Composites Formed from Thermoresponsive Polymers and Conductive Nanowires for Transient Electronic Systems

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Supporting Information

ABSTRACT: The disintegration of transient electronic systems after a preprogrammed time or a particular stimulus (e.g., water, light, or temperature) is fundamentally linked to the properties and behavior of the materials used for their construction. Herein, we demonstrate that polymers exhibiting lower critical solution temperature (LCST) behavior can work as thermoresponsive substrates for circuitry and that these materials can be coupled with conductive nanowires to form a transient electronics platform with unique, irreversible temperature-responsive behavior. The transient systems formed from composites of LCST polymers and conductive nanowires exhibit stable electrical performance in solution (T_solution > LCST) for over 24 h until a cooling stimulus triggers a rapid (within 5 min) and gigantic (3−4 orders of magnitude) transition in electrical conductance due to polymer dissolution. Using a parylene mask, we are able to fabricate thermoresponsive electrical components, such as conductive traces and parallel-plate capacitors, demonstrating the versatility of this material and patterning technique. With this unique stimulus-responsive transient system and polymers with LCSTs above room temperature (e.g., poly(N-isopropylacrylamide), methyl cellulose), we have developed a platform in which a circuit requires a source of heat to remain viable and is destroyed and vanishes once this heat source is lost.

KEYWORDS: transient electronics, poly(N-isopropylacrylamide) (PNIPAm), methyl cellulose (MC), silver nanowires (AgNWs), parylene mask

INTRODUCTION

Transient electronics are an emerging platform of electronic circuitry purposefully designed to disintegrate and irreversibly lose function.1 The transient system is fabricated such that it exhibits stable electrical behavior until a stimulus, such as light,2 temperature,3 or a solvent,4 is applied. Transient systems composed of nontoxic, decomposable, and biocompatible materials are promising platforms with applications in several areas including bioresorbable electronics,5–7 energy storage devices,8–10 and secure storage systems.11,12 A critical aspect of a transient system is the mechanism for disintegration, which is fundamentally linked to the properties and behavior of the materials used for its construction. Herein, we report a type of thermoresponsive transient electronics based on entirely disintegrable and biocompatible polymers and conductive nanowires. The transient system exhibits stable electrical behavior when immersed in the warm water, but quickly dissolves when the temperature of the surrounding solution drops below a certain threshold temperature. In other words, by utilizing polymers with thermal transitions above room temperature, we are able to fabricate a conducting composite that requires energy input (in the form of heat) to prevent irreversible dissolution and loss of function. Employing standard fabrication techniques, we have successfully fabricated various passive electronic components and multilayer devices.

When dissolution was triggered by low solution temperature, these transient components exhibited a gigantic loss of electrical conductivity. Composites formed from nonconducting polymers and conducting particles have been used for a wide variety of applications, as such systems leverage both the enhanced or unique mechanical/optical/thermal properties of the polymeric matrix and the electrically conducting properties of the embedded particles. Examples of such composite systems include the use of conductive nanowires deposited on elastomeric and/or transparent substrates (to obtain stretchable and/or transparent conductors),13,14 epoxies loaded with conductive particles (to obtain castable conductive adhesives),15,16 and transient electronic systems formed from conductive particles and soluble polymers.1,17 In each of these systems, the matrix serves as a binder that holds the conductive network of particles together or otherwise provides mechanical support; the resulting bulk behavior of the material is a combination of the matrix behavior (mechanical, optical, thermal, chemical) and the particle behavior (generally, electrical conductivity). In some systems, the goal is to couple...
response of the matrix to some environmental factors to a change in electrical performance. In particular, in transient electronic systems, the electrical behavior of the device is designed to change irreversibly as a response to some environmental change (e.g., exposure to solvent or light). In this work, we leverage the lower critical solution temperature (LCST) behavior of certain polymers to obtain a conductive composite material that requires energy input (in the form of heat) to stay viable. Loss of energy input results in cooling, which subsequently results in dissolution and loss of function. Although others have demonstrated materials systems wherein energy input causes destruction (e.g., using photosensitive films), the composite material discussed herein is the first to require energy input to prevent destruction and loss of conductivity.

To date, the majority of transient electronics systems are based on the concept of transience induced by immersing the devices in an aqueous environment. The loss of function is due to the dissolution or destruction of construction materials.2 Stimulus-responsive systems that maintain a stable state but quickly disintegrate upon exposure to a specific stimulus may enable more complex behaviors and sharper transitions between the stable, functional state and the disintegrated state. Rogers and colleagues have investigated a range of these stimulus-responsive polymeric binders, we employ high aspect ratio silver nanowires (AgNWs) to form a percolating conductive network. The main advantages of using AgNWs as conductive materials are their excellent electrical conductivity, biocompatibility, and high anisotropy (which minimizes the effects of polymer swelling on the bulk conductivity).31–33 The AgNW suspensions exhibit excellent compatibility with existing micropatterning techniques. The AgNW/polymer composite exhibits stable electrical performance when immersed in a warm water bath (Twater > LCST), but disintegrates within 5 s when a cooling thermal stimulus triggers the transient behavior (Figure 1a–c). After characterizing the thermoresponsive electrical conductance of these composites, we demonstrate the ability to pattern (both macroscopically and microscopically) conductive AgNW traces in thermoresponsive insulating substrates and form various transient passive components. A transient platform, composed of various passive components on a thermoresponsive transient substrate, is built to demonstrate the versatility of this system.
RESULTS AND DISCUSSION

To characterize the transient behavior, we cast various formulations of AgNWs and LCST polymer onto interdigitated gold electrodes34,35 and monitored their electrical conductance. When immersed in a warm water bath (T_{water} > LCST), the polymeric binder is hydrophobic and thus enables stable electrical conductance with negligible change over 24 h. When the water bath is allowed to cool and the temperature drops below the LCST, the polymeric binder becomes hydrophilic and dissolves, releasing the embedded AgNWs into solution, irreversibly destroying the circuit and rendering it untraceable. Unless otherwise indicated, deionized water (DI water) with electrical resistivity of 18 M\( \Omega \) cm (produced using a Milli-Q Integral ultrapure water system) was used as the solvent in this study. The timeframe for disintegration in previous transient systems that rely on slow and steady dissolution of their components is on the order of hours or days,36 and similar timeframes were observed with photosensitive transient systems.2 Using our AgNW/LCST polymer platform, we obtain extremely rapid (within 5 s) loss of function upon cooling. To tune the threshold temperatures of our thermoresponsive transient systems, we can choose polymers with different LCSTs. For example, PNIPAm and MC have a LCST around 32 and 45 °C, respectively; these polymers have been widely used as temperature-sensitive scaffolds for tissue engineering and drug delivery.37,38 The temperature-dependent electrical behavior of devices formed from MC with three different molecular weights (14 000, 41 000, 88 000), as well as a device formed from MC with molecular weight of 41 000 but 10X thicker than the others, was compared. We did not observe any obvious relationship between disintegration temperature and either film thickness or molecular weight (Figure S3a−d).

It is known that the LCST of MC changes only slightly (a few degrees Celsius) with varying molecular weight.39,40 This small variation in LCST may affect the temperature at which the MC film begins to disintegrate to a small extent, but this was not observable in this study with any significance due to the rate of cooling of the water bath in relation to the disintegration rate. Moreover, it is known that the rate of thermogelation is only marginally dependent on molecular weight,39 and swollen films formed from MCs of different molecular weight may, upon cooling, disintegrate at different rates. However, the dependence of these behaviors on molecular weight was not so dramatic as to be observable in this study. Because the 3 \( \mu \)m thick AgNW networks are attached only on the surface of MC (i.e., the nanowires are not distributed throughout the entire device thickness), the conductance loss due to the dissolution of the MC film is not related to the thickness of the polymer substrate.

Figure 2a shows a SEM image of AgNWs embedded in a MC film. When the MC solution is poured on the AgNW pattern, the liquid infiltrates the AgNW network but maintains the pattern of the conductive AgNW network. After drying overnight, the resulting transparent polymer film with AgNWs buried below the polymer surface can be peeled off the Si substrate. The conductivity of the resulting AgNW/MC film is 6250 S cm\(^{-1}\) (sheet resistance of \( \sim \)0.4 \( \Omega \)/sq), similar to values reported in previous studies using AgNWs as conductors in stretchable electronics, strain sensors, and soft robotics16,42−44 and higher than values reported in previous transient electronics studies using pastes of polymer and conductive tungsten microparticles (\( \sim 400 \) S cm\(^{-1}\)).21 This value is also higher than the conductivity of commercial silver epoxy (\( \sim 140 \) S cm\(^{-1}\) or resistivity of 0.007 \( \Omega \)).
cm for MG Chemicals 8331 silver epoxy). Negligible resistance change was observed after repeated bending of 180° by hand, as the AgNW network holds its shape while embedded within the MC matrix (Figure S4). This behavior is similar to that observed for AgNW networks used as conductors for stretchable electronics applications.31

The electrical conductance of the transient system depends on the density of the AgNWs embedded in dielectric polymeric matrix.45 We compared the electrical percolation threshold of two different varieties of AgNW (aspect ratios \(L/D\) of 100 and 200−400) to determine the optimal mass ratio of AgNW/polymer for each size of AgNW in our conductive composite system. We spun coated thin films of various AgNW/PNIPAm formulations onto interdigitated gold electrodes (Figure S2) to measure their conductance in both dry and wet states. The measured resistance was then converted into the film conductivity based on the geometry of the interdigitated gold electrodes using the following equation

\[
\sigma_f = \frac{1}{R_f} \frac{d}{(N - 1)t}
\]

where \(d\) is the gap between the interdigitated electrodes, \(t\) the thickness of the film, \(l\) the length of the individual electrode, and \(N\) the number of teeth.34,46 Figure S5 shows conductivity as a function of AgNW/polymer mass ratio and the result agrees, within an order of magnitude, with the 3D theoretical electrical percolation prediction for isotropically oriented conductive cylinders with high aspect ratios for \(L/D > 100\).47,48 The 3D percolation theory assumes isotropically oriented nanowires in 3D space, whereas the 2D percolation theory model would be appropriate for nanowires oriented entirely within a plane (i.e., no out-of-plane orientation components). In our work, the AgNW/polymer composite was deposited onto the interdigitated gold electrodes via spin coating, and thus the radial liquid flow during coating likely yields a preferred orientation in the plane (i.e., a somewhat anisotropic distribution of AgNW orientation). As a result, the threshold observed in our experimental results lies, as expected, between the bounds set by the 3D and 2D models.

To test the transient performance of this platform, a MC substrate containing patterned AgNW networks with dimensions of 50 mm in length, 4 mm in width, and 0.08 mm in thickness was submerged in a warm water bath and the electrical conductance was measured using gold-coated kelvin clips applied to the two ends of the AgNW/MC trace. Figure 2b shows the change in conductance of the AgNW/MC film over a 24 h period. After the heat source was turned off, the conductance was stable until \(T_{water} < LCST\), at which point a significant loss of conductance can be seen over a 5 min period.

![Figure 3](image-url)
(the sampling period of the measurement) (Figure 2c). Faster transient behavior, with a dramatic loss of conductivity in a timeframe as short as 5 s, can be seen in Figure S3. It is worth noting that once the device is immersed in the water bath, it cannot be retrieved and dried because it has become too fragile. This transient behavior was reproducibly observed in multiple AgNW/MC samples. Optical images corresponding to the change in morphology of the AgNW/MC film at different temperatures are provided in Figure 2d–f. Figure 2d shows the AgNW/MC layer immersed in a warm water bath (60 °C). It can be seen that water swelled the MC film but the embedded AgNW network was mechanically stable and electrical performance was not lost. When the temperature of the water bath dropped below the LCST, the MC substrate became soluble in water, removing the mechanical support for the AgNW network and thus causing the destruction of the conductive network. Figure 2f shows the disintegration of the AgNW/MC film when the water bath temperature had cooled to room temperature (22 °C).

Figure 3a shows a patterned AgNW/MC thermoresponsive transient conductor with linewidths of 2 mm and 500 μm. The inset image shows the deformed film in hand, illustrating that this is a flexible electronics system not unlike previous flexible electronics employing AgNWs patterned on elastomers.1,49,50 Zigzag patterns were also fabricated (Figure 3b). Using a parylene mask, we were able to fabricate microscopic zigzag patterns with linewidth as small as 50 μm (Figure 3b inset). In Figure 3c, we employ parallel AgNW/MC traces to construct a simple circuit to light a light-emitting diode (LED). We also powered a surface-mount device LED with an AgNW/MC trace with linewidth of 1 mm (Figure S6). With transient conductive AgNW/MC traces, we then built a temperature-sensitive LED circuit composed of a red LED connected in series with a piece of AgNW/MC trace (Figure 3d). The red LED remained continuously lit for 12 h while the AgNW/MC conductor was submerged in a warm water bath (Twater > LCST). After the heat was turned off, the red LED turned off when the colder solution temperature triggered the dissolution of the MC film, leading to the destruction of the AgNW/MC circuit (Figure 3e). We note that LCST polymer-based substrates may have the potential to integrate with other materials, such as Mg, Zn, and Si NMs, to enable additional varieties of thermoresponsive transient electronics.

To demonstrate the ability to form multilayer devices, we fabricated a thermoresponsive parallel-plate capacitor (Figure 4a). The device was composed of a MC slab with two patterned AgNW traces, embedded in the top and bottom surfaces, as two conductive electrodes (Figure S7). The thickness of the AgNW layer on each side was ~4 μm, with a ~110 μm MC film in the middle. To achieve the desired alignment of two AgNW/MC films, we spin coated fresh MC solution onto patterned AgNW traces, 2 mm in width, on a silicon wafer and immediately put another prefabricated dry AgNW/MC film down (with AgNWs facing upwards) on top of this fresh coating. Careful adjustment of the position of the top AgNW/MC film using tweezers allowed us to achieve the desired alignment needed to form a parallel-plate capacitor. When the device was immersed in a warm water bath, we measured a stable capacitance for 24 h (Figure 4b). As before, the destruction of the capacitor was triggered when the water bath temperature decreased below the LCST. The change in capacitance was rapid and occurred within 5 min (Figure 4c). In the dry state, the capacitance was in good agreement with the theoretical prediction, given by
micrometer scales. Finally, a temperature-responsive LED circuit and a capacitor were built using the AgNW/MC conductors. With stable electrical performance in a warm water environment, thermally induced disintegration (e.g., heat is required for the circuit to remain viable), and compatibility with standard fabrication techniques, the reported thermo-responsive transient conductive composites open up new possibilities for exciting applications employing stimulus-responsive transient electronic devices.

**EXPERIMENTAL SECTION**

**Fabrication of Thermoresponsive Transient Electronics.** To characterize the percolation threshold of AgNW/polymer composites, PNIPAm (Sigma-Aldrich, Mn 20 000−40 000) was dissolved in isopropanol (5% w/v) and mixed with AgNW suspensions at various mass ratios; this solution was then cast onto interdigitated gold electrodes. To form patterned conductors, we first deposited parylene C onto a clean Si substrate (PDS, Specialty Coating System) to form ~3 μm thick film (3 g of parylene dimer used). Standard photolithography was used to pattern photosensitive (S1813, 1000 rpm for 1 min) on top of the parylene to serve as an etch mask. Oxygen plasma etching (Oxford RIE PlasmaPro 100 Cebra, descum for 250 s) was used to remove exposed parylene. AgNW (ACS Material, AgNWs-300 and AgNWs-L50) suspension was cast onto the patterned AgNW traces at 100 rpm for 1 min) on top of the parylene to serve as an etch mask. Oxygen plasma etching (Oxford RIE PlasmaPro 100 Cebra, descum for 250 s) was used to remove exposed parylene. AgNW (ACS Material, AgNWs-300 and AgNWs-L50) suspension was cast on the wafer and left exposed in a fume hood for 1 h to allow the isopropanol solvent to evaporate. Patterned AgNW traces were obtained via carefully peeling off the parylene mask (Figure S1). MC (Sigma-Aldrich 15, 40 000 cP) dissolved in trfluoroethanol (Fisher, 2,2,2-trifluoroethanol) was spun coated onto the patterned AgNWs at 100 rpm. After drying overnight, the MC film (with embedded AgNWs) was gently peeled off the silicon wafer. To fabricate a parallel-plate capacitor, MC solution was spun coated on patterned AgNW traces at 100 rpm and then another dry piece of AgNW/MC film (with AgNWs facing upward) was immediately placed on the still-wet MC film with the alignment as desired. Afterward, the whole substrate was placed in a fume hood overnight. In this way, the top and bottom surfaces of the MC film may contain parallel conductive AgNW traces to work as electrodes.

**Characterization of Transient Electronics.** Computer-controlled hot plates (IKA/RET control-vic) were used to heat the water baths in which the transient devices were immersed. A LabVIEW program was used to acquire data from the electrical characterization hardware (Sourcemeter or LCR meter) and water bath temperature measurements from the hot plates (using the hot plate’s external temperature probe), and to turn off the hot plate heat source at a specific time. A Keithley 2450 Sourcemeter was used to measure the electrical conductance of the AgNWs/polymer composite in both dry and wet states. Capacitance was measured using a computer-controlled LCR meter (Keithley U1731C) connected to the device using gold-coated Kelvin clips (Allied Electronics).

**ASSOCIATED CONTENT**

* Supporting Information
   The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b04748.
   Experimental details, supplemental figures, and additional experiments (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge the Vanderbilt Trans-Institutional Programs (TIPs) funding program for supporting this work. Portions of this work were performed using the shared resources of the Vanderbilt Institute of Nanoscale Science and Engineering (VINSE).

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