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Morphology and Pore Characteristics of Bacterial Cellulose/Multiwalled Carbon Nanotube Composite Cryogels

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Bacterial cellulose/multiwalled carbon nanotube (MWCNT) composite cryogels were prepared via sol–gel chemistry using epichlorohydrin as a crosslinker. Their morphology and pore characteristics were examined under various conditions. The bacterial cellulose/MWCNT composite cryogels had a macroporous structure that contained mesopores and micropores due to the MWCNTs that were homogeneously incorporated in the macroporous network structure.

Keywords: Multiwalled Carbon Nanotube, Cryogel, Bacterial Cellulose, Porosity.

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1. INTRODUCTION

Aerogels are highly porous materials that are filled with air within their network structure. They have many interesting properties, such as a high surface area, an extremely low density, and low heat conductivity. These novel characteristics give them good application potentials in various fields, such as as adsorbents, heat insulators, and catalysts.[1–3] Aerogels are normally prepared using sol–gel processes with an organic or inorganic precursor and special drying methods, such as supercritical drying or freeze-drying.[3] Resorcinol-formaldehyde (RF) and phenolic-furfural (PF) aerogels are well-known organic areogels.[4, 5] The precursors for preparing organic aerogels are not cost-effective enough, though, for their widespread use. Aerogels that were prepared using freeze-drying are known as cryogels. Freeze-drying is a more economical and practical as well as a relatively milder method than supercritical drying.

In this study, bacterial cellulose/multiwalled carbon nanotube (MWCNT) composite cryogels were prepared via sol–gel chemistry using epichlorohydrin as a crosslinker. The bacterial cellulose/MWCNT composites were produced using *in situ* methods, wherein bacterial cellulose was dissolved in an NaOH/urea/water solvent system[6] with pre-dispersed MWCNTs. According to the quantity of the MWCNTs and the bacterial cellulose, the morphology of the bacterial cellulose/MWCNT composite cryogels were microscopically changed, as were their pore characteristics from a macroporous (>50 nm, IUPAC) structure to a macroporous structure that contained mesopores (2–50 nm, IUPAC) and micropores (<2 nm, IUPAC). These porous materials have many advantages in many fields according to their pore type. Therefore, bacterial cellulose/MWCNT composite cryogels with a range of morphologies and pore characteristics according to their pore type will be useful in many fields.

2. EXPERIMENTAL DETAILS

2.1. Materials

Bacterial cellulose pellicles were prepared using a procedure reported in an earlier study.[7] The MWCNTs (purity: 95%, from Iljin Nanotech, Korea) were produced via thermal chemical vapor deposition (CVD). The as-received MWCNTs were treated with acid to remove impurities such as metallic catalysts, using a procedure that was reported in an earlier study.[8]

2.2. Preparation of the Bacterial Cellulose/MWCNT Solution

A certain quantity of the acid-treated MWCNTs was predispersed in distilled water using an ultrasonic generator (Kyungill Ultrasonic Co., Korea). The bacterial cellulose pellicles in distilled water were cut into pieces and then disintegrated using a homogenizer. The water in the bacterial cellulose was squeezed out softly, after which the bacterial cellulose was immediately immersed in a mixture of

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NaOH, urea, distilled water, and MWCNTs that had been pre-cooled to −6 °C for 2 h and stirred for approximately 5 min at ambient temperature.

2.3. Gelation of the Bacterial Cellulose/MWCNT Solution

Epichlorohydrin was used as a crosslinker for the gel formation of the bacterial cellulose/MWCNT solutions. A certain amount of epichlorohydrin was slowly injected into the solutions with vigorous stirring at 2,500 rpm. The bacterial cellulose/MWCNT solutions that had a certain amount of epichlorohydrin were then moved into a 60 °C oven and aged overnight.

2.4. Preparation of the Bacterial Cellulose/MWCNT Cryogels

The bacterial cellulose/MWCNT gels were placed in a distilled water bath to remove their solvents. The water was periodically changed and then flash-frozen in liquid nitrogen (−196 °C) for a few seconds to freeze the liquid. The resulting mixture was immediately freeze-dried in a lyophilizer (LP3, Jouan, France) at −50 °C and 0.045 mbar for 48 h.

2.5. Characterization

The morphologies of the bacterial cellulose/MWCNT composite cryogels were observed via field emission scanning electron microscopy (FESEM, S-4300SE, Hitachi, Japan) at an accelerating voltage of 15 kV after the samples were pre-coated with a homogeneous Pt layer via ion sputtering (E-1030, Hitachi, Japan). The presence of MWCNTs in the pore structure was examined via transmission electron microscopy (TEM, CM200, Philips, Netherlands) at an accelerating voltage of 100 kV.

The porous properties were analyzed from the nitrogen adsorption–desorption isotherms that were obtained using a surface area and porosimetry analyzer (ASAP 2020, Micromeritics, USA) at −196 °C. Then the Brunauer-Emmett-Teller (BET) surface areas (S_{BET}) were calculated. The micropore surface area (S_{mic}) and the micropore volume (V_{mic}) were obtained using the *t*-plot theory. The mesopore surface area (S_{mes}), the mesopore volume (V_{mes}), and the mesopore diameter (D_{mes}) were calculated using the Barrett-Johner-Halendar (BJH) theory.

Table I. Reaction conditions for the bacterial cellulose and the bacterial cellulose/MWCNT composite cryogels.

Sample name	Solution (g)	Concentration (wt%)	ECH volume (ml)	MWCNTs (wt%)
Gel-1	30	0.5	3	0.1
Gel-2	30	0.5	3	1
Gel-3	30	1	3	0.1
Gel-4	30	1	3	1

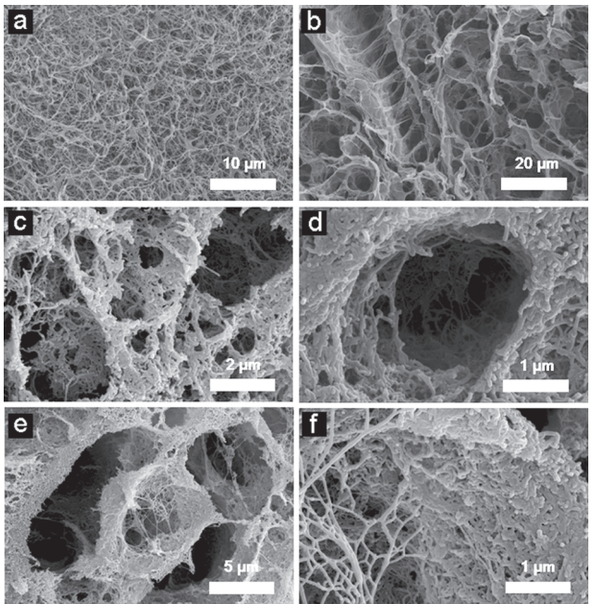

Fig. 1. SEM images of the bacterial cellulose/MWCNT composite cryogels: (a) Gel-1, (b) Gel-3, (c) and (d) Gel-2, and (e) and (f) Gel-4.

3. RESULTS AND DISCUSSION

In this study, bacterial cellulose/MWCNT composite cryogels (BCMCCs) with different quantities of MWCNT and bacterial cellulose were prepared.

Table I shows the conditions under which the samples were prepared. There were two variables. One was the concentration of the bacterial cellulose, and the other was the quantity of the MWCNTs.

Figures 1(a and b) show a SEM image of the bacterial cellulose cryogels with 0.1-wt% MWCNTs. The macroporous structures of both Gel-1 and Gel-3 were virtually unaffected by the MWCNTs that were incorporated in the cryogels. It was difficult to find the MWCNTs that were incorporated in the cryogels because most were embedded in the network structure. Figures 1(c–f) show SEM images of the bacterial cellulose cryogels with 1-wt% MWCNTs. Totally dense macroporous structures, unlike those of the bacterial cellulose cryogels without MWCNTs, were

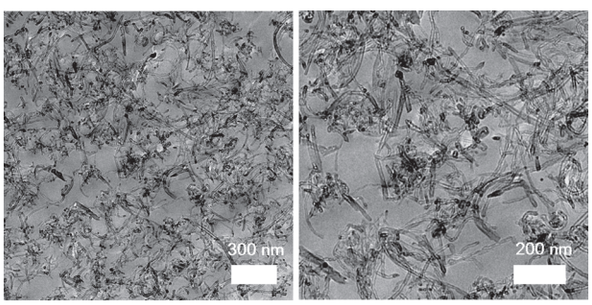

Fig. 2. TEM images of the bacterial cellulose/MWCNT composite cryogel with 1-wt% MWCNTs.

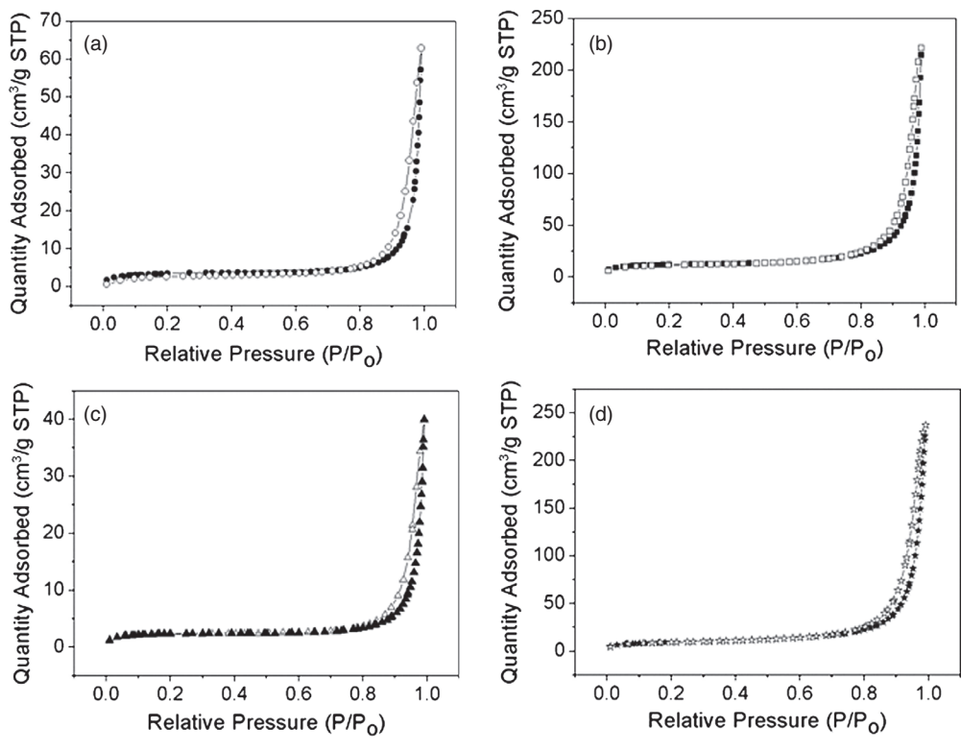

Fig. 3. Nitrogen adsorption–desorption isotherms of the bacterial cellulose/MWCNT composite cryogels: (a) Gel-5, (b) Gel-6, (c) Gel-7, and (d) Gel-8.

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induced by the large amount of MWCNTs. The MWCNTs homogeneously covered the macroporous network structure.

In the NaOH/Urea/water solvent system, the urea formed an inclusion complex (IC) of bacterial cellulose. The urea encased the bacterial cellulose macromolecules at a low temperature.[9] Had the bacterial cellulose been dissolved in the NaOH/Urea/water solvent system with homogeneously dispersed MWCNTs, the MWCNTs would have been uniformly dispersed in the IC. Therefore, in the process of gelation, the MWCNTs were physically or chemically incorporated in the network structure of the cryogels. It can thus be said that MWCNTs can be homogeneously incorporated in the inner or outer network structure of cryogels.

The inner morphology of the bacterial cellulose/MWCNT composite cryogels was observed via TEM to confirm the existence of the MWCNTs and to determine how they were embedded in the solid structures (Fig. 2).

The nitrogen adsorption–desorption isotherms revealed the porous properties of the BCMCCs. Their isotherms were similar to those of the IUPAC-type IV with an adsorption hysteresis (H1), which indicated a mesoporous structure produced by agglomerates or compacts of approximately uniform spheres in a fairly regular array (Fig. 3).

Table II shows porous properties of the bacterial cellulose/MWCNT composite cryogels. The pore sizes, which were calculated using the BJH method, approximately ranged from 30 to 44.2 nm. The pore size distribution and surface area of the BCMCCs depended on the quantity

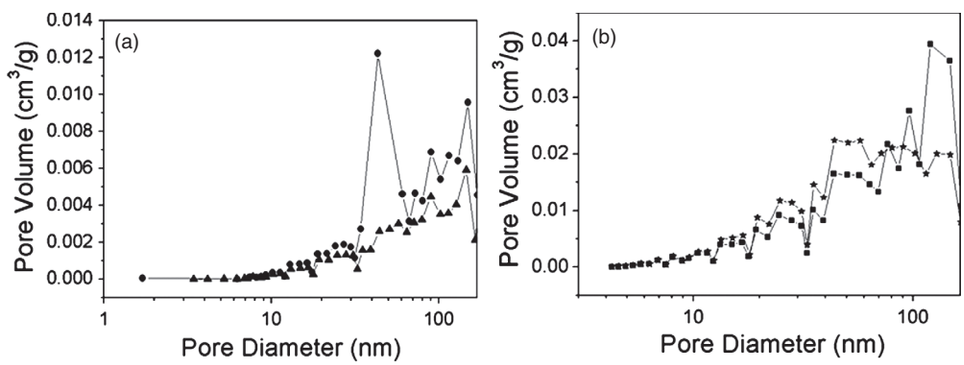

Fig. 4. Pore size distribution of the bacterial cellulose/MWCNT composite cryogels: (a) Gel-5 and Gel-6, and (b) Gel-7 and Gel-8.

Table II. Porous properties of the bacterial cellulose/MWCNT composite cryogels.

	S_{BET} (m^2/g)	S_{Mic} (m^2/g)	S_{Meso} (m^2/g)	D_{Meso} (nm)	V_{Mic} (cm^3/g)	V_{Meso} (cm^3/g)
Gel-1	11.1	2.8	8.3	31.9	0.0017	0.0953
Gel-2	38.4	19.4	19.0	34.7	0.0101	0.3361
Gel-3	7.5	3.8	3.7	30.0	0.0020	0.0601
Gel-4	31.6	6.7	24.9	44.2	0.0034	0.3648

of the MWCNTs. The mesopores and micropores of the bacterial cellulose cryogels that contained 1-wt% MWCNTs were significantly larger than those of the bacterial cellulose cryogels that contained 0.1-wt MWCNTs. Moreover, according to the quantity of the incorporated MWCNTs, the Gel-1 pore size distribution was similar to that of Gel-3, and the pore size distribution of Gel-2 was similar to that of Gel-4 (Fig. 4). In contrast, the bacterial cellulose cryogels without MWCNTs contained only macroporous structures that consisted of small mesopores and micropores with <3 m^2/g surface areas (data not shown).

This suggests that the mesopores and micropores of BCMCCs are induced by the MWCNTs that are incorporated in them, and particularly by the agglomerates rather than the shapes of their incorporated MWCNTs. Overall, it can be concluded that macroporous materials with controlled quantities of mesopores and micropores can be produced by changing the quantity of their incorporated MWCNTs.

4. CONCLUSIONS

Bacterial cellulose/MWCNT composite cryogels were prepared via sol–gel chemistry using epichlorohydrin as a crosslinker. The MWCNTs in the bacterial cellulose/MWCNT composite cryogels were homogeneously incorporated in the macroporous network structure. The nitrogen adsorption–desorption isotherms of the bacterial cellulose/MWCNT composite cryogels were similar to those of the IUPAC-type IV with an adsorption hysteresis (H1), which indicates that a mesoporous structure was formed by agglomerates or compacts of approximately uniform spheres in a fairly regular array. Both the mesopores and micropores of the bacterial cellulose/MWCNT composite cryogels were significantly affected by the quantity of the incorporated MWCNTs. In conclusion, this study showed that macroporous cryogels with mesopores and micropores have potential applications in various fields, such as as scaffolds and catalysts, in adsorption and separation, as electrodes in electro-chemical devices, for sensing, and for various nanotechnologies.

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