

PVA/PAAc/MULTI-WALLED CARBON NANOTUBES COMPOSITE HYDROGELS COATED WITH POLYANILINE AND THEIR ELECTROCHEMICAL ACTUATOR CHARACTERISTICS

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Introduction

One of the primary requirements for designing advanced artificial materials is a change of their properties in response to external stimuli. Materials that can be used as artificial muscles must respond to an electric field, pH, temperature, ionic strength, and/or light with a corresponding change in their shape and size [1]. Recent literature shows an emerging interest in hydrogel-based actuating systems because of their stimuli-responsive behavior [2-4]. However, the poor electrical conductivity of hydrogels results in a poor response time and a high operational voltage limits their applicability in devices.

Carbon nanotubes (CNTs) have attracted much attention recently as a conducting material suitable for use in biomaterial fabrication. The published articles have been doubled each year for the application of CNTs in biomedical applications. However, the aggregation of CNTs in the polymer matrix is always a big problem in the preparation of composites. Electrospun nanofiber can serve as good candidate materials for enhancing the performance of CNT dispersion. Also, electrospun nanofiber templates provide high surface area and porosity, which are ideal for the diffusion of ions. Because nanofibers have stronger mechanical properties compared to the bulk polymer, nanofibrous templates can maintain their mechanical stability despite of their porous structure even in the hydrogel fibrous templates.

Among many materials proposed for actuators, conducting polymers have received considerable attention as promising candidates for actuator design owing to their moderately high actuation strain at low operational voltages below 1V [2,3]. Conducting polymers undergo expansion and contraction during electrochemical redox reactions depending on the cycle of potential due to the exchange of solvated ions with the electrolytes.

Despite of being good candidates for designing actuators, the brittleness and poor elongation at break of conducting polymers limit their practical applicability in devices. Methods to improve the electrical and mechanical properties of conducting polymer-based actuators using CNTs have been proposed. In this study, poly(vinyl alcohol)(PVA)/poly(acrylic acid)(PAAc) hydrogel containing multi-walled carbon nanotubes (MWCNTs) was prepared by electrospun method. And then, to improve the conductivity of the composite hydrogel further, conductive polymers, polyaniline, were

coated on PVA/PAAc/MWCNTs composite hydrogel templates by in situ polymerization. Polyaniline-coated PVA/PAAc/MWCNTs composite hydrogels provide larger surface area, higher porosity for the diffusion of ions, and higher electrical property.

Experimental

PVA was dissolved in deionized water and heated at 90 °C for 6 h to make 20 wt. % aqueous solution. PAAc was dissolved in deionized water at room temperature for 1 h. PAAc solutions were prepared to have 10 wt. % concentration. The mixed aqueous solution of PVA (10 wt. %, 20 ml) and PAAc (10 wt. %, 10 ml) was slowly added to the mixture of GA (1 ml) and ketoprofen (0.5 g) with stirring for 30 min at room temperature. The mixture procedures were replicated with MWCNTs (0.01, 0.05, 0.1 and 0.2 g) in order to vary their electrical conductivity.

The reaction mixture was stirred for 3 h at room temperature. Subsequently, nitrogen was bubbled through the mixture for 30 min to remove the oxygen dissolved in the reaction mixture. The polymer solution was injected into a 30 cm³ syringe having a capillary tip which has a gauge 18 needle (inner diameter: 1.27 mm). Polymer solution was electrospun into a fiber web using an electrospinning system equipped with power supply (NT-PS-25K, NTSEE Co., Korea). Polymer solution was electrospun with following conditions [voltage: 20 kV, syringing rate: 1.5 cm³/h, collector rotation speed: 300 rpm and tip to collector distance: 15 cm]. Electrospinning of hydrogel fibers was carried out at 100 °C for 1 h in air in order to produce a semi-IPN hydrogel polymer structure.

The PANi-coated PVA/PAAc/MWCNTs composite hydrogel was synthesized using in situ chemical oxidative polymerization. In typical synthesis process, PVA/PAAc/MWCNTs composite hydrogel (10 mm (wide) x 50 mm (length) x 1 mm (thick)), aniline monomer, and equal volumes of HCl solution were sonicated for 10min to form uniform suspensions. Then the required amounts of APS were dissolved in HCl solutions separately, and added slowly into the above suspensions to initiate the polymerization. The resulting reaction mixtures were allowed to react for 6 h at 0-4 °C with stirring in order that aniline could be fully polymerized. The synthesized PANi-coated PVA/PAAc/MWCNTs composite hydrogel was separated and rinsed several times with distilled water, acetone, and methanol. The various kinds of PANi-coated PVA/PAAc/MWCNTs composite hydrogel are classified as shown in Table 1.

Table 1. Classification of PVA/PAAc/MWCNTs composite hydrogel and PANi-coated PVA/PAAc/MWCNTs composite hydrogel

Amount of MWCNT (g)	PVA/PAAc/MWCNTs composite hydrogel	PANi-coated PVA/PAAc/MWCNTs
0.01	F1	PCF1
0.05	F5	PCF5
0.1	F10	PCF10
0.2	F20	PCF20

Results and Discussion

The surface morphologies of hydrogel fibers involving MWCNTs were presented in Fig. 1 to investigate the effects of MWCNT additives. The smooth surface was observed in all cases, but the average diameter of hydrogel fibers measured by soft program (installed in SEM apparatus) was decreased as the amount of MWCNT increased. This reduction in diameters originated from the enhanced conductivity of the polymer solution with higher content of MWCNTs. This allows higher electric current during electrospinning and induces higher charge accumulation in the solution jet, resulting in strong electrostatic repulsion among jet sprays. This repulsive force easily overcomes the surface tension of the jet to reduce diameters of the polymer nanofibers.

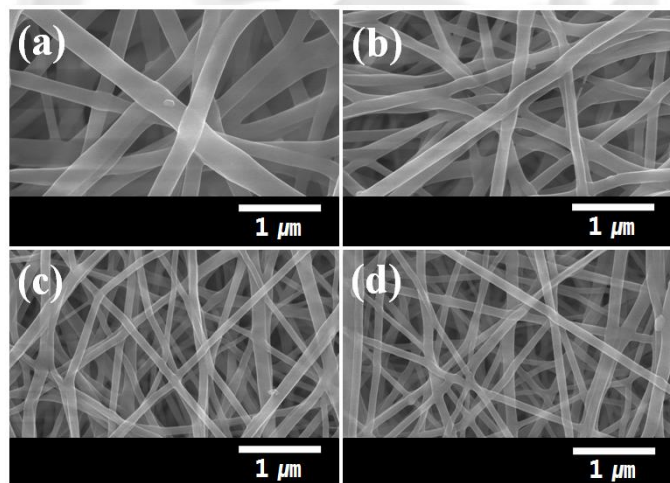


Fig. 1. SEM images of PVA/PAAc/MWCNT composite hydrogel (a) F1, (b) F5, (c) F10, and (d) F20.

The surface morphologies of PANi-coated PVA/PAAc/CNT composite hydrogel were presented in Fig. 2. The cross-section of PANi-coated PVA/PAAc/CNT nanofibers was studied by SEM in order to investigate the polymerization of aniline on the PVA/PAAc/CNT composite hydrogel. The nanowire-typed PANi was synthesized successfully on the PVA/PAAc/CNT composite hydrogel nanofibers without giving any damage on nanofiber templates.

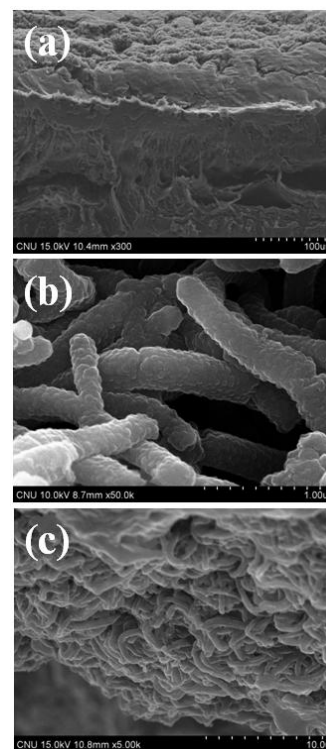


Fig. 2. SEM images of cross-section (a) PANi-coated PVA/PAAc/MWCNT nanofibers, (b) PANi, and (c) PVA/PAAc/MWCNT composite hydrogel.

Conclusions

Poly(vinyl alcohol)(PVA)/poly(acrylic acid)(PAAc) hydrogel containing multi-walled carbon nanotubes (MWCNTs) was prepared using electrospinning method. To improve the conductivity of the composite hydrogel, conductive polymers like polyaniline were coated on PVA/PAAc/MWCNTs composite hydrogel templates by in situ polymerization. The electrical conductivity of composite nanofibers increased by higher amount of MWCNT additives and PANi coating. The bending rate and angle of hydrogel nanofibers increased by PANi coating, CNT addition, and applying voltage.

References

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