High Dielectric Performances of Flexible and Transparent Cellulose Hybrid Films Controlled by Multidimensional Metal Nanostructures

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Various wearable electronic devices have been developed for extensive outdoor activities. The key metrics for these wearable devices are high touch sensitivity and good mechanical and thermal stability of the flexible touchscreen panels (TSPs). Their dielectric constants ($k$) are important for high touch sensitivities. Thus, studies on flexible and transparent cover layers that have high $k$ with outstanding mechanical and thermal reliabilities are essential. Herein, an unconventional approach for forming flexible and transparent cellulose nanofiber (CNF) films is reported. These films are used to embed ultralong metal nanofibers that serve as nanofillers to increase $k$ significantly (above 9.2 with high transmittance of 90%). Also, by controlling the dimensions and aspect ratios of these fillers, the effects of their nanostructures and contents on the optical and dielectric properties of the films have been studied. The length of the nanofibers can be controlled using a stretching method to break the highly aligned, ultralong nanofibers. These nanofiber-embedded, high-$k$ films are mechanically and thermally stable, and they have better Young’s modulus and tensile strength with lower thermal expansion than commercial transparent plastics. The demonstration of highly sensitive TSPs using high-$k$ CNF film for smartphones suggests that this film has significant potential for next-generation, portable electronic devices.

Flexible displays have immense potential in next-generation electronic devices,[1–2] such as wearable smart devices,[3–6] augmented or virtual reality devices,[7,8] smart living,[9] and automotive electronics for smart cars.[10] Despite the remarkable developments in this field, corresponding progress has not been made in the development of flexible touchscreen panels (TSPs) with outstanding mechanical durability. Such development is important because the TSPs of wearable electronic devices, including smart watches, wrist bands, smart glasses, and fitness or medical monitors, can be exposed to various outdoor activities. Thus, a protective cover layer is required to withstand wear and scratch damage without affecting touch performance. Therefore, TSPs with high sensitivity and reliability are essential requirements for the success of future flexible displays. Among diverse touch-sensing methods, such as resistive,[11] infrared ray,[12] surface acoustic wave,[13] and capacitive methods,[14,15] the capacitive TSP has practically dominated the market due to its multitouch functionality.[16,17] When a finger or a conductive stylus approaches an electrode of the capacitive TSP, it disturbs the electromagnetic field and alters the capacitance.[18] This TSP detects touch by measuring the capacitance at each addressable electrode, and, thus, the dielectric constant of the protective cover layer, which is located between the active touch-sensor surface and the touching object (i.e., human fingers or touch pens), is related directly with touch sensitivity.[19]
Glass has high optical transmittance (~90%), outstanding mechanical reliability, and a high dielectric constant (gorilla glass, \( k \approx 7.2 \)).\(^{[20]}\) It has been used extensively for this protective layer. However, flexible TSPs can no longer use glass because of its fragility, and the inevitably result has been the use of plastic films as the layer for flexible TSPs. Unfortunately, commercially transparent plastic films, such as polyethylene terephthalate (PET; \( k \approx 3.1 \)), polyethylene (PE; \( k \approx 2.2 \)), polyimide (PI; \( k \approx 3.4 \)), and polycarbonate (PC; \( k \approx 2.9 \)), have relatively low dielectric constants and modest mechanical properties. For example, the nanofibers with high aspect ratio (\( \approx 700 \)) showed a significant enhancement in \( k \) with a relatively small filler content of 1.2 wt% \((k = 9.2)\) at 120 kHz, compared to the cases of nanoparticles \((k = 4)\) at 120 kHz or nanowires with lower aspect ratios \((k = 5.5)\) at 120 kHz. The large open space between the long nanofiber network (high aspect ratio) can provide optical transparency as high as 90% in the visible light regime and a high \( k \) value \((k = 9.2)\) while still preserving the outstanding mechanical robustness (Young’s modulus of 4.3 GPa and tensile strength of 205 MPa) and thermal stability (CTE of 8.4 ppm K\(^{-1} \)) of the CNF matrix. Using this high-\( k \) CNF film, we demonstrated the fabrication of highly sensitive, flexible TSPs. Real-time measurements of the change in the relative capacitance during finger touch using this high-\( k \) film showed 2–3 times higher sensitivity than the cases using metal nanoparticle- or nanowire (with lower aspect ratio)-based CNF films. These results provide clear evidence for its potential and widespread application in next-generation, flexible electronics.

For the conducting nanofillers, the length of the AgNFs can be controlled by a stretching method for cracking highly aligned, ultralong AgNFs (Figure 1a). After spin-coating a polyvinylpyrrolidone (PVP; MW = 10 000) sacrificial layer (thickness = 700 nm) on a 1 mm thick polydimethylsiloxane (PDMS) substrate (width = 5 cm, length = 10 cm), this PDMS film was wrapped onto the outer surface of a drum collector. Alignment of the AgNFs was obtained by electrospinning an AgNP suspension (average diameter of AgNPs = 45 nm, solvent: \( \alpha \)-Terpineol, AgNP concentration = 54%) on the rapidly rotating drum collector\(^{[23]} \) with a rotation rate of 3000 rpm, and then, this electrospun PDMS film was detached carefully from the drum collector. After thermal sintering of the electrospun AgNPs at 180 °C in air for 2 h, they were coalesced into electrically conductive AgNFs with an average diameter of \( \approx 300 \) nm. The thermal expansion of PDMS at this annealing temperature (180 °C) was not large enough to break the AgNFs. To control the length of the AgNFs, these annealed AgNFs on the PDMS film were stretched uniaxially up to 50% in the direction parallel to the AgNF alignment as a function of stretching rate (12.5, 25, 37.5, and 50 cm s\(^{-1} \)) by using a motor controller (ECOPIA), as shown in Figure 1a. For the case of a brittle thin film on an elastic substrate as like our system (the PVP layer on PDMS substrate), cracks can be formed with uniformly spacing normal to the stretching direction when they are under the uniaxial stress state\(^{[38]} \) As shown in Figure 1b–e, most cracks are formed normal to the stretching direction and spacing between them is relatively uniform. At the areas close to side edges and gripping parts, however, nonuniform cracks can be generated due to the nonuniaxial stress state by mechanical constraints (Figure S1a, Supporting Information). Figure S1b (Supporting Information) presents the statistical analysis on the alignment of cracks by measuring the angular distribution of 500 cracked lines (measurement area: 50 \( \times \) 50 mm). Here the line 0° refers to being normal to the stretching direction, based on which the acute between the cracked line and reference line. The average angle between the cracked line and reference line was \(-0.1°\) \( \pm \) 0.4°. Also, the distance between the cracked lines of the PVP layer and the length of the AgNFs were dependent on the stretching rate. The average spacings between cracks...
were 51 ± 2.2, 102 ± 4.2, 148 ± 3.7, and 198 ± 5.7 μm, corresponding to the stretching rates of 12.5, 25, 37.5, and 50 cm s⁻¹, respectively, and this spacing increased with the stretching rate, as shown in Figure S1c (Supporting Information). Figure S2 (Supporting Information) clearly shows that more cracks are generated and the spacing between the separated PVP segments becomes narrower, as the stretching rate decreases. Because PVP is much more brittle than PDMS, these cracks are introduced in the PVP layer during stretching, which determines the length of AgNFs. At lower stretching rate, secondary cracks are initiated and propagated before the primary cracks initiated at weakest spots propagate into long cracks that release stress in neighboring PVP segments. At higher stretching rate, however, primary cracks initiate and develop into long cracks quickly and therefore secondary cracks lose chances to be initiated statistically. Consequently, lower stretching rate reduces the average length of the PVP segments (separated by cracks), with resulting in shorter AgNFs. (Higher stretching rate increases the average length of the PVP segments with resulting in longer AgNFs.) Subsequently, dissolving this PVP sacrificial layer by soaking this sample in DI water produced an aqueous dispersion of the AgNFs with controlled lengths. The average lengths of these cracked AgNFs were 50 ± 5, 95 ± 10, 145 ± 17, and 200 ± 20 μm (aspect ratios = 167, 350, 483, and 700, respectively) corresponding to stretching rates of 12.5, 25, 37.5, and 50 cm s⁻¹, respectively, as shown in Figure 1f and Figure S3 (Supporting Information). The difference between the fiber length and crack spacing is due to the misalignment of Ag nanofibers (Figure S4, Supporting Information).

Figure 1a–c shows size distribution graphs and scanning electron micrographs (SEMs) (insets) of the conductive nanofillers. Zero-dimensional AgNPs with diameters of 100 ± 24 nm (aspect ratio = 1), 1D AgNWs with an average length of 10 ± 3.1 μm and an average diameter of 100 nm (aspect ratio = 100), and long AgNFs with an average length of 200 ± 20 μm and an average diameter of 300 nm (aspect ratio = 700) were formed by the stretching method and used for producing high-k CNF films. In contrast to AgNPs and AgNWs that exhibited broad size or length distributions (the deviation of AgNP = 24% of average diameter, the AgNW case = 31% of the average length), the AgNFs showed relatively sharp distributions in length (deviation = 10% of the average), indicating that the stretching method can produce relatively uniform lengths of AgNFs, compared to the bottom-up synthesis methods for AgNPs or AgNWs. In this study, we used 2,2,6,6-tetramethyl-1-piperidine-1-oxyl-oxidized CNFs (0.3 wt% in H₂O, University of Maine, Orono, ME, USA) with diameters of ~20 nm and lengths of ~1 μm. To produce high-k and transparent CNF films, these AgNPs, AgNWs, and AgNFs were mixed in the aqueous suspension of CNFs (0.3 wt%) with various concentrations, followed by vacuum filtration. The obtained CNF films were dried thoroughly by hot pressing at 60 °C for 10 h under the pressure of 10 MPa, and, then, they were peeled off of the filter. These CNF films are vulnerable to water, as indicated by high haze values and rough surfaces (Figure S5, Supporting Information), which can degrade the optical properties of the films. Mixing hydrophobic epoxy polymers with CNF films can solve these issues to match refractive indices, and an epoxy-based hard polymer (SU-8, Microchem) was coated to these CNF films using a dip-coating method to produce the CNF-epoxy hybrid films in which either AgNPs, AgNWs, or AgNFs were embedded (film thickness = 50 μm). The final films that were produced contained very small contents of epoxy (below 5%). Figure 2d shows photos of the CNF films that contained 1.2 wt% of AgNPs (left), AgNWs (middle), and AgNFs (right). The optical properties of these films, showing transmittance and haze values as a function of nanofiller contents, are presented in Figures 2e–f. Among these three films, the AgNP sample exhibited the lowest transmittance (29% at a wavelength of 550 nm) and the highest haze values (35%).
Figure 2e,f shows that increasing the content of AgNPs decreased the transmittance of the CNF films and increased their haze values significantly. In contrast to the AgNP case, both the AgNW- and AgNF-based samples had high transmittance (above 90%) with low haze (below 5%) even though the content of AgNWs or AgNFs was increased up to 1.2 wt%. This significant difference in transmittance and haze between the AgNP sample and the other two films (AgNW- or AgNF-based films) can be explained by the discrepancy in their light scattering through these nanofillers. To elucidate the origin of the distinct transmittance, we calculated the scattering efficiencies (wavelength = 550 nm) of single Ag spheres (for AgNPs) and cylinders (for AgNWs or AgNFs) with diverse diameters ranging from 20 to 400 nm by conducting finite-difference time-domain simulations (see Figure S6a, Supporting Information).

The simulation result shows the scattering efficiencies of the Ag spheres much larger than those of the Ag cylinders at all of the diameters considered, indicating an optical characteristic differed by the dimension of Ag structures. A side-to-side comparison of electric field profiles clearly reveals the enhanced light-matter interaction from the Ag sphere (Figure S6b, Supporting Information). The direct calculation of transmittance with arrays of Ag spheres and cylinders with the same diameter of 100 nm supports well the measured data (Figure S6c, Supporting Information); for the Ag cylinders, the slight fluctuation observed at the Ag volume fraction smaller than 0.2 is due to an interference effect, which would not appear in the practical, randomly dispersed structures. Taken together, such low transmittance of the AgNP-CNF film is ascribed to strong scattering of light by their nanoparticle shapes. We also investigated optical properties of the CNF films according to film thickness. The pristine CNF film (with no additional nanofiller) did not show significant change in transmittance or haze even when the thickness increased from 50 to 100 µm. This is because the pristine CNF film is inherently transparent. On the other hand, the addition of nontransparent metallic nanofillers on the light-path can cause severe light scattering. As a result, the nanofiller-embedded CNF films exhibited notable degradation in optical properties with increasing thickness as shown in Figure S7 and Table S1 (Supporting Information).

The capacitive networks formed by the conductive nanofillers and dielectric CNFs can improve the dielectric constants (k) of the films effectively due to the free charges entrapped at the interface between the nanofillers and CNFs. The SEM images in Figure 3a–c show the morphologies of the AgNP-, AgNW-, and AgNF-embedded CNF films (content of these nanofillers = 1.2 wt%) before coating the epoxy polymers to observe their embedded structures. These three types of nanofillers (AgNPs, AgNWs, and AgNFs) were dispersed uniformly inside the layers of the CNF with negligible aggregations. After coating the epoxy polymer, the k values of these films were measured at 120 kHz, which is within the operating frequency range of commercialized TSPs (Figure 3d). Compared to the pristine CNF-epoxy hybrid film (k = 3.3), the addition of these nanofillers to the CNF-epoxy film can improve k significantly as their concentrations are increased, despite the degradation of their optical transmittance. In contrast with the zero-dimensional AgNPs (aspect ratio ≈ 1) that had a relatively less dominant contribution to increasing k, the higher aspect ratios of the 1D metal nanostructures that had lower percolation thresholds of electrical conductivity were advantageous in improving k without significant reduction in the optical transparency of the
films. For example, the AgNF-embedded film with an AgNF aspect ratio of 700 exhibited optical transmittance of 80%, and, when the AgNF content was 2 wt%, it had a drastically increased $k$ value of 12.9, which was approximately four times larger than the $k$ value of the pristine CNF-epoxy hybrid film, while still preserving the low dielectric loss of this film. (See the Supporting Information and Figure S8.) This $k$ value of 12.9 is sufficiently high, compared to the $k$ values of commercialized glass (gorilla glass, $k = 7.2$) or other high-$k$ polymers, such as pure poly(vinylidene fluoride) ($k = 7.9$) and high density polyethylene ($k = 5.0$). Also, as shown in Figure S9 (Supporting Information), dielectric constants of the nanofiller-embedded CNF films are not changed by film thickness significantly because the fraction occupied by nanofillers per unit volume is the same. To achieve both high transparency ($T = 90\%$) and high $k$ for the protective cover layer of capacitive TSPs, the maximum concentration of the nanofillers was optimized as 1.2 wt% in our experiments, and the optimized transmittance (at 550 nm) and $k$ values (at 120 kHz) of these films (at 1.2 wt%) are compared in Figure 3e. Among these AgNP-, AgNW-, and AgNF-embedded films, the AgNF sample with the highest aspect ratio of 700 presented a high $k$ of 9.2 with high transmittance of 90%, which indicated that it had potential for the realization of TSPs with good sensitivity.

For the reliable operation of flexible TSPs for wearable electronic devices, such as smart watches or wrist bands that can be exposed to diverse outdoor activities, the mechanical and thermal reliabilities of the protective cover layers are important. For this purpose, the mechanical and thermal properties of the AgNP-, AgNW-, and AgNF-embedded CNF-epoxy hybrid films were characterized. Figure 4a shows outstanding mechanical robustness of these high-$k$ films, which had high values of Young’s modulus ($E = 4.3$ GPa, $T = 90\%$) and high $k$ values (at 120 kHz) of these films (at 1.2 wt%) are compared in Figure 3e. Among these AgNP-, AgNW-, and AgNF-embedded CNF-epoxy hybrid films.
TS = 205 MPa). Using these functional nanofillers (AgNPs, AgNWs, and AgNFs) in CNF-epoxy hybrid films did not degrade the mechanical robustness of the CNF-based films significantly. And these mechanical properties were superior to those of conventional plastic films, such as PET (E = 2 GPa, TS = 55 MPa) and PI (E = 2.5 GPa, TS = 68 MPa). Figure 4b shows the reliability of the AgNF-embedded film (film thickness: 50 µm, k = 9.2, T = 90%) against mechanical bending with a bending radius of 0.5 mm (bending-induced strain = 5%) during 10 000 bending cycles and a frequency of 0.5 Hz. After 10 000 bending cycles, the k value of this film was maintained constantly with negligible reduction (3.2% decrease) from the initial k value of 9.2, which indicated that the embedded AgNFs sustained their formation within the CNF matrix against this bending deformation, thereby exhibiting the outstanding flexibility of this high-k film. In addition to the mechanical properties, thermal stability also is an important factor to determine the reliable operation of flexible electronic devices. In contrast to rigid glass layers with a low CTE (CTE < 10 ppm K⁻¹), most plastic films for flexible electronics, such as PET, PI, PC, and polyethylene naphthalate, have relatively high CTEs, i.e., exceeding 50 ppm K⁻¹. The difference in CTE between the plastic films and the components of a device that contain multiple inorganic layers of metals or ceramics induces thermal stress to the device region during thermal fabrication processing or long-term device operations with repetitions of thermal cyclic loading-unloading, which can lead to device failure and degrade their reliability eventually. Thus, relatively low thermal expansion, high k values, and good mechanical robustness are desirable properties for the protective cover layers of flexible TSPs. Figure 4c shows that the AgNF-embedded film (k = 9.2, T = 90%) had an extremely low CTE value of 8.4 ppm K⁻¹, which was comparable to the levels of conventional glasses (CTE of 9 ppm K⁻¹) or pristine CNF-epoxy hybrid film (CTE of 8.3 ppm K⁻¹). The similar, low thermal expansion properties of Ag and CNFs and the minimal content of epoxy can result in this low CTE value of the AgNF-embedded CNF-epoxy hybrid film.

The AgNP-, AgNW-, and AgNF (aspect ratio = 700)-embedded CNF-epoxy hybrid films (with the same thickness of 50 µm) were applied as the protective cover layer of flexible, capacitive TSPs in order to compare their sensitivities to touch (Figure 5). The basic principle of capacitive touch sensing is to detect the changes in mutual capacitance between the intersections of the X–Y electrodes. When a conductive object, such as a human finger or a conductive stylus, approaches the intersections, the fringing electric field above the intersections is disturbed.
because the object disturbs some charges from the initial $C_0$ (Figure 5a). In the capacitive TSP, the impact of the $k$ value of the protective cover layer on the sensor’s sensitivity can be described theoretically by Equation (1)[46]

$$T_v = \frac{t}{k} \quad (1)$$

where $T_v$ is the thickness of the vacuum for an electric field conduction equivalent to that of the protective cover layer that has the thickness and dielectric constant of $t$ and $k$, respectively. Here, $1/T_v$ is proportional to touch sensitivity, and the $k$ value ($=1/T_v$) also has a linear relationship with touch sensitivity. To verify this linear relationship between $k$ and touch sensitivity, we measured the sensitivity of capacitive TSPs experimentally according to different $k$ values of the protective cover layers. After integrating these three different types of cover layers ($k$ of the AgNP sample = 4.0; $k$ of the AgNW sample = 5.5; and $k$ of the AgNF sample = 9.2) on the capacitive TSPs, the change in capacitance ($\Delta C$) attributed to finger touch was measured by a TSP inspection system, as shown in Figure 5b. Figure 5c shows the sensing performance, which was visualized by measuring the relative change in capacitance ($\Delta C/C_0$), which also can be referred to touch sensitivity

Relative change in capacitance, $\frac{\Delta C}{C_0} (%) = \frac{(C_0 - C_{\text{touch}})}{C_0} \times 100\% \quad (2)$

where $C_0$ is the reference capacitance, and $C_{\text{touch}}$ is the capacitance when the finger is touched. Figure 5c shows that $\Delta C$ is nearly zero ($C_0 = C_{\text{touch}}$) with no finger touch, while the finger touch leads to decreased capacitance. For the multitouch function, both coordinates, i.e., (X11, Y12) and (X16, Y8), were touched simultaneously, and the sensor detected the touch signal accurately at the corresponding location (Figure 5c and Figure S10, Supporting Information). In the 2D mapping images of Figure 5c, (X11, Y8) and (X16, Y12) are undesirable electrical artifacts that present negative values of $\Delta C$; these artifacts are called signal retransmissions in capacitive multitouch sensors, and these unintended positions can be ignored by designing the program to detect only positive values of $\Delta C$.[47] Among these three films (AgNP-, AgNW-, or AgNF-embedded films), the AgNF sample with the highest $k$ showed the largest change in capacitance ($\Delta C/C_0$: 62%), while the AgNW-CNF and AgNP-CNF films showed changes of 36% and 24%, respectively. (The pristine CNF-epoxy hybrid film and the AgNF (aspect ratio = 350)-embedded sample showed $\Delta C/C_0$ of 20% and 52%, respectively, as indicated in Figure S10, Supporting Information.) Figure 5d shows that there was a linear relationship between touch sensitivity ($\Delta C/C_0$) and $k$ of the cover layer. A large change in capacitance is desirable for highly sensitive TSP operations so that the noise in sensing systems can be disregarded. Figure 5e shows the AgNF-embedded (aspect ratio = 700) film attached to a commercial smartphone as the protective cover layer after the original glass cover was removed.

In conclusion, the work described here demonstrated the fabrication of transparent and flexible CNF films with high $k$ values by incorporating ultralong metal nanofibers. Aligned arrays of these metal nanofibers were produced continuously by electrospinning a suspension of metal nanoparticles onto a rotating drum collector, and their lengths were controlled by a stretching method for cracking these aligned fibers. Embedding these metal nanofibers into cellulose hybrid films resulted in transparent films with significantly high $k$ values (above 12.9), compared to the $k$ values of conventional glasses and plastics. Also, the remarkable mechanical and thermal stabilities of the cellulose hybrid films made them suitable for use as the protective cover layers of flexible and sensitive TSPs in wearable electronic devices that are exposed to diverse outdoor activities. We believe this approach provides a promising strategy for next-generation, wearable electronics.

**Experimental Section**

Experimental details are given in the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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