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Electrically Conductive Polymeric Membranes by Incorporation of Carbon Nanotubes

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Electrically conductive polymeric membranes were prepared by incorporation of multi-walled carbon nanotubes (MWNTs) onto microbial cellulose membranes cultured by Acetobacter xylinum*. To minimize the damage to the inherent properties of the individual MWNTs induced by the chemical modification, we chose to use a surfactant for the purpose of dispersing MWNTs in water. Sodium dodecylbenzene sulfonate was selected for the process of dispersing MWNTs in water. Using scanning electron microscopy and transmission electron microscopy, the individual MWNTs were found to strongly adhere to the surface and the inside of the cellulose membrane. We also investigated electrical conductivity of the cellulose membranes containing well-dispersed MWNTs.*

Keywords: adsorption; cellulose membranes; electrical conductivity; multi-walled carbon nanotubes; surfactant

INTRODUCTION

Improving the electrical conductivity of bulk polymers is important in a number of applications. For example, static electrical dissipation is needed in applications such as computer housings and exterior automotive parts [1,2]. By introducing small amounts of carbon nanotubes

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(CNTs) into the polymers, the mechanical strength, electrical conductivity, and thermal conductivity of polymer composites can be improved tremendously compared with those of the pristine polymer [3–6]. However, since CNTs are extremely flexible and possess a high aspect ratio, it is extremely difficult to disperse them using ordinary composite fabrication methods. CNTs generally form stabilized bundles due to van der Waals forces, resulting in the formation of hollow ropes [3]. Therefore, obtaining a good dispersion of CNTs is known to be one of the key issues involved in using CNTs in composites [3,4]. In order to optimize this process, the dispersion of CNTs in the polymer matrix has been studied from different points of view, including both the non-covalent and covalent functionalization of the CNTs [5,6].

In this work, CNTs were incorporated uniformly into the microbial cellulose membranes using an aqueous CNT dispersion with a surfactant. *Acetobacter xylinum* bacteria are known to produce cellulose extracellularly. This microbial cellulose is expected to become a new industrial material, because of its unique structure and properties in terms of its purity and high crystallinity [7,8]. To minimize the damage to the inherent properties of the individual MWNTs induced by the chemical modification, we chose to use a surfactant for the purpose of dispersing the MWNTs in water. We also investigated the morphology and electrical conductivity of the cellulose membranes containing well-dispersed MWNTs.

EXPERIMENTAL

Preparation of Microbial Cellulose Membranes

Acetobacter xylinum was used to produce the microbial cellulose membranes. Hestrin & Schramm (HS) medium was selected as the most suitable medium for this microorganism. The stationary culture method was adopted to harvest the cellulose membranes. The cells used for inoculation were cultured in a test tube containing 5 mL of HS medium at 30°C for $3 \sim 4$ days. All of the cells pre-cultured in the test tube with a small cellulose membrane on the surface of the medium were inoculated into a 500 mL Erlenmeyer flask containing 100 mL of HS medium. Culturing was performed in an incubator at 30°C for 14 days. The cellulose membranes were dipped into 0.25 M NaOH for 48 h at room temperature to extract the cells and the pH was then lowered to 7.0 by repeated washing with distilled water. The purified cellulose was stored in distilled water at 4°C to prevent drying.

Preparation of MWNT Dispersion

The MWNTs (Iljin Nanotech Co., Korea) were synthesized by the thermal chemical vapor deposition (CVD) method. The purity of the as-received pristine MWNTs was 97%. In order to eliminate the impurities present within them (such as metallic catalysts), the MWNTs were treated in 3 M HNO_3 at 60°C for 12 h, followed by refluxing in 5 M HCl at 120°C for 6 h. The purity of the acid-treated MWNTs was found to be 99% using thermogravimetric analysis (TGA, Polymer Lab., TGA1000, UK). The purified MWNTs were dispersed in pure water (0.5 mg/mL) with a sodium dodecylbenzene sulfonate (NaDDBS) surfactant (0.3 wt% in water). Ultrasound was then applied to the MWNT dispersion using an ultrasonic generator (Kodo technical research Co., Ltd, Japan) with a nominal frequency of 28 kHz and a power of 600 W for 7 h at 25°C.

Characterization

The surface morphology of all of the samples was observed using field emission scanning electron microscopy (FESEM, S-4300, Hitachi, Japan). Transmission electron microscopy (TEM) was performed using a Philips CM 200 unit, operated at an acceleration voltage of 120 kV. The electrical conductivity of the MWNTs-incorporated microbial cellulose membrane was measured by the four-probe method using a picoammeter with an internal voltage source (487, Keithley, USA) and an impedance analyzer (4284A, HP, USA).

RESULTS AND DISCUSSION

The image in Figure 1 shows the microbial cellulose membrane cultivated for 2 weeks using glucose as the sole carbon source. The

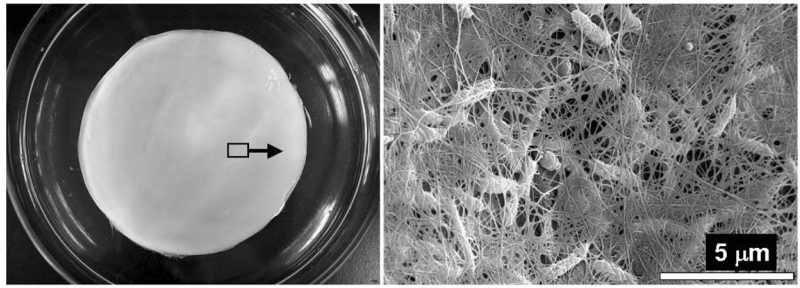

FIGURE 1 Image of microbial cellulose membrane cultured for 2 weeks (left) and FESEM image of freeze-dried surface of microbial cellulose membrane (right).

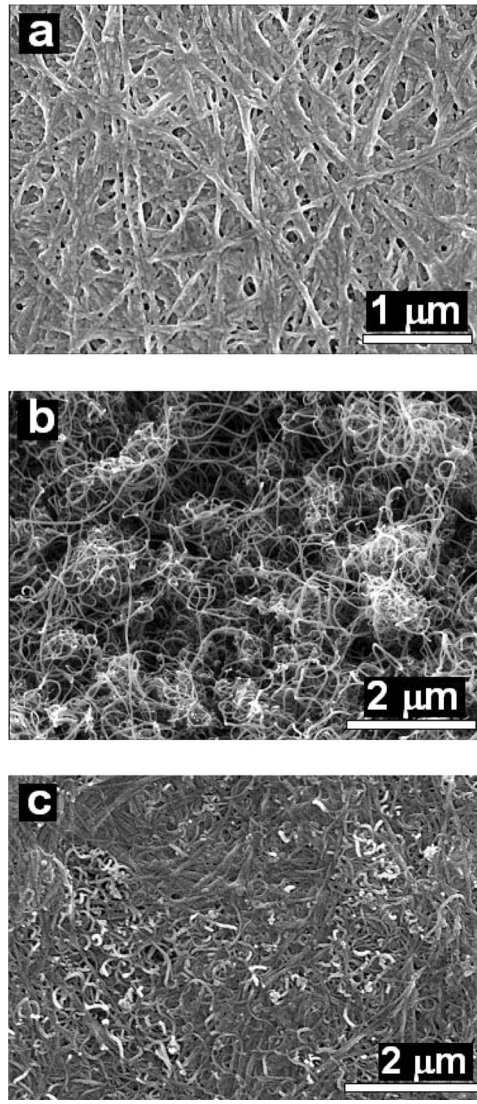

FIGURE 2 FESEM images of (a) vacuum-dried microbial cellulose membranes, (b) purified MWNTs and (c) MWNTs-incorporated microbial cellulose membrane.

water-swollen cellulosic gel was shown to comprise a random assembly of microfibrils with a diameter of about 10 nm by the analysis of the FESEM image of the freeze-dried gel surface shown in Figure 1. After extracting the cells in 0.25 M NaOH solution for 48 h, the yellowish

cellulose membrane turned into the white one shown in Figure 2(a). The cellulose membrane had a kind of non-woven nanofibrous membrane structure.

The MWNTs were sonicated in aqueous solutions of NaDDBS surfactants to stabilize them against van der Waals attraction. The optimum concentration of surfactant was approximately 0.3 weight % in case of the 0.05 wt % dispersion of MWNTs. At the optimum concentration of the surfactant in aqueous solution, the homogeneous dispersion of MWNTs formed a single phase. Once a homogeneous aqueous dispersion of MWNTs was obtained, the water-swollen gel-like microbial cellulose was dipped in a bath containing the MWNTs dispersion with NaDDBS for 24 h, withdrawn, rinsed several times in a deionized water bath so that the surfactants were desorbed, and air-dried at room temperature overnight. The morphology of the MWNTs-incoporated cellulose membrane was observed using FESEM (Fig. 2(c)). The MWNTs were densely embedded on the surface of the cellulose membrane. The TEM image provided strong evidence of the interaction between the cellulose membranes and MWNTs, even after sonication for 24 h in water (Fig. 3), although the exact mechanism of their interaction is uncertain.

We measured the electrical conductivity of the MWNTs-incoporated cellulose membrane. The four-probe electrical measurements of the membrane gave a DC conductivity (σ_{DC}) at room temperature of about

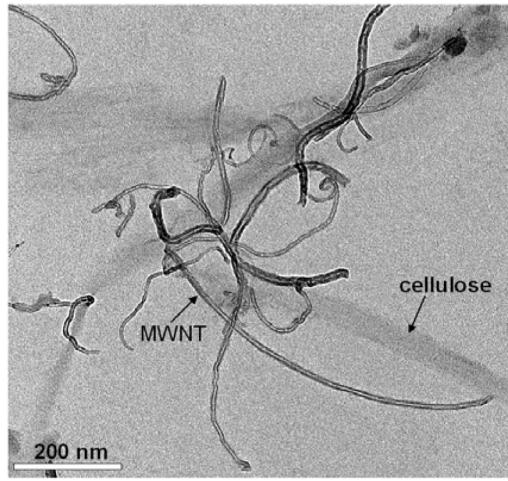

FIGURE 3 TEM images of the MWNTs-adsorbed microbial cellulose after sonication in water for 24 h.

4.2×10^{-1} S/cm. It should be pointed out that most of the MWNTs were well-dispersed in the cellulose membranes, although the porosity of the non-woven nanofibrous cellulose membranes may have contributed to the lowering of the electrical conductivity. It should also be noted that the electrical conductivity of the pure MWNTs used in this study is about 2.3×10^{1} S/cm. We attempted to determine the amount of MWNTs incoporated in the cellulose membrane using thermogravimetric analysis (TGA) under a nitrogen atmosphere. However, this measurement was unsuccessful, because the cellulose membrane charred after burning at temperatures of up to 600°C and did not decompose completely [9].

CONCLUSIONS

We prepared MWNTs-incoporated microbial cellulose membranes by effectively dispersing the MWNTs by dipping the cellulose membrane in the aqueous MWNT dispersion with NaDDBS surfactant. This composite process produced an electrically conductive polymeric membrane with well-dispersed and embedded MWNTs within the cellulose membranes as observed by electron microscopy. The electrical conductivity of the cellulose/MWNT composite membranes was measured by the four-probe method at room temperature and was found to be about 4.2×10^{-1} S/cm, although the porosity of the cellulose membrane may have caused this value to be reduced. It was found that the adsorption process was a useful method not only of dispersing the MWNTs in the non-woven nanofibrous membranes, but also of enhancing the electrical conductivity of the polymeric membranes.

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