

ULTRAFAST MEASURES ULTRASMALL: INTERFACIAL STRUCTURAL PROPERTIES DETERMINED FROM FREE VOLUME ELEMENT DISTRIBUTIONS IN POLY(ETHER IMIDE) ALUMINA NANOCOMPOSITES.

Significance

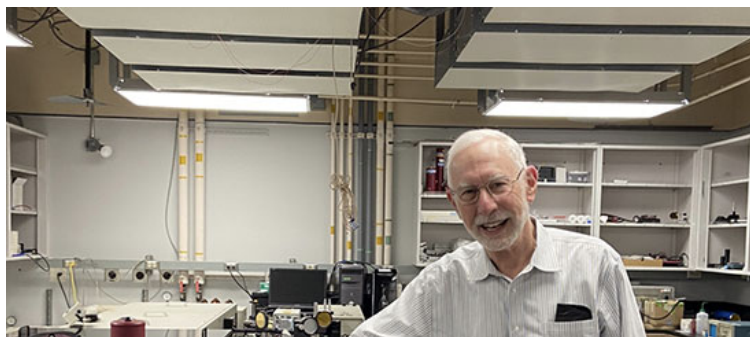
Polymer nanocomposites, often called PNCs, are becoming a big deal in material science these days. They bring some pretty amazing improvements to mechanical strength, heat resistance, and electrical properties. What makes them stand out is that you do not need a lot of nanofillers to see these benefits. Even with just a small amount mixed into a polymer matrix, these composites can perform better than traditional materials. Perhaps more important, you do not have to synthesize a new polymer to get new properties. Plus, they are super customizable, which makes them a perfect fit for a range of cutting-edge applications, like high-temperature dielectrics or next-gen energy storage. Still, despite their growing importance, scientists are puzzled over exactly *how* these improvements happen. A big part of the magic seems to come from a special layer between the polymer and the nanofillers, often called the interphase that have different properties from the bulk material. It has its own set of physical and chemical quirks, shaped by the way the polymer chains interact with the surface of the filler particles. These interactions mess with how the chains pack together, how much space they leave between each other, and how freely they can move. All these factors end up having a huge impact on the overall properties of the material. While we know the interphase is key, figuring out its exact details has been a tough nut to crack. Their tiny sizes and complexity make the polymer coatings of the nanoparticles really hard to measure, and existing methods often give conflicting results. Depending on the approach, people have reported interphase thicknesses ranging anywhere from just a few nanometers to several tens of nanometers. Part of the problem is that current methods, like small-angle X-ray scattering and broadband dielectric spectroscopy, only give a partial picture. They might pick up on things like density changes or electrical behavior, but they miss the bigger story of what is really happening structurally and dynamically. On top of that, we do not fully understand how nanofillers affect the free volume elements (FVEs)—tiny empty spaces in polymers that influence chain movement and packing. These gaps are super important, but how they change when nanoparticles are added is still in the realm of mystery.

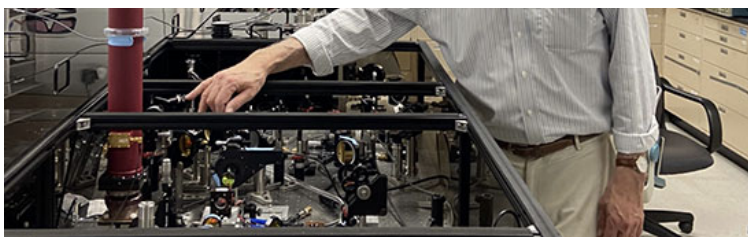
A new research paper published in *Macromolecules Journal* led by Professor Michael Fayer from the Department of Chemistry at Stanford University and conducted by PhD candidates Junkun Pan and

Aaron Charnay, focused on poly(ether imide) (PEI) nanocomposites, adding alumina nanoparticles to see how the polymer's microstructure shifted. Using an advanced technique called restricted orientation anisotropy method (ROAM), they zoomed in on the size and behavior of FVEs in these materials using ultrafast infrared spectroscopy. Their work is a step toward unraveling how nanocomposites really work at the nanoscopic level. The research team created nanocomposite samples with different amounts of tiny 20 nm alumina nanoparticles. They tested weight percentages of 0.5%, 1%, and 2% to see how these additions affected the polymer matrix. To make sure the particles were spread evenly throughout the polymer, they used a solvent casting method, followed by vacuum drying to remove any leftover solvents, and observations using scanning electron microscopy (TEM). To dig into the tiny FVEs—essentially the little gaps inside the polymer—they turned to an innovative tool: phenyl selenocyanate (PhSeCN). This compound acted as an infrared vibrational probe, allowing the team to use ROAM. It's a sensitive way to pick up on the nanoscale voids and movement within the material. Their first step was to analyze how the sizes of these FVEs were distributed, which tells you a lot about how the polymer chains are packed and moving, especially near the nanoparticles. What they found was pretty striking. The pure PEI sample had a wide range of FVE sizes, meaning a mix of small and large voids. But as soon as they added the alumina nanoparticles, things started to shift. The average size of the FVEs got bigger, and the range of sizes became much narrower. For example, with 2% alumina filler, the average radius increased from 2.43 Å in pure PEI to 2.51 Å, while the distribution's width shrank from 0.56 Å to 0.47 Å. This narrowing pointed to the nanoparticles' role in creating a more consistent packing of the polymer chains around them. To back this up, they used SEM to look closely at how well the alumina particles were spread throughout the samples. The SEM images showed excellent dispersion, even at higher filler concentrations, with only a tiny bit of aggregation. This even spread made sure that the changes they observed in the polymer properties were due to the nanoparticles themselves, not clumping effects. They also used Fourier transform infrared spectroscopy to confirm that the PhSeCN probe stayed embedded in the polymer matrix and didn't change its natural dynamics. One of the most eye-opening findings was how the nanoparticles affected the interfacial layer, the zone where polymer dynamics are completely different from the bulk material. Lastly, the researchers noticed a linear relationship between the amount of nanoparticles added and the interfacial volume fraction. From this relationship, the authors calculated that this interphase region was 19.2 ± 0.5 nm thick—much larger than the immediate layer where polymer chains stick tightly to the particle surface. This shows that the nanoparticles influence a substantial part of the polymer around them. The FVE sizes in this region were also more uniform and slightly larger, suggesting that the nanoparticles disrupted irregularities and created a smoother packing of the polymer chains. Additionally, being able to quantify the interphase with this level of accuracy opens up new possibilities for fine-tuning

materials. It gives scientists and engineers a better way to evaluate and optimize composites, especially since the interphase plays such a big role in improving a material's mechanical strength, thermal stability, and dielectric performance. The results give a clearer picture of how nanocomposites work and could pave the way for better designs in the future.

In conclusion, the new work led by Professor Michael Fayer is an important step forward in discovering the complexities of PNCs, especially when it comes to understanding the interfacial properties. Professor Fayer said, "It is amazing that measuring picosecond dynamics can determine sizes with a few hundredths of an Å resolution." What's exciting is that the approach they developed isn't limited to just one type of material—it provides a framework that can be applied to many other nanocomposite systems. From a practical standpoint, this research could lead to some advancements in high-performance materials. The results show that even tiny amounts of nanofillers—like the alumina nanoparticles used in this study—can cause big changes in the polymer matrix's structure. This explains why PNCs often display impressive improvements in their properties, even with low amounts of filler. This kind of efficiency is a win for industries, as it reduces costs and simplifies production while delivering top-notch performance. Another key takeaway is how the narrowing of the free volume RPDs as nanoparticle concentration increases reflects the ability of nanofillers to create a more uniform polymer chain structure. This uniformity is essential in applications like energy storage devices, where stability and predictability are critical. Plus, the consistent FVE sizes make these materials more reliable under stress, making them especially appealing for sectors like aerospace and automotive industries, where durability and consistency are critical. On a broader scale, the authors' work showcases how nanoparticles interact with polymer structures and how those interactions translate to macroscopic property changes. The successful use of ROAM to capture these intricate dynamics paves the way for its application in other polymer-nanoparticle systems, including those with more complex geometries like carbon nanotubes or layered silicates. Moreover, the ability of the new method to differentiate between bulk properties and interphase behavior could drive the development of innovative multi-functional composites with properties tailored for a wide range of advanced applications.





About the author

Michael D. Fayer received his Ph.D. in chemistry from the University of California at Berkeley (1974). He started at Stanford University in 1974, and today, he is the David Mulvane Ehrsam and Edward Curtis Franklin Professor of Chemistry. He has been married to Terry M. Fayer for 56 years and has two children and two grandchildren. Fayer is a pioneer in developing and applying ultrafast non-linear laser techniques for studying complex molecular systems ranging from solids at liquid helium temperatures to room temperature materials with mesoscopic structures. In the last several decades, his primary focus has been on the molecular dynamics studied with ultrafast infrared non-linear experiments. He has played a central role in developing and applying two-dimensional infrared spectroscopy. His work has profoundly impacted modern physical chemistry and materials science, and his methods have spread worldwide. Fayer is a Fellow of the National Academy of Sciences, American Academy of Arts and Sciences, and a Foreign Fellow of the Indian National Science Academy. He has received the Peter Debye Award in Physical Chemistry (ACS), William F. Meggers Award (OSA) the Pittsburgh Spectroscopy Award (SSP), Ahmed Zewail Award in Ultrafast Science and Technology (ACS), Arthur L. Schawlow Prize in Laser Science (APS), Ellis R. Lippincott Award (OSA), E. Bright Wilson Award for Spectroscopy (ACS), Earl K. Plyler Prize for Molecular Spectroscopy (APS).

Principal Research Interests

The Fayer group is involved in research on the dynamics and interactions of molecules in complex molecular materials. Systems with mesoscopic structures and other types of complex structures and dynamics are common in nature and have properties distinct from typical bulk material, e.g., lithium ions in complex environments such as polymer electrolytes, gel polymer electrolytes, and concentrated salt solutions. To study such systems, we are applying a variety of ultrafast nonlinear experiments, including two-dimensional infrared vibrational echo spectroscopy, other ultrafast IR methods, and ultrafast visible and UV experiments. We are exploring dynamics and intermolecular

interactions of molecules in liquids, liquids in nanoscopic environments, room temperature ionic liquids, polymers, polymer membranes, and perovskites. We also study solute-solvent dynamics and interactions such as complex formation and dissociation. A prominent area of our research is water dynamics in nanoconfinement and its interactions with interfaces and ions. Proton transfer in water and other liquids and nanoscopic systems. We are also investigating highly concentrated aqueous salt solutions. We develop methodologies and theories of ultrafast multidimensional vibrational spectroscopy and other ultrafast optical methods for general probes of structural dynamics in complex molecular systems. We also develop and apply statistical mechanics theory of molecular systems and experimental observables.

Reference

Junkun Pan, Aaron Charnay, Michael D. Fayer. **Poly(ether imide) Alumina Nanocomposites: Interphase Properties Determined from Free Volume Element Radius Distributions.** *Macromolecules* 2024, 57, 14, 6492–6501

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