

All-CELLULOSE COMPOSITE WITH HIGH THERMAL CONDUCTIVITY USING NANODIAMONDS

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Abstract

An all-cellulose composite with ND was prepared by immersing uniaxially aligned cellulose fibers in ND aqueous suspension, following by impregnation with cellulose solution. The structure, mechanical and thermal properties of the composites were investigated using a scanning electron microscope, a thermogravimeter, an X-ray diffraction, a tensile test, a dynamic mechanical analysis, a differential scanning calorimeter, and thermal conductivity measurements. The storage modulus of the composite with 6.3 wt % of ND was 30 GPa at 250 °C. In addition, the thermal conductivity of the composite with 6.3 wt % of ND parallel to the fiber direction was 8.4 W/(m · K). The composites are shown to have excellent mechanical and thermal performances. Accordingly, the composites with ND had excellent properties derived from ND and cellulose. In addition, these were intrinsically environmentally-friendly composites.

1. Introduction

Composite materials, typically glass fibers or carbon fibers embedded into epoxy resin or unsaturated polyester, show excellent mechanical and thermal properties; thus, they are widely use in various applications ranging from aerospace to vehicles to sports utensils [1]. However, in recent years, oil depletion becomes more serious. Therefore biomass resources have attracted attention as alternatives to petroleum-based materials.

Cellulose is the most abundant natural homopolymer, and it plays a significant role in the structure support of plant cell walls because of its high mechanical properties. [2] Together with a relatively high elastic modulus of 138 GPa for the crystalline regions in the direction parallel to the chain axis [3] and a high degree of polymerization, the liner orientation of native cellulose (cellulose I) molecules contribute to the mechanical high performance of the plant cell wall. In addition, inter / intrahydrogen bonds stabilize the molecule itself, and connect it tightly to neighboring ones. The maximum macroscopic Young's modulus of plant cellulose (up to 128 GPa) [4] is higher than those of aluminum (70 GPa) and glass fiber (76 GPa). The excellent mechanical property of cellulose has brought about the current trend toward eco-composites focusing on the best use of cellulose fibers, e.g., poly-L-lactic acid reinforced with natural plant fiber (hemp [5], kenaf [6], and flax [7] etc.). We proposed the

development of a novel material, an *all*-cellulose composite, in which the incorporated fibers and the matrix were both made of cellulose. It was prepared by impregnating the cellulose solution into uniaxially aligned cellulose fibers. This *all*-cellulose composite is shown to have excellent mechanical properties and thermal performances [8].

Carbon-based nanomaterials, such as carbon nanotubes, are well-known for their incredibly high mechanical properties (Young's modulus ≥ 1 TPa and tensile strength = 100-150 GPa), and they have attracted interest as reinforcing fillers for polymer nanocomposites [9-12]. However, the success of the reinforcement has been limited because of their tendencies to form agglomerates in polymer matrices. [13, 14] Recently, nanodiamond (ND) has been produced by several procedures, such as by explosion, and it has been exploited as one kind of new nanocarbon family in some field of nanotechnology. [15, 16] Diamond is well-known for its excellent properties, such the highest bulk modulus and thermal conductivity, high wear resistance, chemical inertness, and good electrical insulating properties. Therefore, ND has been expected to offer polymer nanocomposites optimal properties due to its own excellent properties [17].

In this study, we proposed a new, environmentally friendly composite using both cellulose and ND. We immersed uniaxially aligned cellulose fibers in the ND aqueous suspension and dried, followed by impregnation with cellulose solution. This method made it possible to absorb ND on fibers easily. Moreover, the ND contents of resultant *all*-cellulose composite could be controlled widely by using aqueous suspensions with various ND contents. Then structure and properties of the composite were investigated.

2. Materials and measurements

2.1 Materials

The cellulose fiber used in this study is refined ramie supplied from Toyobo Co., Ltd. The ND aqueous suspension was supplied from Bando Chem. Ind.; the ND content is 2.75 wt %. ND powder was synthesized by the detonation of explosive compounds, including TNT (2-methyl-1,3,5-trinitrobenzene) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine), under an inert atmosphere. The detonation soot was purified by oxidation with the strong acids, such as permanganic acid, nitric acid, and sulfuric acid, followed by annealing. After rinsing, the ND powder was dispersed in water by wet milling process in bead mill. For the matrix, we used a filter paper for quantitative chemical analysis (Toyo Roshi Kaisha, Ltd.).

2.2 Sample preparation

Filter papers were pretreated. The pretreatment was performed by immersing them in distilled water, acetone, and DMAc (*N,N*-dimethyl acetamide), each for 24 h at room temperature, successively. Then, the pretreated filter papers were dissolved in DMAc containing LiCl (8 wt %) solvent with a cellulose concentration of 1.5 wt %. Non-pretreated ramie fibers were aligned parallel one another and fixed at both ends. After that, the uniaxially aligned fibers were immersed in ND aqueous suspension which was diluted with distilled water (ND content : 0.1, 0.5, 1.0 wt %) and ultrasonicated for 1h. Then the fibers with ND were dried for 6 h at 120 °C, and impregnated with the cellulose solution. The solution started gelation by exposing it to an ambient condition for 12h. After another 12 h, the fiber-incorporated gel was

immersed into methanol to extract DMAc and LiCl, then dried at room temperature for 12 h, and further dried in a vacuum at 60 °C for 24 h.

2.3 Measurements

The surface of ramie fiber and the ND particles were observed using a scanning electron microscope (SEM), JSM-5610LVS (JEOL) at an accelerating voltage of 15 kV. Pt/Pd was deposited on the surface prior to the observation. The ND content of composite was measured by a thermogravimeter (TG), TG/DTA-220U (Seiko Instrument Inc.) at the heating rate of 10 °C/min under N₂ flow. X-ray diffraction photographs were taken by a flat camera with a camera length of 60.3 mm. The CuK α radiation, generated with RINT-2000 (Rigaku Co.) at 40kV, 20 mA, was irradiated on specimen perpendicular to the fiber orientation. The equatorial diffraction profile was detected using an X-ray goniometer with a symmetric reflection geometry. Tensile properties were determined using a tensile tester, Autograph AGS-1kND (Shimadzu Co.) ; the initial length of the specimen was 40mm, and the extension rate was 2 mm/min. The toughness (K) was determined as the area surrounded by the stress (σ) – strain (ε) curve. The cross-section area of the composite was determined by measuring the weight, the length, and the density. The density of composites were determined by floatation method (carbon tetrachloride/ benzene system at 30°C) at room temperature. Dynamic mechanical analysis (DMA) was performed with a dynamic mechanical analyzer, DVA-220S (ITK Co., Ltd.) from 25 to 300 °C ; the initial length of the specimen was 20 mm. A heating rate of 6 °C/min, and a frequency of 10 Hz were employed. The tensile deformation (0.25 %) was applied to the specimen in the direction parallel to the fiber orientation. The specific heat capacity was measured by a differential scanning calorimeter (DSC) (Rigaku Co., DSC8230). A heating rate of 10 °C/min was employed under N₂ flow. The specific heat capacity C_p (J/(g · K)) can be obtained from the equation

$$C_{ps} = \frac{C_{pr} \times m_r}{Y_r} \times \frac{Y_s}{m_s} \quad (1)$$

where C_{ps} is C_p of sample (J/(g · K)), C_{pr} is C_p of reference, m_s is weight of sample (g), m_r is weight of reference, Y_s is difference of sample and empty pan (mW), and Y_r is difference of reference and empty pan. Al₂O₃ was used as reference. The thermal diffusivity was measured by thermal diffusivity measurement system, Thermowave Analyzer (Bethel Co., Ltd. Hudson Laboratory). The surface of the composite was coated with graphite spray. The thermal conductivity λ (W/(m · K)) can be obtained from the equation

$$\lambda = \alpha \times C_p \times d \quad (2)$$

where α is thermal diffusivity (m²/S), and d is density (g/m³).

3. Results

3.1 Characterization

Figure 1 shows SEM micrographs of (a) the ramie single fiber and (b) the ND absorbed ramie single fiber. The surface of the ramie single fiber was smooth, but after immersing in ND aqueous suspension, the surface was covered with ND. Thus, this simple immersion method made it possible to absorb ND particles on fibers easily.

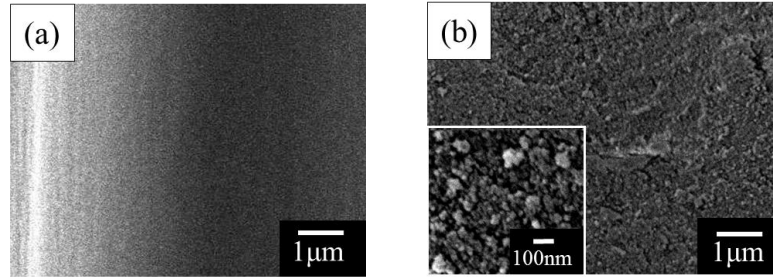


Figure 1 Scanning electron micrographs of (a) the ramie single fiber and (b) the ND absorbed ramie single fiber.

Figure 2 shows the thermogravimetric traces of the ND and the composites. The weight of loss of ND was negligible, but the composites were thermally decomposed mainly through the decomposition of cellulose. Moreover, with increasing the amount of ND (with using high concentration ND aqueous suspension), residual weight after heating increased. From the difference between the residual weight of the *all-cellulose* composite and the *all-cellulose* composites with ND, the ND contents of the composites were calculated. The results are summarized in Table 1. For example, when we employed 1.0 wt % ND aqueous suspension, ND contents in the composite was 6.5 wt %. Thus, the ND contents of the *all-cellulose* composites with ND could be controlled widely by using aqueous suspension with various ND contents.

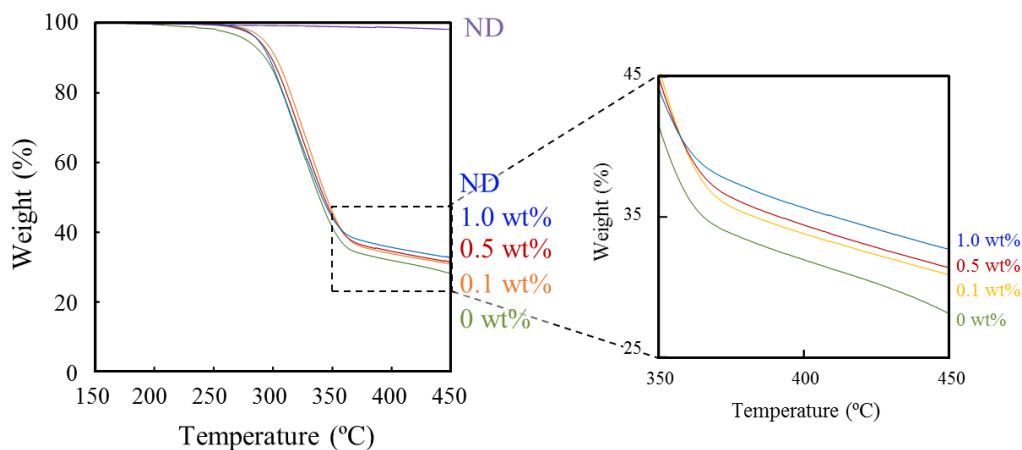


Figure 2 Thermo-gravimetric trace of ND and composites.

ND aqueous suspension wt%	ND in composite wt%
0	0
0.1	3.9
0.5	4.6
1.0	6.5

Table 1 ND content in aqueous suspension and in composite.

Figure 3 shows X-ray photographs of (a) a ramie fiber, (b) the matrix film, (c) the *all-cellulose* composite, and (d) the *all-cellulose* composite with ND. The X-ray photograph of a ramie fiber showed high crystallinity and a high degree of the crystallite orientation. The

ramie fiber belongs to cellulose I, which is typical for natural plant cellulose [18]. On the other hand, the photograph of the matrix film showed the noncrystalline scattering. The matrix cellulose was converted into noncrystalline condition through dissolution and re-solidification and belonged to cellulose II. The diffraction pattern of the *all*-cellulose composite clearly showed a specifically uniaxially oriented fiber pattern with high crystallinity. Comparing with that of ramie fiber, high crystallite orientation was maintained. Moreover, that of the *all*-cellulose composite with ND also showed a specifically uniaxially oriented fiber pattern with high crystallinity.

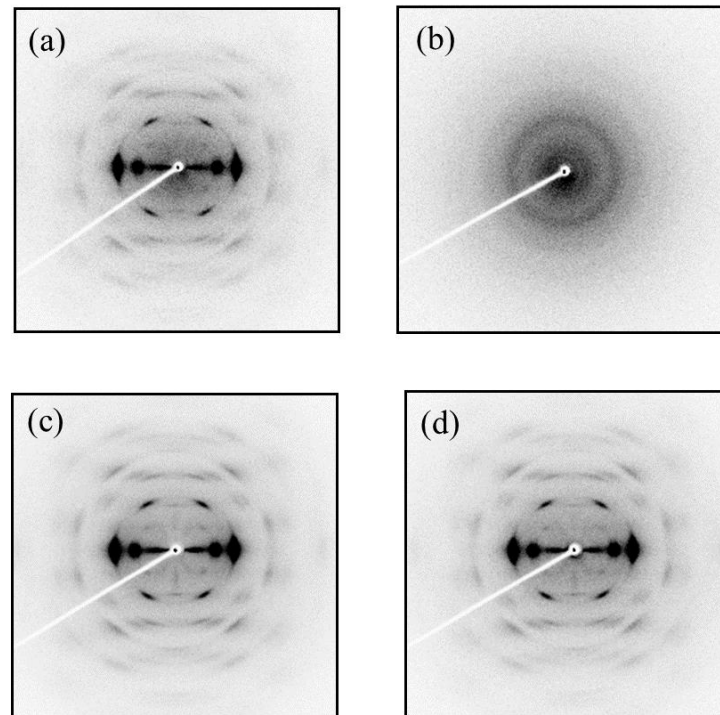


Figure 3 X-ray photographs of (a) a ramie fiber, (b) the matrix film, (c) the *all*-cellulose composite, and (d) the *all*-cellulose composite with ND.

3.2 Mechanical properties

Figure 4 shows the stress-strain curves of *all*-cellulose composite and *all*-cellulose composites with ND. The *all*-cellulose composite possesses high mechanical properties (tensile strength (σ_{\max}) 440 MPa, toughness (K) 9.5 J/g). Mechanical properties of *all*-cellulose composites with ND were as high as those of *all*-cellulose composite (the composite with 4.6 wt% of ND : σ_{\max} 490 GPa, K 10.1 J/g). In particular, the σ_{\max} increased even with a small amount of ND loading. These high mechanical properties and the increase of σ_{\max} were derived from *all*-cellulose composite and ND effects.

Figure 5 shows the temperature dependence of the storage modulus (E') of the composites. The E' value of the *all*-cellulose composite decreased from 31 GPa at 30 °C to 20 GPa at 250 °C. The E' value of the *all*-cellulose composite with ND was higher than *all*-cellulose composite. In particular, E' of the composite with 6.5 wt % of ND was 47 GPa at 30 °C. Furthermore, even though the E' value of the composite with 6.5 wt % of ND decreased with heating, the drop was limited to 30 GPa at 250 °C. This thermal/mechanical performance is

extremely high among polymer-based composites, which originates from the intrinsically excellent properties of both the ramie fibers and ND themselves.

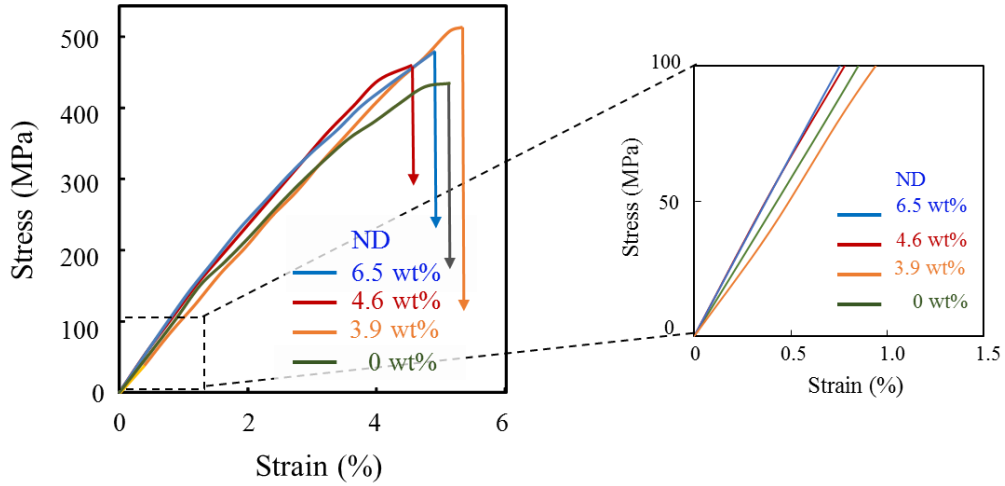


Figure 4 Stress-strain curves of the *all-cellulose* composite and the *all-cellulose* composite with ND.

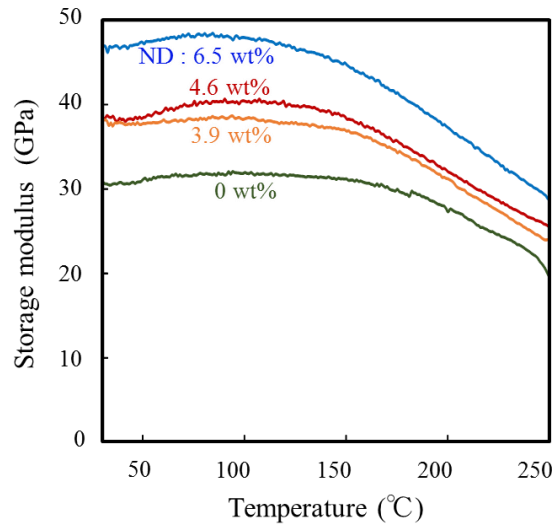


Figure 5 Temperature dependence of the storage modulus of the *all-cellulose* composite and the *all-cellulose* composite with ND.

3.3 Thermal properties

Table 2 shows ND content in the composites, C_p and the density of the composites. These values were calculated from the results of DSC measurement and the floatation method. The results of thermal diffusivity α ($10^{-6} \text{ m}^2/\text{s}$) of the composites in the fiber direction, perpendicular direction, and the thickness direction are shown in Table 3. The thermal conductivity λ ($\text{W}/(\text{m} \cdot \text{K})$) of the composites were calculated from the values in Table 2 and 3 using eq 2.

Figure 6 (a) shows the relationship between the observed thermal conductivity and the ND contents of *all*-cellulose composites with ND. The thermal conductivity of the *all*-cellulose composite parallel to the fiber direction was higher than those in the perpendicular and thickness direction. Moreover, in fiber direction, the thermal conductivities of the composites with ND showed a further increase. For example, the composite with 6.5 wt % of ND reached 8.4 W/(m · K), which is about 50 % higher than that of the *all*-cellulose composite. This is because that ND particles were located alongside fibers, which made thermal conducting channels, and contributed to the increase of anisotropic thermal conductivity of the composites (Figure 6 (b)).

ND content (wt%)	C _p @25°C (J / g / K)	Density (g/cm ³)
0	1.32	1.503
3.9	1.26	1.519
4.6	1.23	1.538
6.5	1.29	1.544

Table 2 ND content in composite, C_p and density of composites.

ND content (wt%)	Thermal diffusivity α (10 ⁻⁶ m ² /s)		
	fiber direction	perpendicular direction	thickness direction
0	2.3	0.36	0.050
3.9	3.3	0.30	0.047
4.6	3.6	0.32	0.050
6.5	4.3	0.43	0.032

Table 3 ND content in composites and thermal diffusivity α of composites in fiber direction, perpendicular direction, and thickness direction.

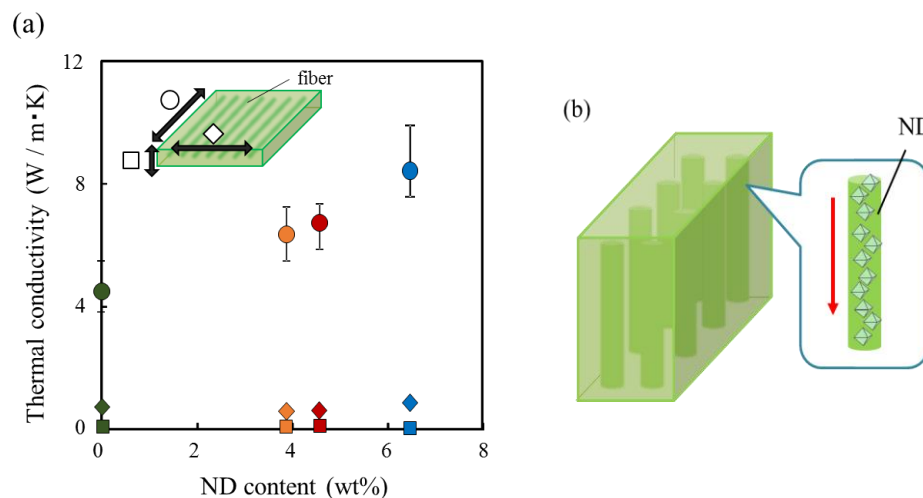


Figure 6 (a) Relationship between thermal conductivity and ND content of *all*-cellulose composites with ND, and (b) the scheme of *all*-cellulose composite with ND.

4. Conclusion

The *all*-cellulose composite with ND was prepared by immersing uniaxially aligned cellulose fibers in ND aqueous suspension, following by impregnation with cellulose solution. This method made it possible to absorb ND on fibers easily. Moreover, the ND contents of the resultant *all*-cellulose composite could be controlled widely by using aqueous suspensions with various contents.

It is revealed that the mechanical properties of the composites with ND are as high as those of the *all*-cellulose composite. In particular, the composites with ND has excellent thermal resistance (E' : 30 GPa at 250 °C). Moreover, the thermal conductivity of the composite with ND parallel to the fiber direction is about 50 % higher than that of the *all*-cellulose composite. This thermal performance is extremely high among polymer-based composites. This is because that ND particles were located alongside fibers, which made thermal conducting channels, and contributed to the increase of anisotropic thermal conductivity of the composites.

Accordingly, these *all*-cellulose composites with ND have excellent properties derived from cellulose and ND. In addition, these are intrinsically environmentally- friendly.

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