

PREPARATION AND PROPERTIES OF CELLULOSE / CARBON NANOTUBE COMPOSITE PAPER

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Introduction

Carbon nanotubes (CNTs) have attracted a lot of attention due to their unique properties. Several studies describe CNT composite materials prepared by dispersing carbon nanotubes in an insulating matrix. These composite materials have some outstanding properties, such as being highly strong, conductive, thermally conductive, and the usage of these materials have been widely investigated [1].

We have been examining them in order to prepare carbon nanotube and paper composite materials by using a papermaking process, and developing applications for this composite paper. In this paper, we will report on our preparation methods and the basic properties of CNT/cellulose composite paper.

Experiments

Material and method

Multi-walled (MW) CNTs were provided by Nanocyl S.A. (Nanocyl 7000). The average diameter of the CNTs was 10 nm, and their average length was 1.5 μm . CNT dispersion was provided by Daido Corporation. An anionic surfactant was used to disperse the CNTs [2], and the CNT concentration was 1%.

Bleached hardwood Kraft pulp (50-wt%) and bleached softwood Kraft pulp (50-wt%) were dispersed in water and beaten using a Tappi standard niagara beater until a freeness of 500 ml was obtained. Then, a 2%-cationized starch (Neotack L-1, from Nihon Shokuhin Kako Co.,Ltd.) water solution was added as a fixer to the pulp, then mixed with the CNT dispersion. Hand-made CNT/cellulose composite paper was prepared using 25 \times 25 cm wire cloth.

As control materials, carbon black (Mitsui Chemicals #41) and carbon fiber (Kureha C-103T) were used instead of CNT to produce composite papers. Plain paper was also prepared in the same way.

Measurements

The tensile strength of the paper was measured in accordance with JIS P 8113 using a tensile tester (Kumagaya Riki Kogyo Co. Ltd.). A four-point contact method was used to determine the electrical conductivity using a Mitsubishi Chemistry Loresta MCP-HT450 in accordance with JIS K7194.

The scattering (S) parameters for the CNT/cellulose composite paper were measured using a vector network analyzer (VNA) at a bandwidth of 67 GHz (Agilent E8361C) and a K-band (18–26.5 GHz) waveguide. A sample piece of paper was inserted in the waveguide. The permittivities of the paper were extracted from the measured S parameters using material measurement software (Agilent 85071E).

Results and discussion

The cellulose fibers had negative charges on their surfaces when dispersed in water. This is due to the carboxyl groups that were generated during the papermaking process, such as cooking or bleaching [3]. Chemicals are usually fixed to cellulose fibers in the paper manufacturing using this electrical charge. When anionic surfactant is used to disperse the CNTs, the surfaces of the CNTs also have negative charges. Therefore, a cationic fixer can be applied to fix the CNTs to the cellulose surfaces. SEM images of the CNT/cellulose are shown in Figure 1. No CNT aggregations were found on the surface of paper (1), and carbon nanotubes can be found on the surfaces of the cellulose fibers connected to each other for paper (2) in the figure. The CNTs easily aggregate due to their Van der Waals' force, so it is important to prevent them from self-agglomerating before bonding with the cellulose. These images show the good interaction between the cellulose fibers and CNTs during the papermaking process.

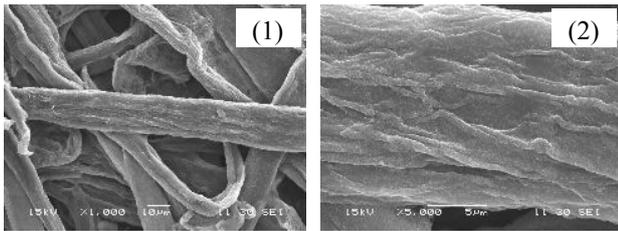


Fig. 1 SEM images of CNT/cellulose composite

The surface resistivities and tensile strengths of each paper are listed in Table 1. When the CNT content was below 5%, the tensile strength of the CNT/cellulose composite paper was almost the same as plain paper. Compared to other carbon materials, the CNT has a lower resistivity with a much smaller loading amount. So, CNTs interfere less with the formation of hydrogen bonding between cellulose fibers, resulting in a highly strong paper.

Figure 2 shows the measured conductivity dependence on the CNT content for CNT/cellulose composite papers. In addition, the conductivities of carbon black (CB)/cellulose and carbon fiber (CF)/cellulose composite papers are shown for comparison. This figure also includes the conductivities for the CNT/polymer composites reported in previous literatures. In the range from 1 to 5-wt% of CNT content, CNT/cellulose composite paper has the highest conductivity ever reported. Figure 3 summarizes the permittivity as a function of the frequency with those reported in previous literatures. In the microwave region, CNT/cellulose composite paper has the highest level. The reason for this high conductivity and permittivity values for composite paper are attributed to the unique network configuration in the paper. CNT creates a conductive nano-network on the cellulose fibers, and the fibers also create networks throughout the entire paper. These two levels of conductive networking result in a higher level of conductivity with only a slight amount of CNT additive.

Table 1 Properties of composite papers

| Material | Content (wt%) | Surface resistivity ($\Omega/\text{sq.}$) | Tensile strength (N/m) |
|--------------|---------------|---|------------------------|
| CNT | 1.0 | 4.51×10^2 | 6.33 |
| | 4.8 | 2.89×10 | 6.40 |
| Carbon black | 23.0 | 4.21×10^2 | 2.03 |
| Carbon Fiber | 30.0 | 4.61×10^2 | 3.20 |
| Plain paper | - | - | 6.33 |

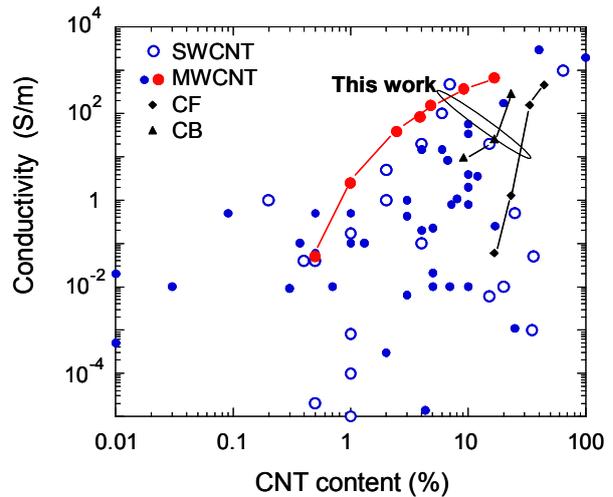


Fig. 2 Measured conductivity dependence

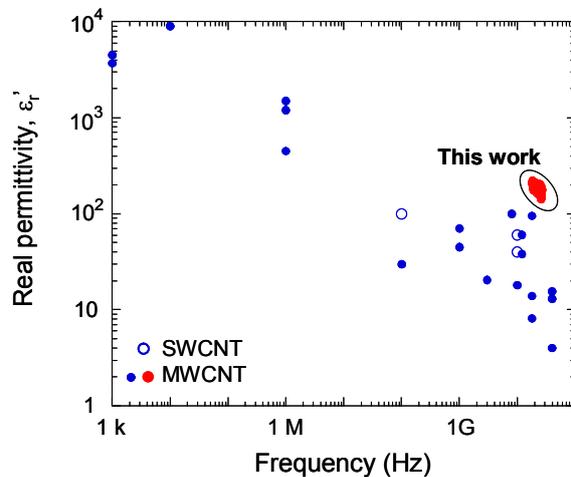


Fig. 3 Real permittivities as function of frequency

Conclusion

We fabricated CNT/cellulose composite papers using a papermaking process. Higher electric conductivity and permittivity values were achieved compared to polymer-based composite materials. This is attributed to the unique CNT network configuration of composite paper.

References

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