pulp sheets and composites were extremely low, at approximately 8 and 10 x 10^{-6} $^{o}C^{-1}$, respectively; these values were about one-eighth of that of acrylic resin. The fibrillated never and once-dried alkali-treated pulp composites had higher CTE values than the fibrillated never and once-dried holocellulose pulp composites. With respect to mechanical properties, the fibrillated never and once-dried holocellulose pulp composites showed remarkable results with a Young's modulus of approximately 16 GPa and a strength of about 280 MPa, exhibiting higher figures than those of the fibrillated never and once-dried alkali-treated pulp composites. These results indicate that hemicelluloses play a role in adhesion between nanofibers, contributing to the thermal stability, stiffness and strength of composites.

In conclusion, 10 to 20 nm wide nanofibers which are thinner than BC were obtained from wood pulp (Fig. 1). Furthermore, the optically transparent nanocomposites exhibiting a light transmittance of 83 % at 600 nm wavelength, a coefficient of thermal expansion of 10 x 10^{-6} $^{o}C^{-1}$, Young's modulus of 16 GPa, and tensile strength of 280 GPa were obtained at a fiber content of 85 wt% using wood pulp nanofibers as reinforcement.

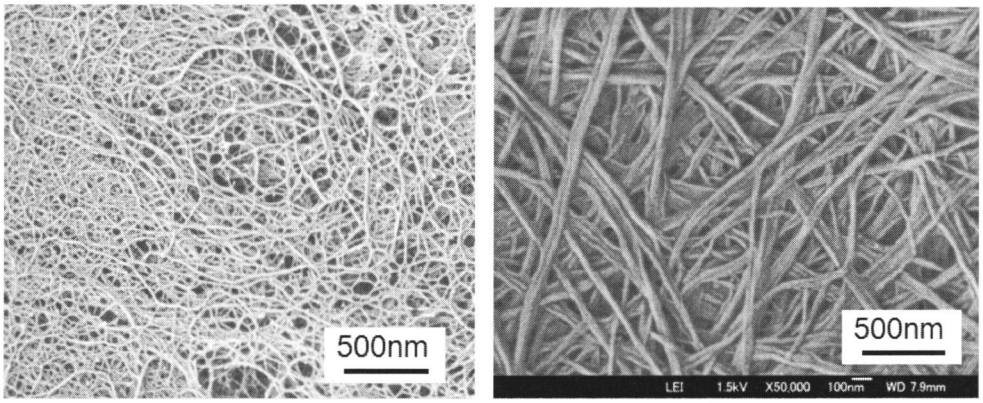

Figure 1. Scanning micrographs of (a) wood pulp and (b) Bacterial cellulose nanofibers.

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