2024

Third 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 17th, 2024 at Texas A&M University

Polymer Technology Industrial Consortium-PTIC

PTIC FALL meeting—October 17th-18th, 2024 Both meetings at Texas A&M University-College Station, TX

Inside the Newsletter

Radiation-Driven Changes in Physical Properties of Polymers

Matt Pharr, Associate Professor and J. Mike Walker '66 Faculty Fellow
Department of Mechanical Engineering

Dr. Matt Pharr's group in the Department of Mechanical Engineering investigates a wide range of problems in mechanics of materials, many of which exhibit a strong coupling between mechanics and other fields, such as electronics, physics, electrochemistry, biology, and chemistry. Several thrusts of his recent research have focused on mechanics of soft materials. This article will summarize one such study in which his team, led by Dr. Kamrul Hasan (currently at PNNL), investigated the effects of alternative sterilization modalities on various properties of polymers.

Single use medical devices implement a variety of polymers and must be sterilized prior to use to destroy microorganisms and prevent disease transmission. Over the past several decades, cobalt-60 gamma irradiation has remained the primary sterilization technique for most medical devices. However, stemming from security threats and shortages in supply associated with cobalt-60, a recent push has emerged to transition towards machine-based sources, such as those of electron beam (e-beam) and x-ray technologies. Prior to large-scale practical deployment, the effects of e-beam and x-ray irradiation on polymer properties must be carefully and thoroughly characterized from several perspectives, including their potential effects on the structural, thermal, optical, and mechanical behavior.

To address these knowledge gaps, Pharr, Hasan, and collaborators from Texas A&M University (Suresh Pillai and David Staack), Pacific Northwest National Laboratory, and several medical device companies (including Becton-Dickinson, Stryker, and Sartorius) have directly compared the effects of sterilization-relevant doses of e-beam, x-ray, and gamma irradiation on ~20 polymers that are commonly used in medical devices (the results have been published here: https://doi.org/10.1016/j.radphyschem.2020.109282; https://www.nature.com/articles/s41529-023-00413-x; https://doi.org/10.1016/j.radphyschem.2021.109505; and https://doi.org/10.1016/j.polymdegradstab.2024.110677). Specimens extracted directly from medical devices themselves, as well as injection molded specimens of their constitutive polymer formulations were utilized in these studies. These polymers/devices were then subjected to various controlled doses of irradiation from e-beam, x-ray, and cobalt-60 irradiation (e.g., at 0, 15, 35, 50, and 80 kGy). After irradiation, the team implemented numerous characterization techniques, including mechanical testing (tension, compression, bending, dynamic mechanical analysis (DMA), and/or

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Dr. Matt Pharr, MEEN

hardness measurements), optical characterization, functional testing (for the devices), gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and Fourier-transform infrared spectroscopy (FTIR). Typical results from these studies for mechanical testing are shown in Figures 1-2.

In the vast majority of the cases, the team observed either (1) insignificant changes in properties for any irradiation modality over the tested dose range, as in Figure 1, or (2) systematic changes in properties with dose but with no relative change among the irradiation modalities (at a given dose), i.e., no radiation source dependence, as shown in Figure 2. Likewise, none of the medical devices that we tested at any dose level for any irradiation modality failed their functional performance tests. However, in a few specific cases, radiation modality dependencies did arise. For instance, in polypropylene homopolymer (PPH) the molecular weight significantly increased upon x-ray irradiation, whereas the melting temperature, glass transition temperature, and elongation at break significantly decreased compared to that of gamma irradiation. Similarly, we observed differences in discoloration that depended on the irradiation modality in a few of the studied polymers. Still, as a whole, we have found that polymer properties and performance are generally uncompromised using e-beam irradiation or x-ray irradiation, as compared to the current gamma (cobalt-60) irradiation. As such, these studies have paved the way toward using safer and more secure modalities of ionizing irradiation to sterilize medical devices.

Beyond the studies listed above, new and ongoing areas of Dr. Pharr's research that are related to polymers include: (1) formulating and implementing a novel top-down methodology to design auxetic (negative Poisson's ratio) polymeric metamaterials from topological principles based on 2D textile weave patterns; (2) studying the interplay between mechanical loading and hydrolysis in biodegradable polymers, e.g., for medical implants and tissue engineering; (3) establishing the feasibility of using small-scale mechanical testing to replace bulk-scale testing of polymers, e.g., to reduce the volume of material required to determine mechanical properties and to accelerate testing times and throughput; (4) utilizing e-beam technologies to promote recycling of polymer waste; and (5) utilizing e-beam technologies to compatibilize waste polymers for integration into large-scale infrastructure applications, particularly in concrete.

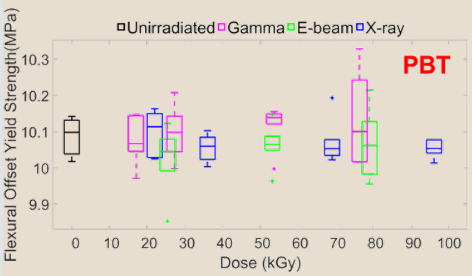

Figure 1: Flexural yield strength as a function of irradiation dose for PBT, showing no change in strength as a function of either the irradiation dose or the irradiation modality.

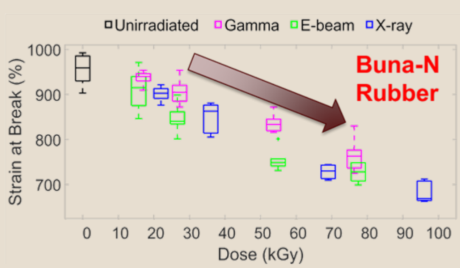

Figure 2: Strain at break as a function of irradiation dose for Buna-N rubber, showing a decrease in strain at break with increasing dose but with no relative change (at a given dose) as a function of the irradiation modality.

Chemistry and Materials Applications of Conjugated Ladder Polymers and Membranes

Lei Fang, Department of Chemistry

Professor Lei Fang leads an active research group in the Chemistry Department at Texas A&M University (TAMU), holding a joint appointment in the Department of Materials Science & Engineering. His research interests primarily focus on chemical innovations related to broadly-defined functional organic compounds and materials. These encompass conjugated ladder polymers, rigid organic pi-systems, porous polymer networks, composite materials, and supramolecular chemistry. His ongoing and prospective research efforts center on fundamental scientific inquiries in the fields of chemical synthesis, physical organic chemistry, polymer science, and materials science. Furthermore, they extend to application development in areas like organic electronics, clean energy, sustainable separation, smart materials, and green catalysis (see Figure). A summary of his main research track record is provided below.

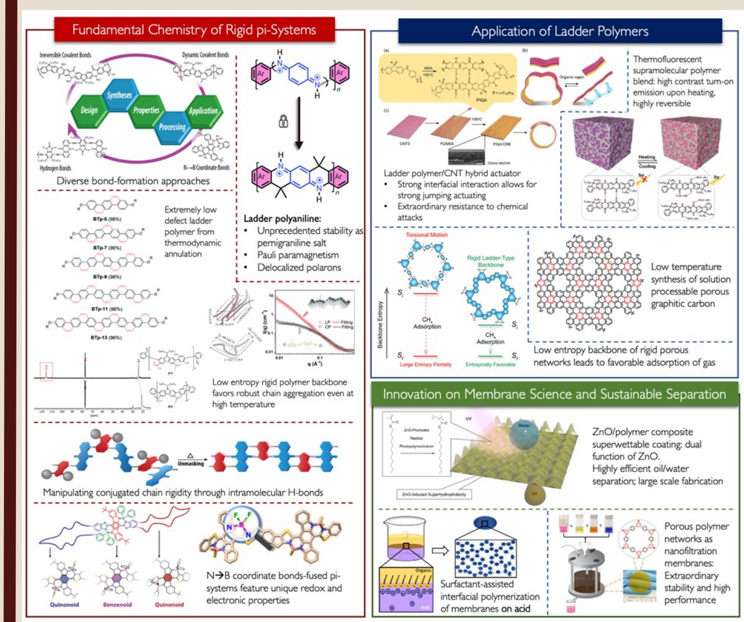

Figure: Graphical summary illustrating the research conducted by Lei Fang's group from 2013 to 2024.

1. Fundamental Chemistry of Conjugated Ladder Polymers and Fused-Ring pi-Systems

Professor Lei Fang's group is among the world's leading teams in the niche area of conjugated ladder polymers. These macromolecules, with multiple bond strands connecting a π-conjugated backbone, offer unique electronic and mechanical attributes, setting them apart from conventional single-stranded polymers. Their synthesis and study, however, pose substantial challenges. Throughout his research journey, Professor Fang's team has achieved groundbreaking contributions in this nontraditional yet fruitful research area.

Synthesis: Professor Fang's achievements span a broad spectrum in ladder polymer synthesis, including defect-free conjugated ladder polymers, ladder polymer analogs of polyaniline, and intramolecular noncovalent bond-bridged ladder polymers (*Acc. Chem. Res.* **2019**). Among their innovative strategies, they employed ring-closing olefin metathesis (*Chem. Sci.* **2016**; *Angew. Chem.* **2017**), utilized imine condensation (*Chem* **2017**; *JACS* **2020**), adopted azaisoindigo for crafting non-covalently bridged molecules (*ACS Materials Lett* **2022**), and incorporated N→B coordinate bonds to assemble extended pi-systems

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(*JACS* **2018**; *J. Org. Chem.* **2021**). They're also advancing the synthesis of fused polypyridine ligands for environmental and sustainability applications.

Properties and Applications: Professor Fang’s synthetic achievements have led to insights into previously uncharted properties of ladder polymers. The low defect levels in their polymers provided foundational data for conjugated, double-stranded polymer physics (*J. Polym. Sci.* **2022**; *J. Mater. Chem. C* **2022**). Their ladder polyaniline analogs introduced stable pernigraniline salt, confirming its conductive nature (*JACS* **2020**) and leading to applications in electrochromic devices (*Chem. Sci.* **2020**), supercapacitors (*Mater. Horiz.* **2023**), and single-molecule switches (*Chem* **2023**). Furthermore, they developed techniques to improve the processability of ladder-type polymers, enabling advanced organic electronic material applications.

2. Applications of Ladder Polymer Materials

Professor Lei Fang's team's foundational work in the synthesis and properties of ladder polymers and fused-ring small molecules has paved the way for innovative materials functions and applications. They have advanced notably in crafting stimuli-responsive materials and functional porous materials.

Stimuli-Responsive Materials: The team integrated a ladder polymer with carbon nanotube sheets, resulting in a high-performing and highly durable jumping actuator with potential for soft robotics applications (*Adv. Mater.* **2021**). Separately, they developed thermally fluorescent polymer composites, which showcase activated fluorescence on heating and excellent reversibility (*Adv. Funct. Mater.* **2020**; *Chem. Eng. J.* **2021**). These materials hold great potential in smart textile applications.

Porous Ladder Polymer Networks: Intrigued by ladder-type backbones for porous polymer networks (*Chem* **2020**), Professor Fang's group recognized their potential in gas storage. They demonstrated an ultra-high methane uptake capacity per unit surface area in a model porous ladder polymer network (*ACS Mater. Lett.* **2020**). Additionally, the team devised an aldol triple-condensation method (*Mater. Chem. Front.* **2018**) leading to porous carbon with high microporosity and a tailored pore size distribution. This innovation, presenting a low graphitization temperature and potential for next-generation electrocatalysts, is set to reshape the world of electrocatalysis (*Chem. Sci.* **2021**; *ACS Appl. Mater. Inter.* **2022**).

3. Supramolecular Chemistry for Membrane Science

Leveraging his core expertise in supramolecular chemistry, Professor Lei Fang's group has innovated new molecular and materials systems for membranes and detergents, beyond his work on ladder-type π-systems.

Separation**:** Utilizing an aldol-triple condensation method, Professor Fang’s group synthesized high-quality membranes of aromatic porous polymer networks with significant molecular sieving properties (*J. Mater. Chem. A.* **2020**) based on supramolecular host-guest principles. Their standout feature is remarkable stability under severe conditions, surpassing conventional membranes. Partnering with Professor Banerjee, the team harnessed ZnO tetrapods to pioneer superwettable coatings (*Mater. Horizons*, **2022**). Resulting in both superhydrophobic and superhydrophilic materials (*Matter* **2024**), this method excels in separating liquid mixtures and degrading organic pollutants. This breakthrough with ZnO composites led to multiple patents, a startup company, and a licensing agreement with TAMU.

New Interfacial Polymerization**:** Professor Fang’s team introduced an economical method for crafting cross-linked cyclodextrin polymer networks (*Chem. Commun.* **2020**) with notable adsorption and electrical sensing capacities (*Mater. Today Chem.* **2022**). Expanding on the surfactant-assisted interfacial polymerization, they developed a unique on-acid interfacial polymerization technique (*Unpublished Result*), broadening its application. The resulting membranes demonstrate promising potential in nanofiltration and are crucial for the chemical, petroleum, and pharmaceutical sectors. This initiative has gained financial supports from TotalEnergies, a 2023 NSF grant, and resulted in a 2022 patent, laying groundwork for further technological advances.

A Celebration of Excellence: Polymer Scientists Inducted as ACS POLY Fellows

This year, the Division of Polymer Chemistry (POLY) within the American Chemical Society (ACS) welcomed seven new fellows, including Texas A&M University's esteemed academics Dr. Jaime Grunlan and Dr. Emily Pentzer.

Reflecting on the honor, Grunlan remarked, “For me, it is like an early lifetime achievement award. The list of those with the POLY Fellow designation are the ‘who’s who’ of the polymer world.”

Pentzer, expressing her gratitude, stated, “I was both surprised and delighted to be selected for this honor. I love the polymer science community and the connection that societies such as the ACS and POLY division help to create, so the recognition of my contributions is very meaningful.”

Full story: **https://rb.gy/t3uryy**

Renowned Researchers Join Texas A&M Engineering Faculty

Drs. Enrique Lavernia and Julie Schoenung have joined Texas A&M University as joint faculty of the Department of Materials Science and Engineering and the J. Mike Walker ’66 Department of Mechanical Engineering.

Both recognized as National Academy of Engineering members, Lavernia and Schoenung come to Texas A&M from the University of California, Irvine.

Full story: **https://rb.gy/shqgjz**

Dr. Enrique J. Lavernia, M. Katherine Banks Chair and Dr. Julie M. Schoenung, Wofford Cain Chair III, both of whom are professors in the Department of Materials Science & Engineering, and in the J. Mike Walker ’66 Department of Mechanical Engineering, have joined forces to write “Metallic Powders for Additive Manufacturing: Science and Applications,” published by Wiley, Inc.

Full story: **https://rb.gy/1r18y2**

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Texas A&M Engineering Leads Nation in Engineering Research Expenditures

Eight departments secured positions in the top 10 among public institutions. Four departments clinched the No. 1 spot in Texas, including biological and agricultural, industrial, materials and nuclear engineering. Materials science climbed three places to claim a spot in the top 10 among public institutions at No. 9.

Full story: **https://rb.gy/yzyuoi**

Texas A&M Awarded More Than 12,000 Diplomas At Spring Commencements

Texas A&M University awarded approximately 12,400 degrees to spring graduates at commencement ceremonies on May 9th, 10th and 11th. Commencements were held at Reed Arena on for undergraduates, master's and doctoral students.

WHOOP! WHOOP!

SPE STUDENT CHAPTER officers for 2023-24

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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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