Improved electrical properties of poly(vinyl alcohol)-based nanofiber electrolytes

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Multifunctional, chemically and physically reactive polymer blends are used as electrical conductive sites to fabricate self-assembled nanofiber structures.

Poly(vinyl alcohol)—PVA—has excellent film-forming, emulsifying, surfactant, and adhesive properties and is thus commonly used to fabricate unique nanofiber compositions for matrix polymers.[1,2] A wide range of potential nanosized fillers can be used for the preparation of high-performance polymer nanocomposites. For instance, organo-modified montmorillonite (ODA-MMT) is typically obtained from octadecylammonium derivatives to produce well-organized nanocomposites.[3] Pristine PVA, however, exhibits low conductivity levels,[4] and methods to increase the conductivity of matrix-PVA-based composite materials are required.

In several past studies, various functional polymers (as partner polymers), as well as organic and inorganic doping agents, have been investigated as ways to improve the conductivity of PVA-based composites (e.g., for polymer nanofiber composites, NFCs).[5,6] In particular, polymer electrolytes can be used to improve the electrical conductivity of these materials. Polymer electrolytes are supramacromolecular systems that contain ion-charged transport sites and have substantial electrical conductivity levels.[7] The conductivity and thermal resistance of solid polymer electrolytes can be further improved through a number of processes (e.g., chemical crosslinking, grafting, graft copolymerization, various modifications to the polymer backbone and side chains, polymer–polymer interactions, blending with other polymers, and the use of doping agents).[8–12]

In this work,[13] we have used multifunctional, chemically and physically reactive polymer blends as electrical conductive sites to produce self-assembled nanofiber structures. In addition, we have developed a new approach to fabricate polymer nanocomposite complexes. In this technique we use a pre-intercalated reactive PVA/ODA-MMT dispersed solution as a matrix nanocomposite, poly(maleic
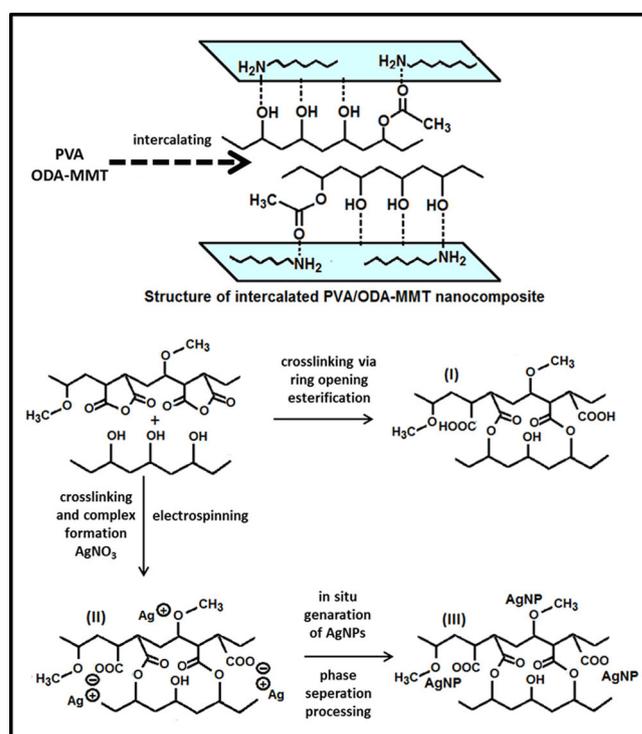

Figure 1. Schematic representation of synthetic pathways and chemistry of the multifunctional nanofiber structures. (I) Intermolecular crosslinking, via ring-opening esterification. (II) Silver (Ag)-carrying crosslinked structure. (III) In situ generation of Ag nanoparticles (NPs) onto polymer chains. PVA: Poly(vinyl alcohol). ODA-MMT: Organo-modified montmorillonite. H_2N/NH_2: Amine group. OH: Hydroxyl group. CH_3/H_3C: Methyl group. O: Oxygen. COOH/HOOC: Carboxylic acid. $AgNO_3$: Silver nitrate.

anhydride-alt-methyl vinyl ether)—poly(MA-alt-MVE)—with a negatively surface-charged solution as a reactive copolymer (partner),
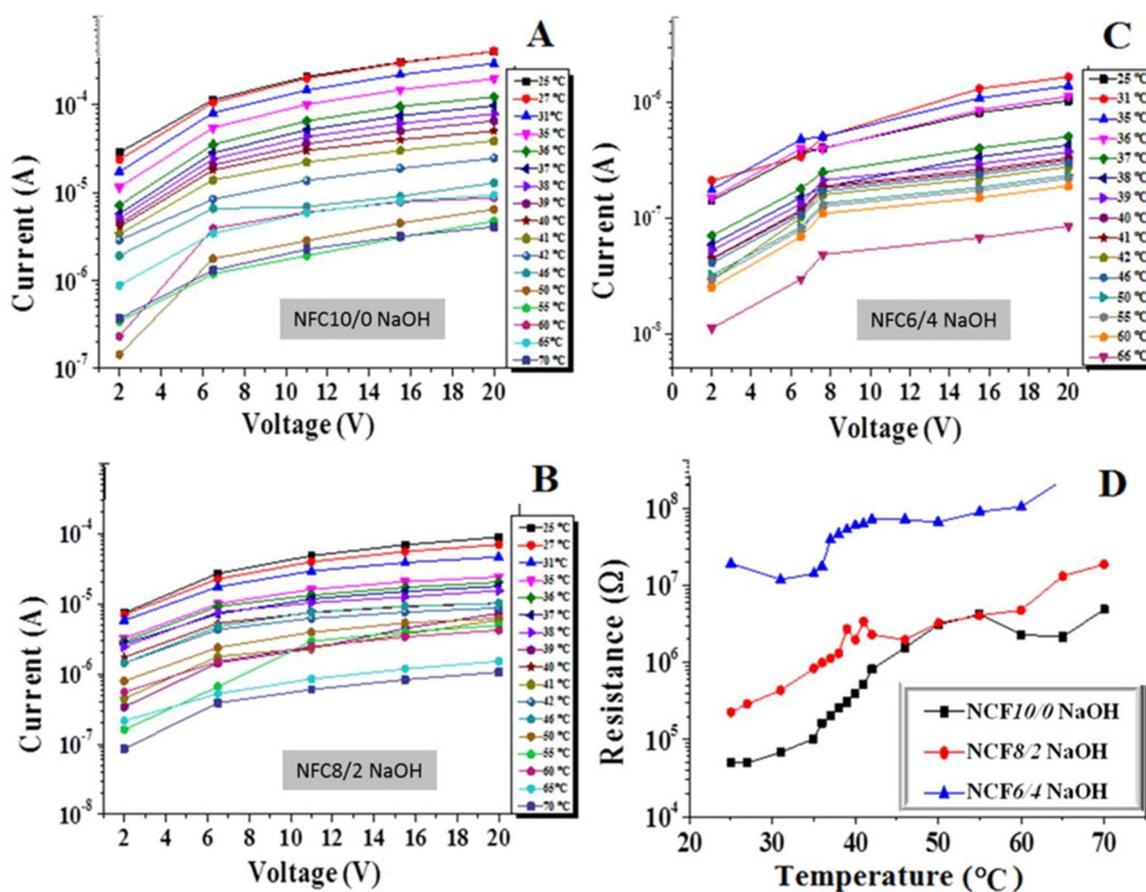
Figure 2. *Plots of current versus voltage for the polymer nanofiber composite (NFC) samples at various temperatures. Results are shown for the NFC samples that contain PVA/ODA-MMT and poly(maleic anhydride-alt-methyl vinyl ether) blended at volume ratios of (A) 10/0, (B) 8/2, and (C) 6/4. These samples were produced with sodium hydroxide (NaOH)-carrying matrix/partner polymer systems. (D) The effect of absorbed NaOH solution on the resistance and conductivity of the fibers, as a function of temperature.*

as well as silver (Ag)- or sodium hydroxide (NaOH)-carrying matrix/partner polymer systems. We have also investigated the electrical properties of our NFCs.

To prepare our matrix/partner polymer composites, we blended the PVA/ODA-MMT and poly(MA-alt-MVE) at various volume ratios (10/0, 8/2, and 6/4). For the preparation of the Ag-carrying matrix/partner polymer complex, we added a given amount of silver nitrate into the polymer complex. We then obtained nanofibers by electrospinning the matrix/partner polymer composites. In addition, we prepared the NaOH-carrying electrospun nanofibers through the absorption of NaOH on the surface of fiber samples in a square shape. The synthetic pathways that we have developed are illustrated in Figure 1.

We measured the current/voltage ratio, i.e., the specific conductivity (σ_{sc}), for the 10/0, 8/2, and 6/4 NFCs (without NaOH) in the 10^{-9}–10^{-11}Scm^{-1} range, at a range of applied currents and voltages.

We find, however, that σ_{sc} of the NFCs increases dramatically to 1.29×10^{-3}, 1.0×10^{-4}, and 2.0×10^{-5}Scm^{-1}, respectively, when they are treated with the NaOH solution for 30 seconds. Moreover, we observe that σ_{sc} depends strongly on absorption time and that the resistance (R) of the NFCs depends on the NaOH absorption time. Indeed, we measure the smallest R for the 10/0 NFC sample and the highest R for the 6/4 NFC sample.

We can also confirm this phenomenon by plotting current/voltage versus temperature, i.e., to estimate direct conductivity (σ_{dc}) values. We have thus estimated (from Figure 2) R values of 6.0×10^{4} ohm, 4.5×10^{5} ohm, and 3.5×10^{7} ohm, as well as σ_{dc} values of 2.4×10^{-4}Scm^{-1}, 4.8×10^{-8}Scm^{-1}, and 7.4×10^{-10}Scm^{-1} for the NFC10/0, NFC8/2, and NFC6/4 samples, respectively. These results indicate that the R

and σ_{dc} parameters strongly responded to changes in the composition and structural factors of our samples. Such factors included the change of colloidal amorphous area, degree of in situ physical and chemical interfacial interactions during electrospinning, diameters, and distributions of NFCs. In particular, the NFC10/0 and NFC8/2 samples exhibit excellent conductivity because of an increase in the number of ionized sites and colloidal amorphous areas after the absorption of NaOH. Our results also indicate that the conductivity of the NFC8/2-Ag sample increased with increasing temperature (from 22 to 50°C) and that its R decreased with the higher applied temperatures. We estimate that the highest conductivity ($5.63\times10^{-9}\,\mathrm{Scm}^{-1}$) and R ($1.56\times10^{-11}$ ohm) values occurred at 22 and 46°C, respectively. Furthermore, when we compare these results to those from pristine PVA, we find that the conductivity of the NFC8/2-Ag sample dramatically increases from $1.25\times10^{-15}\,\mathrm{Scm}^{-1}$ (i.e., for a neat PVA film at room temperature) to 5.63–$5.12\times10^{-9}\,\mathrm{Scm}^{-1}$ in the 22–46°C temperature range.

In summary, we have developed a new method for the fabrication of polymer nanocomposite complexes, in which we use multifunctional, physically and chemically reactive polymer blends as electrical conductive sites. Through our investigation of the NFC electrical properties, we have found that conductivity and pressure resistance properties of nanofiber electrolytes strongly depend on several factors. These factors include the amount of loaded reactive organoclay or silver nanoparticles, the fraction/origin of the partner copolymer, as well as structural factors (e.g., a partially crosslinking network of the fibers). We also find that increases in ion mobility—which depend on increased interlayer spacing and crosslinking/alternating structures with regularly repeating functional units—are important factors in the formation of supramacromolecular conductive sites on fiber surfaces. In our future studies we will investigate the effects of different partner polymer systems on the electrical properties of PVA-nanofiber-based solid electrolytes.

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