2023
Second Quarter
PTC Newsletter

Polymer Technology Consortia

UPCOMING EVENTS

Mark Your Calendars for the PTC Fall meetings.

Scratch Behavior of Polymers Consortium-SCRATCH

SCRATCH FALL meeting-October 12th, 2023
Texas A&M University-College Station, TX

Polymer Technology Industrial Consortium-PTIC

PTIC FALL meeting—October 12th & 13th, 2023
Texas A&M University-College Station, TX

Inside the Newsletter

"Research on active polymeric films for food packaging applications"

Elena Castell-Perez and Rosana Moreira, BAEN Food Engineering Lab

According to the Centers for Disease Control and Prevention (CDC), there have been hundreds of cases in the last five years related to consumption of fresh spinach and other leafy greens. Thus, the need to develop pathogen decontamination strategies for use in fresh produce. An initial study from the Food Engineering research lab of the Biological and Agricultural Engineering (BAEN) department at Texas A&M University assessed the antimicrobial effectiveness of zeolitic imidazolate framework-8 (ZIF-8) nanoparticles as a means to reduce the amount of chemical sanitizer used during fresh produce processing. Although effective, the nanoparticles which were directly sprayed on the leafy green, were visible to the eye and affected the firmness of spinach shelf life (Figure 1). Furthermore, the potential toxicity of ZIF-8 encapsulated makes this method unsuitable for direct applications to foods. Thus, the need to incorporate the antimicrobials into the produce packaging film to avoid negative produce quality issues.

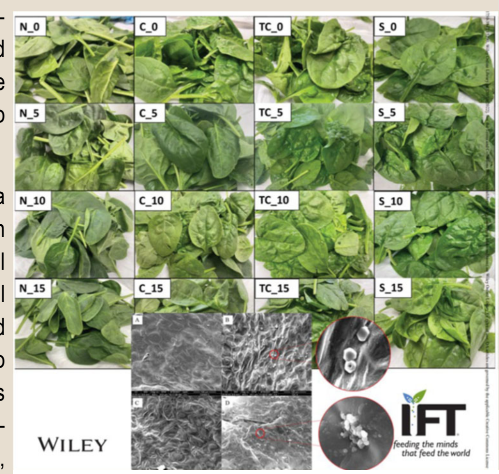

Fig. 1. Overall appearance of fresh spinach leaves; controls (N) and samples treated with 1 chlorine (C), trans-Cinnamaldehyde (TC), and 0.5TC@ZIF-8_PL (S) over 15 days of storage at 4°C https://doi.org/10.1111/1750-3841.16294.

Dr. Elena Castell-Perez, BAEN professor, along with Dr. Rosana Moreira, BAEN professor and their graduate students, are working on development and testing of polymeric materials for use as antimicrobial produce packaging. Poly (vinyl alcohol) (PVA) has excellent chemical resistance, high crystallinity, film forming, and hydrophilic properties, and it is non-toxic. However, due to its hydrophilic properties, PVA tends to attract water resulting in poor stability in aqueous and organic solutions and even dissolving in water at room temperature). Effective antimicrobial delivery systems are necessary to maximize solubility, bioavailability, stability, and masking of stronger flavors of the packaged foods. The main reason for using ZIF-8 nanoparticles is that zeolitic imidazolate frameworks (ZIF) are a subclass of metal-organic frameworks (MOFs),

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consisting of inorganic metal ions in tetrahedral environments bridged by imidazolate ligands. These highly porous compounds have high microporosity, crystalline structure, high surface area, and relatively high chemical and thermal stability, making them attractive candidates for industrial applications including development of antimicrobial food packaging. The superior stability under aqueous physiological conditions allows ZIF-8 to avoid premature drug release and increase cellular uptake, helping it as a drug carrier. Drug delivery stimuli from ZIF-8 can be controlled through various parameters in the environment, such as pH, temperature, enzymes, and reductive environments. Nevertheless, most ZIF-8 research and development has been conducted in the medical field for targeted drug delivery for treatments, but not much has been applied to the food industry, let alone incorporation of these nanoparticles into food packaging systems.

A recent study completed the assessment of functionality and antimicrobial effectiveness of poly (vinyl alcohol) (PVA) films with embedded ZIF-8 nanoparticles carrying a natural antimicrobial, *trans*-cinnamaldehyde (TC). The ZIF-8 nanoparticles are synthesized using a sonochemical method and incorporated into polymeric matrices at several mass ratio concentrations of ZIF-8@TC to PVA. Solutions are mixed, cast onto petri dishes and dried for 12 hours at 37oC in a ventilated oven and film samples stored in airtight containers at room temperature until tested. The engineering properties of the PVA/ZIF-8@TC films are very comparable with those of commercial low-density polyethylene (LDPE) film commonly used for packaging of spinach leaves. Although the composite films have different tensile properties from the LDPE film, embedding ZIF-8@TC into PVA films improves the tensile strength by 17%, making the films suitable for the low loads found in food packaging situations. All tested films were effective at inhibiting the test microorganism both from disk diffusion (Figure 2) and controlled release experiments when leaves were placed in PVA-composite packages (Figure 3).

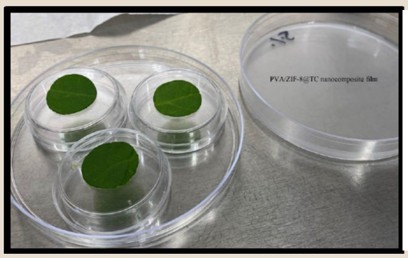
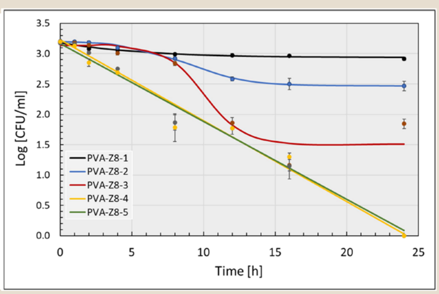


Figure 2. Setup used for studying the antimicrobial effectiveness of films on spinach leaves inoculated with E. coli MG1655. Hara, Castell-Perez & Moreira. (2023). Antimicrobial Properties of Poly (vinyl alcohol) (PVA) Films with Zeolitic Imidazolate Framework (ZIF-8) Nanoparticles for Food Packaging. Journal of Food Science. In press.

Figure 3. Growth inhibition of E. coli MG1655 by nanocomposite films with embedded ZIF-8@TC nanoparticles. Tests at 37C to assess effectiveness of films at microorganism optimum temperature. Initial E. coli MG1655 population of 3.2 log CFU/mL. PVAZ8-1 to 5 represent concentration of trans-cinnamaldehyde (TC). Hara, Castell-Perez & Moreira. (2023). Antimicrobial Properties of Poly (vinyl alcohol) (PVA) Films with Zeolitic Imidazolate Framework (ZIF-8) Nanoparticles for Food Packaging. Journal of Food Science. In press.



These studies offer new insights into the use of ZIF-8 nanoparticles as active compound carriers for food packaging applications. Future implications of this study include the development of systems that are safe to humans, biodegradable, inexpensive and scalable for commercial applications.

"Soft Polymer Nanocomposites-enabled Flexible Neuromorphic Devices"

Shiren Wang, Department of Industrial & Systems Engineering

Dr. Shiren Wang is a professor in the Department of Industrial and Systems Engineering and is dedicated to soft polymer nanocomposites for flexible electronics. Recently, his group has developed a flexible neuromorphic device based on soft polymer nanocomposites through collaboration with Dr. Mark Zoran (Department of Biology at Texas A&M University), Dr. Jenny Qiu(Department of Mechanical Engineering, Texas A&M University), and Dr. Cory Merkel(Department of Computer Science, Rochester Institute of Technology). (This work has been published in *Advanced Composites and Hybrid Materials*, 6,14(2023); *https://doi.org/10.1007/s42114-022-00599-9.)*

The need for multifunctional composites is growing due to their synergistic functions suitable for increasingly complex application scenarios. Recent advances in flexible and wearable electronics drive the development of multifunctional composites that combine good electronic and mechanical performances. Upon deployment, it is imperative that the massive amount of data generated by electronic devices can be stored and processed efficiently. Memristor-based artificial synapses are promising for energy-efficiency neuromorphic computing. Particularly, nanocomposite materials having nanoscale fillers embedded in organic matrices are promising for flexible neuromorphic electronics due to their mechanical flexibility, biocompatibility, and simple fabrication process. Also, flexible memristor units with low energy consumption have been sought-after. Several attempts to achieve high energy efficiency against mechanical deformation were based on incorporating natural materials, which could achieve ~10^{-10}-Watt resistive switching power consumption with a working bending radius of curvature of 15mm. Although natural materials have been widely explored for flexible memristive devices, these natural materials lack diversity for structural customization or require additional chemical modification to exhibit neuromorphic behaviors. For example, it would take weeks to harvest protein nanowires from the bacterium Geobacter sulfurreducens in a strictly controlled environment to fabricate a protein-nanowire film-based active layer.

In this collaborative work, polydimethylsiloxane (PDMS)/Carbon nanotubes(CNT) nanocomposites were prepared by simple solution processing with an extra low loading of CNT, and their neuromorphic functionalities were studied. By tuning the PDMS crosslinking density, the resultant memristor's operation voltage can be adjusted as low as 0.7 V, and a stitching power consumption of 1.40 x 10^{-10} W with a high bending radius of curvature of 5mm. The memristive performance also demonstrated good stability against cyclic switching and the ability to mimic the biological synapse behavior.

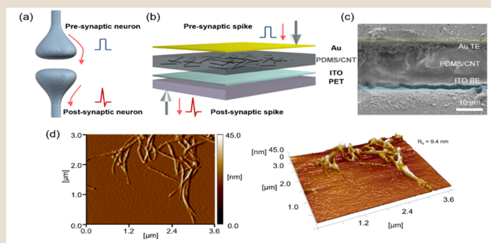


Figure 1 Structure of the composite memristor device. (**a**)Illustration of the structure of a synapse. (**b**) Illustration of the architecture of CNT/PDMS nanocomposite memristor with Au top electrode, ITO bottom electrode, and PET substrate to simulate the neuromorphic function. (**c**) Cross-sectional SEM image of the CNT/PDMS nanocomposite memristor with a 10 μm scale bar. (d) AFM images of well -dispersed 0.1 wt% CNT-PDMS active layer with root-mean-square roughness of 9.4 nm

The structure of the neuromorphic composite is inspired by the synapse, where signals are transmitted from presynaptic axons to postsynaptic dendrites through a synaptic cleft (Figure 1). The sandwich-structured composite consists of a bottom electrode (BE), an active middle layer, and a top electrode (TE) to simulate the synapse function. A commercially available flexible electrode, indium tin oxide (ITO)-patterned polyethylene terephthalate (PET) membrane, was used as the bottom electrode. The ITO/PET as BE is commercially available and low-cost, offering flexibility and an excellent interface for BE and PDMS-based middle layers. CNT-dispersed in PDMS was spin-coated on ITO/PET BE with 20 μm thickness, which serves as an active middle layer for non-volatile bipolar resistive switching behavior.

Vertically assembled sandwich-structured devices exhibit bipolar resistive switching behavior with continuous voltage sweep experiments at a rate of 170 mV s^{-1}, under an ambient environment (Figure 2a-c). The electrical performance of fabricated memristors was characterized using a Keithley 2400 SMU semiconductor analyzer. In a representative voltage sweep loop, the devices

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exhibited bipolar resistive changing behavior, the transition from the high resistance state (HRS) to the low resistance state (LRS) at each turn-on voltage (V_{on}). At 0 V, device A demonstrated an HRS until the voltage of 4.4 ± 0.3 V (± standard deviation) was applied. The current curve experienced a spiking increase of up to three times magnitude, indicating a conductivity transition from the HRS to the LRS. When exceeding the V_{on}, device A stayed in LRS. The LRS state was retained at reversing voltage sweep until it was switched off at a turn-off voltage (V_{off}) of - 4.3 ± 0.3 V (Figure 2a). The device then remained in the HRS until the next voltage sweeping, after which the cycle was repeated. Also, device B switched from HRS to LRS at 3.2 ± 0.4 V (V_{on}) and LRS to HRS at -3.8 ± 0.1 V (V_{off}), as illustrated in Figure 3b. Most importantly, device C demonstrated V_{on} at 0.6 ± 0.01 V and V_{off} at - 0.7 ± 0.5 V (Figure 2c), decreasing crosslinking density of active layer from (7.3 ± 0.9) x 10^{-3} mol cm^{-3} (device A) to (4.4 ± 1.1) x 10^{-3} mol cm^{-3} (device B) and (1.95 ± 0.32) x 10^{-3} mol cm^{-3} (device C) (Figure 2d) leads gradual reducing of both V_{on} and V_{off} of all devices from 4.7 V to 0.7 V (Figure 2e). Despite the CNTs content being the same at all devices, the difference in switching voltage indicated that the structure of the PDMS matrix affects the transport phenomena of electrons between the CNTs under external electrical fields.

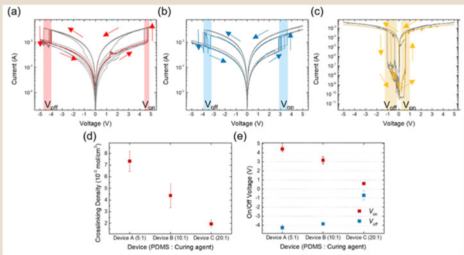


Figure 2 Molecular structure dependence of the resistive switching behavior. Current-Voltage (I-V) curves under 5 voltage sweep cycles of device A (**a**), device B (**b**), and device C (**c**). Arrow indicates the voltage sweep path. (**d**) Crosslinking density of devices with different mixing ratios. (**e**) Molecular structure dependence of On and Off voltages, 5:1 for device A, 10:1 for device B, and 20:1 for device C (PDMS: Curing agent ratio)

The electronic performances are tested to demonstrate the potential of our device to serve in flexible electronic applications. Stability against voltage stress is essential in electrical performance in resistive switching devices. The cyclic stability of Au/CNT-PDMS/ITO devices with different crosslinking densities was developed by measuring the current at the On state (I_{on}) and Off state (I_{off}) with the eclipse of cycles at the reading voltage of 0.2 V after each writing voltage of 5 V and erasing voltage of - 5 V up to 10^4 times (Figure 3) under ambient condition. Device A was stable for 10^4 cycles, and device B was also steady with no visible degradation of the On/Off ratio (Figure 5a, c). Also, the I_{on} of device C, a low crosslinking density device (20:1), was maintained for 10^4 cycles. The statistical distributions of I_{on}/I_{off} and log-normal relevant results (Figure 5b, d, f) indicate the average values of I_{on} increase from 0.985 ± 0.019 μA (device A) to 1.075 ± 0.018 μA (device B) and finally reach 1.159 ± 0.028 μA (device C) as crosslinking density decreases, with the ratio of current at each HRS and LRS (I_{on}/I_{off}) increases from 2.62 for device A to 2.67 for device B and finally 3.06 for device C. The higher ratio between I_{on}/I_{off} promises a low misreading rate and high device accuracy during operation.

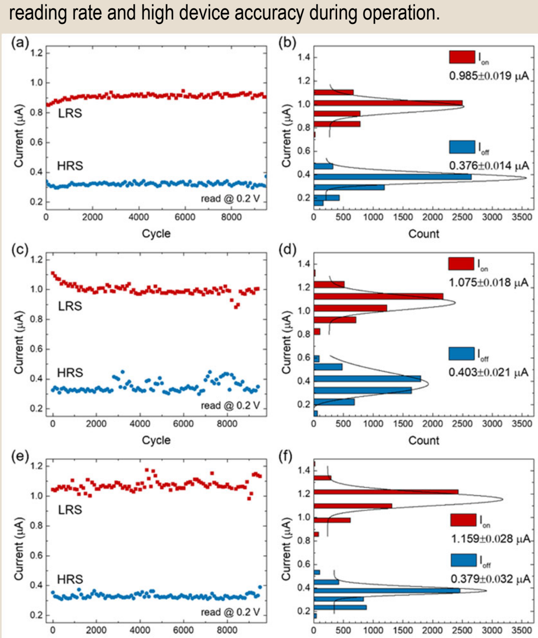


Figure 3 The cyclic stability of the nanocomposite memristor and histogram of currents at On and Off states with different crosslinking densities. Device A (**a, b**), device B (**c, d**), and device C (**e, f**). The black lines are log-normal fits to the distributions.

The mechanical flexibility of the CNT-PDMS memristor was evaluated by bending the devices on semicylindrical molds with different radii of curvature (Figure 4). The characteristic currents at HRS and LRS of the devices were measured from flat to bending state with a radius of curvature of R=15, 12.5, 10, 7.5, 5 mm, respectively, and returned to a balanced state as shown in Figure 7a. During the deformations of bending and relaxing, the currents in each bending state were kept stable (Fig. 7b-d). Irrespective of the bending deformations, the resistance between HRS and LRS of the device remained constant 3 times within 1.3 % (device A), 1.5 % (device B), and 4.6 % (device C) changes, respectively, from a pristine flat state. The PDMS-CNT memristor thus demonstrates good electrical stability against mechanical deformation for wearable applications.

We compared the performance of the CNT-PDMS devices with other memristors on a two-dimensional space constructed with the power consumption within resistive transition and radius of curvature at maximum deformation. The device C optimized in this experiment, which performs the stable resistive switching at a radius of curvature of 5 mm, achieved a low power consumption of 1.4 x 10^{-10} W during operation. The device’s flexibility is well below the trend line, reaching a relatively low operating power consumption variance compared to other flexible memristors.

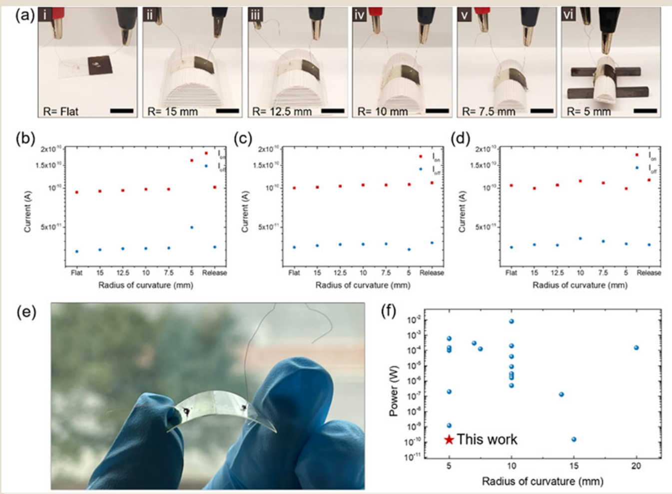
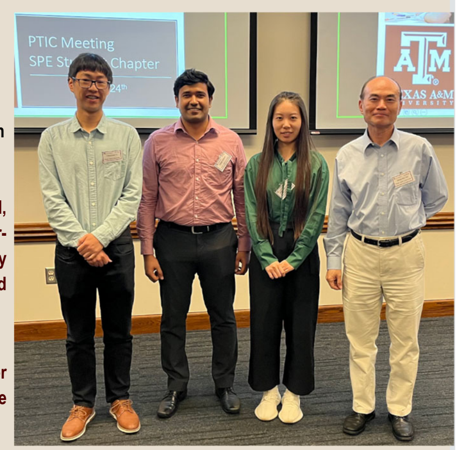


Figure 4 The performance of flexible memristor under bending deformation. (**a**) Sequential electrical measurement for the flexible device under different radii of curvature (R) from flat (i) to 15(ii), 12.5 (iii), 10 (iv), 7.5 (v), 5 (vi) mm, respectively, with 10 mm scale bar. (**b-d**) Current at On state (I_{on}) and Off state (I_{off}) of device A (**b**), device B (**c**), and device C (**d**) under flexural deformation. (**e**) The photograph image of the mechanical flexibility of the device. (**f**) The power consumption versus minimum radius of curvature of flexible memristors.

PTIC student poster session

The Polymer Technology Industrial Consortium (PTIC) Student Poster Session was held on March 23rd-24th and the winners are as follows:



L-R: 3rd Place—Chenxuan Li, CHEM, poster titled: "Photopolymerized Superwettable Coatings Enabled by Dual-purpose ZnO for Liquid/liquid Separation"

2nd Place—Sumit Khatri, MSEN, poster titled: "Algae Biofilm induced Surface Erosion of Acrylic Coatings"

1st Place—Yifei Wang, MSEN, poster titled: "3D Printing of Bijel Ink for Wearable Conductive Porous Materials"

Dr. Hung-Jue Sue, MSEN, Professor and PTC Director

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PTC is delighted to welcome our newest SCRATCH member to the SCRATCH Behavior of Polymer Consortia, please welcome:

LYB LyondellBasell

PTC is also delighted to welcome our newest Polymer Technology Industrial Consortia-PTIC member, please welcome:

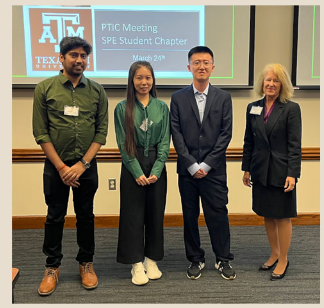
EASTMAN

2023 SPE scholarship recipients

SPE South Texas section

L-R: Donna Davis, SPE Liaison; Yufeng Quang, CHEN received the SPE Henry Kahn memorial scholarship

L-R: Barbara Carrillo, CHEN, received the SPE scholarship; Sara West, MSEN, received the Dale Walker memorial scholarship; Dr. David Hansen, SPE Liaison



L-R: Ratul Mitra Thakur, CHEN and Yifei Wang, MSEN received the SPE scholarship; Hengxi Chen, MSEN received the Henry Kahn memorial scholarship; Donna Davis, SPE Liaison

L-R: Hunter Syas, BMEN, received the SPE Dale Walker memorial scholarship; Dr. David Hansen, SPE Liaison

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Polymer Specialty Certificate Updates

Students that have applied for the Polymer Specialty Certificate	87
Students that have received the Polymer Specialty Certificate	75

For more information, please visit: http://ptc.tamu.edu/polymer-specialty-certificate/

Have Questions?

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Materials Science & Engineering

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