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ARTICLE *in* ACS MACRO LETTERS · NOVEMBER 2011

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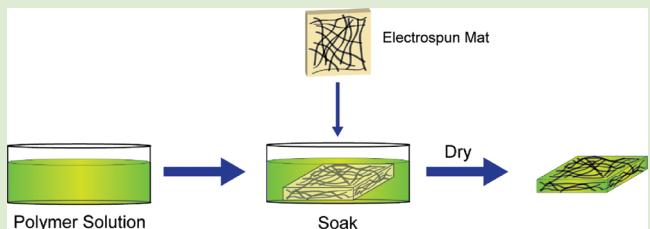
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Supporting Information

ABSTRACT: Stimuli-responsive materials are desired for a wide range of applications. Here, we report the design and fabrication of all-organic, stimuli-responsive polymer composites using electrospun nanofibers as the filler. The incorporation of 4 wt % of filler into the polymer matrix increased the tensile storage modulus by 2 orders of magnitude. Upon exposure to water, the filler fibers plasticize and no longer provide mechanical reinforcement. The tensile storage modulus subsequently diminishes 2 orders of magnitude to the value of the neat matrix polymer.



Materials that can change their mechanical properties on command upon exposure to specific stimuli are desired for a wide variety of applications, including drug delivery, sensors, actuators, and shape-memory materials.^{1–7} Many different strategies have been developed to impart stimuli-responsive properties into soft and hard materials upon exposure to a variety of stimuli.⁸ One of the most interesting approaches to dynamic materials is using stimuli-responsive filler materials for polymer composites. Because the filler is responsible for the dynamic response, it can be blended with a wide variety of polymers to impart stimuli-responsive properties to materials that are otherwise mechanically static.^{9,10} As an example, Rowan and colleagues demonstrated significant mechanical switching in a variety of polymers using cellulose nanowhiskers as filler for polymer nanocomposites inspired by the dermis of a sea cucumber.^{11–14} Here, we report all-organic, stimuli-responsive polymer composites fabricated using an electrospun mat of poly(vinyl alcohol) (PVA) as the filler, which undergoes a 2 orders of magnitude change in the storage modulus upon exposure to water.

Electrospinning uses electrostatic forces to produce continuous polymer nanofibers that have been used for a variety of applications from cell scaffolds to filtration membranes and electronic devices to drug delivery vehicles.^{15,16} In electrospinning, fibers are generated by applying an electric field between a polymer solution and a grounded collector. When the electrostatic force overcomes the surface tension of the polymer solution, a stable jet or “Taylor cone” can be formed. As the jet travels toward the collector, it is constantly subjected to a stretching movement, producing nanofibers of tunable diameter.¹⁷ Outside of the uses for the fibrous mat, nanofibers fabricated via electrospinning have also been used as the filler component in polymer nanocomposite materials.^{18,19} The

incorporation of electrospun nanofibers into a polymer matrix was found to increase the strength of the composite films compared to the corresponding neat polymers. More recently, stimuli-responsive polymer composites have been fabricated from electrospun mats. Luo and Mather have demonstrated shape memory and actuation properties of electrospun polymer composites using poly(*ɛ*-caprolactone) and carbon nanofibers, respectively, as filler materials.^{20,21} To the best of the authors' knowledge, a controlled change in material modulus has not been demonstrated using electrospun fibers as fillers in polymer nanocomposites.

Composite films comprised of a rubbery 1:1 ethylene oxide/epichlorohydrin copolymer (EO-EPI) as the matrix and electrospun poly(vinyl alcohol) (PVA, 99% hydrolyzed, 130 kg/mol) (structure shown in Figure S1 of the Supporting Information) were fabricated to realize stimuli-responsive composite materials. EO-EPI was used as the matrix because it has a low storage modulus and does not swell substantially in water. Furthermore, due to the hydrogen-bond accepting nature of the ether functionality of the copolymer, a strong interaction between the alcohol groups of the PVA filler and the polymer is expected. For the filler, PVA was chosen due to its high strength (storage modulus ~1.6 GPa for the mat), fiber diameter in the nanometer range when electrospun, and hydrolytic stability of the fibers upon treatment with methanol. Treating the PVA mat with methanol is known to prevent the dissolution of the electrospun mat in water by increasing the crystallinity of the fibers that also results in an increase in the storage modulus of the mat.²²

Received: September 1, 2011

Accepted: October 21, 2011

Published: November 17, 2011



The fabrication process for the polymer composites is shown schematically in Figure 1a. To obtain uniform films, an

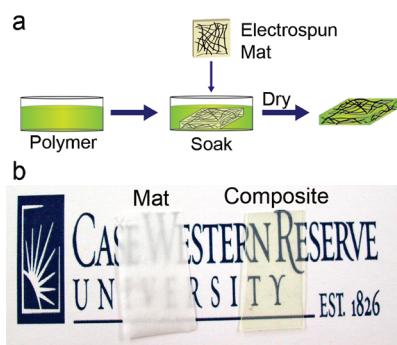


Figure 1. (a) Schematic of the composite film fabrication. (b) Photograph of the native electrospun mat and polymer composite film showing the increase in transparency of the composite film. Reprinted with permission from Case Western Reserve University.

electrospun PVA mat was placed into an EO-EPI solution (100 mg/mL in toluene) in a Teflon mold. Well-interfaced composites were easily obtained utilizing 4 wt % PVA filler. The solution was then dried under ambient conditions and removed from the mold, yielding a uniform film \sim 300 μm thick. Composite EO-EPI/PVA films were found to be significantly more transparent than the corresponding electrospun mat (Figure 1b), indicating strong matrix–filler interaction, which is necessary for mechanical reinforcement.

Scanning electron microscopy (SEM) revealed the structure of the composite films as shown in Figure 2. Upon

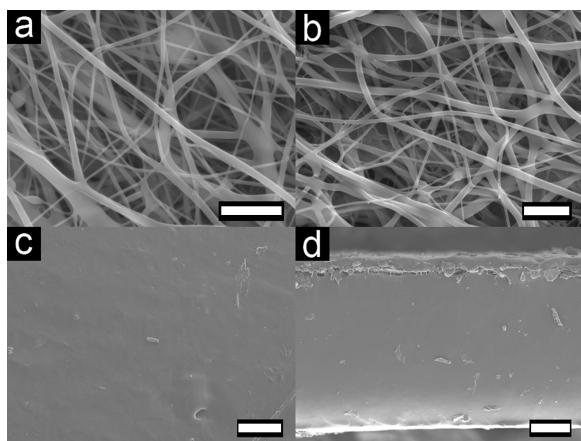


Figure 2. SEM images of (a) the native electrospun PVA mat (scale bar 10 μm), (b) the PVA mat after methanol soaking (scale bar 10 μm), (c) the surface of the composite film (scale bar 75 μm), and (d) the cross-section of the composite film (scale bar 75 μm).

electrospinning, the PVA mat was found to consist of one-dimensional fibers with a wide range of diameters (508 ± 216 nm). Similar distributions of fiber diameter have been reported in the literature²² by the authors, and a more uniform fiber distribution can be obtained by optimizing the spinning conditions and PVA solution properties.²³ Methanol soaking was found to increase the fiber diameter slightly to 716 ± 197 nm. Composite films were observed to be smooth on the surface, indicating the electrospun mat is fully incorporated into the film. Cross-sectional SEM revealed a sandwich-type

structure in the composite film with regions of neat polymer on both sides of the electrospun mat. The EO-EPI polymer also appears to be well-interfaced with the electrospun mat, displaying only a few regions of delamination.

To probe the stimuli-responsive mechanical behavior, dynamic mechanical thermal analysis (DMTA) was used to obtain the tensile storage modulus (E') in the dry and wet state. At room temperature, EO-EPI is above its glass transition temperature ($T_g = -35^\circ\text{C}$) and, thus, in a rubbery state, resulting in a low tensile storage modulus of $E' = 2.4 \pm 0.3$ MPa (Figure 3a). With the inclusion of 4 wt % of PVA electrospun

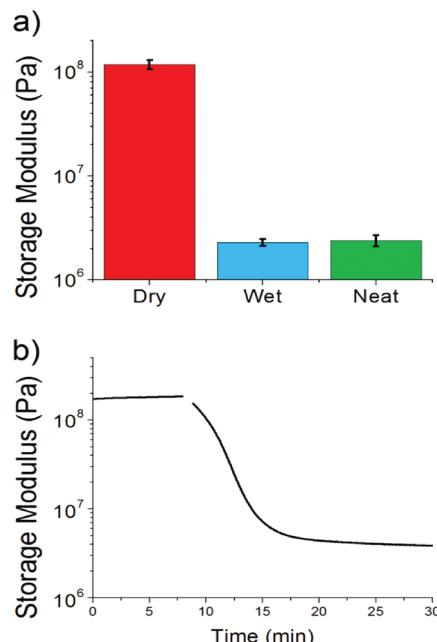


Figure 3. (a) Tensile storage modulus of EO-EPI with PVA composite dry, EO-EPI with PVA composite wet, and the neat EO-EPI polymer dry. (b) Storage modulus change as a function of time after the addition of water. The line break in the plot corresponds to the addition of water.

mat, the tensile storage modulus increased 2 orders of magnitude to $E' = 118 \pm 12$ MPa. Subsequent to exposure to water, the tensile storage modulus was found to dramatically decrease to $E' = 2.3 \pm 0.2$ MPa, which is similar to the tensile storage modulus of the neat polymer, without a substantial increase in swelling. At room temperature, neat EO-EPI swells $19.3 \pm 1.9\%$ w/w in water, while the composite swells $28.3 \pm 3.6\%$ w/w. The modulus change occurs over the course of 10–20 min as shown in Figure 3b. In the composite film, upon uptake of water, the PVA fibers soften so that no reinforcement to the polymer matrix occurs. Since the PVA fibers no longer reinforce the composite film, the mechanical properties return to those of the EO-EPI matrix. Drying of the film did not restore the storage modulus fully, resulting in a one-directional responsive system.

To rule out delamination of the matrix and filler causing the stimuli-responsive softening, cross-sectional SEM of the dried composite material after water soaking (Figure 4) was performed. Significant delamination between the filler and matrix was not observed. Thus, irreversible loss of crystallinity is likely the most significant factor in the reduction of storage modulus and one-directional behavior of composites. To further explore the one-directional behavior of composites, a

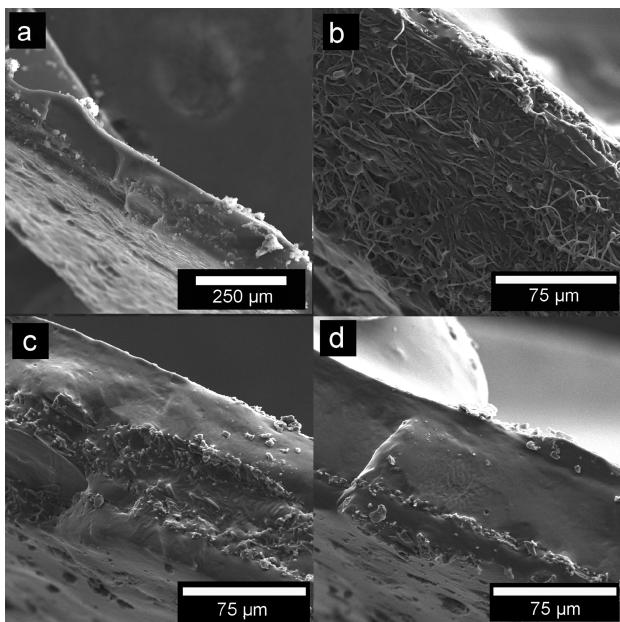


Figure 4. Cross-sectional SEMs of (a) composite film after water immersion and drying, (b) upper left portion, (c) middle portion, and (d) bottom right portion.

DMTA analysis of individual components is performed as shown in Figure 5. At room temperature, neat PVA is below its

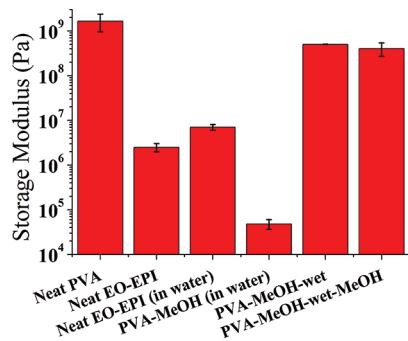


Figure 5. Tensile storage modulus of individual components of the composite.

glass transition temperature (75°C) and, thus, in a glassy state resulting in a higher storage modulus ($\sim 1700 \text{ MPa}$). The PVA mat tested under water submersion had a storage modulus decrease of 5 orders of magnitude to $\sim 0.05 \text{ MPa}$. The softening of wet PVA explains the overall reduction of storage modulus of the composite when exposed to water. A substantial, but incomplete, increase of storage modulus ($\sim 500 \text{ MPa}$) was noticed after drying the water soaked PVA mat. The inhibition of water movement out of PVA fibers through the EO-EPI matrix was likely the factor preventing restoration of the storage modulus of composite resulting in a one-directional responsive system. Differential scanning calorimetry (DSC) revealed a total loss of PVA crystallinity after drying of the water-soaked EO-EPI/PVA composite, while the neat PVA mat regained 77% of crystallinity after water soaking and drying (Figure S2 of the Supporting Information).

Tensile testing was performed on neat EO-EPI and the EO-EPI/PVA composite to determine the tensile strength, elastic modulus, elongation-at-break, and toughness, as shown in

Figure 6. As mentioned above, neat EO-EPI is in the rubbery state at room temperature and showed higher elongation-at-

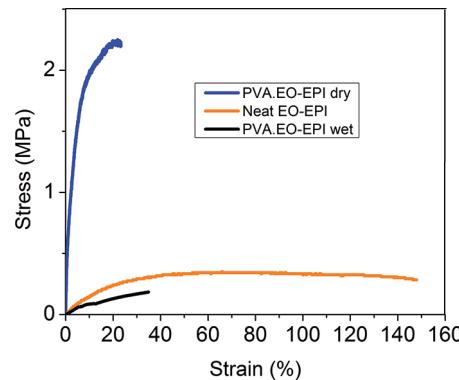


Figure 6. Tensile stress–strain curve for neat EO-EPI, EO-EPI/PVA composite dry, and EO-EPI/PVA composite wet.

break ($\sim 150\%$) and lower tensile strength ($\sim 0.33 \text{ MPa}$). The reinforcement of the EO-EPI matrix upon addition of 4 wt % PVA mat filler was indicated by its higher elastic modulus ($\sim 104 \text{ MPa}$), tensile strength ($\sim 2.45 \text{ MPa}$), and toughness ($\sim 0.42 \text{ MJ/m}^3$). Although a reduction in extensibility was observed as expected, strong interactions between the high modulus, crystalline PVA electrospun mat, and the rubbery EO-EPI matrix led to effective stress transfer and enhancement of the overall strength of the material.

In summary, we report the initial fabrication and mechanical properties of an all-organic, stimuli-responsive composite film. An electrospun mat of PVA was incorporated into a soft polymer (EO-EPI) matrix by mixing the mat with a polymer solution and evaporating the solvent. The resulting composite film was found to be more transparent than the initial mat, indicating good matrix–filler interactions. Upon the incorporation of 4 wt % of PVA mat as filler, the storage modulus was found to increase 2 orders of magnitude. Exposure to water was found to plasticize the PVA fibers, thus negating the reinforcement effect of fiber inclusion. The hydrated composite film was found to have a tensile storage modulus equivalent to the neat dry polymer, demonstrating the ability to change the storage modulus upon exposure to a specified trigger. Since electrospinning is a robust technique capable of forming nanofibers from a wide variety of polymers to be used as fillers, this general strategy could create stimuli-responsive composites using an assortment of stimuli. Currently, work is underway to explore the range of stimuli that can be used to trigger modulus changes in composite films.

ASSOCIATED CONTENT

S Supporting Information

Film fabrication, chemical structure of polymers, DSC, TGA, % transmittance, and variable temperature DMTA plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge Army contract W911QY-08-C-0142, 3M Nontenured Faculty Grant, and The Sherwin Williams Company for support. N.R.W. is supported by a Bayer Fellowship and NSF BRIGE EEC-0824333. We would also like to thank the Center for Layered Polymeric Systems (CLiPS, NSF STC DMR-0423914) for use of their SEM and UV-vis spectrometer.

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