Conducting Paper Sheet Made of Polypyrrole, Pulp Fiber and Cellulose Nanofiber Toward Electrodes for Electronic Paper

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ABSTRACT

We have prepared conducting paper sheets made of polypyrrole, pulp fiber and cellulose nanofiber that utilize polypyrrole as conducting parts and pulp/cellulose nanofibers as flexible part. The sheets have a potential that can be utilized as back electrodes for electronic paper.

1 Introduction

There has been an increasing interest in conducting paper sheets, which is low cost and can be mass produced, in the field of printed electronics. Conducting paper sheets have been used as a substrate for electronic devices.

Beneventi *et al.* prepared conducting paper composite of polypyrrole with cellulose fibers [1]. In this preparation, there are problems such as high cost and time-consuming due to the multi-step synthesis process. As a simple and novel method, we have prepared the composite of polypyrrole with pulp fibers [2] instead of cellulose fibers. In this approach, the pulp fibers act as a high surface area substrate for the precipitating polypyrrole. Then, we reported the characterization of the sheets made of the polypyrrole-pulp fibers and discussed the applications of these sheets in the field of electronic paper.

However, the electrical conductivities of these composites were not enough to be applied in the field of electronic papers. We think that the improvement of the conductivities could be possible by adding cellulose nanofiber (CNF) to the composite of polypyrrole and pulp fibers. In the present work, we report the preparation of composites made of polypyrrole, pulp and CNF, and their higher conductivities relative to those of the composite prepared in the absence of CNF previously reported.

2 Experiment

2.1 Preparation of Conducting Paper Sheets made of Polypyrrole-Pulp-CNF Fibers

The polypyrrole-pulp-CNF fibers were prepared as follows: 0.30 g (dry weight) pulp fibers (Daio paper corp., elleair toilet tissue) and 0, 1.67, 8.33, and 16.67g (dry weight) CNF (Daio paper corp. ELLEX-S(A), 3% in water) were added to a solution of FeCl₃ (4.55 g) in de-ionized water (total solvent volume = 50 ml) at 25 °C with constant

stirring. Pyrrole (0.5 ml) was then injected via syringe into this stirred solution turned black within 5 minutes. The polymerization was allowed to proceed for 2 hours. This reaction mixture was then centrifuged at 16500 r.p.m. for 30 minutes. using a ASONE AS165W instrument and the resulting black sediment was redispersed in de-ionized water using an ultrasonic bath.

Conducting paper sheets were then made by mixing and drying the polypyrrole-pulp-CNF fibers using a dry oven (MASUDA SA31 DRYING OVEN) at 50°C, 12 hours. The sheets were cut in a round shape (3 cm of diameter).

2.2 Characterization of Conducting Paper Sheets made of Polypyrrole-Pulp-CNF Fibers

The surface electrical resistances of the sheets were measured using DIGITAL MULTIMETER (Sanwa Electric Instrument Co., Ltd.; CD770) Scanning electron microscopy (SEM) studies were made on the conducting paper sheets made of polypyrrole-pulp-CNF fibers using a (JEOL Ltd., JCM-6000Plus NeoScope) instrument at an operating voltage of 10 kV. The chromaticity studies of these sheets were carried out using a spectrophotometer (X-Rite 962). Results and Discussion.

2.3 Electrical conductivities of the paper sheet

The electrical conductivities of the paper sheets made of polypyrrole-pulp-CNF fibers are summarized in Table 1. The electrical conductivities of the paper sheets containing CNF are much higher than that without CNF. We confirmed that CNF improved the electrical conductivity on these paper sheets dramatically.

 Table 1 Electrical conductivities of the paper sheets

 made of polypyrrole-pulp-CNF fibers

Sheet No.	Initial Content			surface
	Pyrrole	Pulp	CNF	electrical
	(ml)	(g)	(g)	resistance(Ω)
No.1	0.5	0.3	0	3000
No.2	0.5	0.3	1.67	44
No.3	0.5	0.3	8.33	7.5
No.4	0.5	0.3	16.67	9.7

2.4 Surface morphologies of the paper sheet

The scanning electron micrograph depicted in Fig.1(a) and (b) are of No.1(in the absence of CNF) and No.4(in the presence of CNF) in Table 1, respectively.

Clearly the surface of the paper sheet made of polypyrrole-pulp-CNF fibers (No.4) is denser than that of the paper sheet made of polypyrrole-pulp fibers (No.1). In other words, the surface area of the fiber component required for adsorption of polypyrrole is larger on the paper sheet made of polypyrrole pulp-CNF fiber (No. 4) than on the paper sheet made of polypyrrole pulp fiber (No. 4) than on the paper sheet made of polypyrrole pulp fiber (No. 1). The smaller fiber of CNF relative to the conventional pulp fiber produces the larger surface area of CNF. Thus, the reason for the decrease in electrical resistance (the increase in electrical conductivity) by the addition of CNF is considered to be the adsorption of a sufficient amount of polypyrrole on the large surface area due to CNF.

We have also observed, in the presence of CNF, that polypyrrole is uniformly coated on the surface of the fibers, while, in the absence of CNF, polypyrrole is easily peeled off from the fibers. Presumably, the addition of CNF improves the adhesive strength between polypyrrole and fibers.



Fig. 1 SEM observations for (a) No.1(in the absence of CNF) and (b) No.4(in the presence of CNF)

2.5 Application Toward Electrodes for Electronic Paper

The chromaticity diagram of conventional pulp sheet and polypyrrole-pulp-CNF sheet is presented in Fig.2. Although the colors of conventional pulp sheet and polypyrrole-pulp-CNF sheet are both achromatic, their brightness is opposite. The polypyrrole-pulp-CNF sheet is very black. These results indicate that the polypyrrolepulp-CNF sheet has potential to be utilized as black flexible electrode.

We are trying to use the polypyrrole-pulp-CNF sheet as electrodes for electronic paper because it is flexible and electrically conductive. For example, we have already demonstrated that the twisting ball which is one of electronic paper systems works when using the polypyrrole-pulp-CNF sheet as electrode at the applied voltage of 30 V [3]. Especially the black color of the polypyrrole-pulp-CNF sheet suggest that it is applicable for back electrode for electronic paper devices including cholesteric liquid crystal displays.



Fig. 2 Chromaticity diagram of conventional pulp sheet and polypyrrole-pulp-CNF sheet

3 Conclusions

We have prepared polypyrrole-pulp-CNF sheets that utilize polypyrrole as conducting parts, and pulp and CNF as flexible part. We found that the addition of CNF dramatically increases the conductivity of the sheets. The polypyrrole-pulp-CNF sheets could be utilized as electrodes for electronic paper due to its flexibility and conductivity.

References

- D. Beneventi et al., "Polymerization of pyrrole on cellulose fibres using a FeCl3 impregnation- pyrrole polymerization sequence", Cellulose, vol. 13, pp. 725-734 (2006).
- [2] N. Takahashi and S. Maeda, "Conducting Sheet Made of Polypyrrole-Cellulose Fibers Toward Electrodes for Electronic Paper", Proc. IDW '20, pp. 761-762 (2020).
- [3] M. Ozawa and S. Maeda, "Conducting Sheet consists of Polypyrrole and Cellulose Nanofiber", Proc. ICFPE 2021, 2Rm104-08-03 (2021).