Thin Films
Room 317 - Session TF1-TuA

VSHOP Fundamentals

Moderators: Prof. Dr. Greg Parsons, North Carolina State University, **Dr. Junjie Zhao**, Zhejiang University

2:15pm **TF1-TuA-1 What Infiltrates What? An Experimental Survey of Precursor-Polymer Vapor Phase Infiltration Chemistries***, **Mark Losego**, Typher Yom,* Georgia Tech

Vapor phase infiltration (VPI) exposes polymers to gaseous inorganic precursors that dissolve into the polymer, become entrapped, and convert the polymer into an organic-inorganic hybrid material. VPI hybrids have unique mechanical, electrical, optical, and chemical properties that make them of interest for applications including EUV resists, membranes, and photocatalysts. However, fundamental predictions of which inorganic precursor chemistries will "successfully" infiltrate into which polymer chemistries is still elusive. Despite various systematic studies, no clear chemical "rules" have yet to be established to make these predictions. In this study, we conduct an experimental survey of "infiltration success" for a range of polymer chemistries, precursor chemistries, and infiltration temperatures to determine if any new insights for prediction can be gained. In total we study 12 different polymers, 3 different precursors, and 3 different infiltration temperatures. We include a range of different heteroatom functional groups on the polymers (e.g., nitrile, carboxylate, pyridine, etc.) as well as some differences in bending rigidity and free volume. Along the way, we note characterization tools best-suited for simple, fast detection and assessment of inorganic loading into polymer films, specifically SEM-EDX and XRF. This talk will show how analyzing the signal-to-noise ratio from these methods can then be used to provide a normalized assessment of inorganic loading. Broadly, the $TiCl_4$precursor is capable of successfully infiltrating into all the polymers that trimethylaluminum (TMA) can infiltrate, but just at a lower concentration, which is often not detectable with EDX alone. In contrast, the diethylzinc (DEZ) precursor does not successfully infiltrate many of the polymers that are successfully infiltrated with $TiCl_4$and TMA, like PMMA and P4VP. However, in certain instances, it appears that this lack of infiltration is not due to a lack of "dissolution" into the polymer, but rather a lack of permanent binding to the polymer. These insights along with efforts to train a machine learning model on this experimental data combined with other literature reports to better address the question of "What infiltrates what?" will be discussed.

2:30pm **TF1-TuA-2 Chemical Stability of Vapor-Phase-Infiltrated Poly(vinylpyrrolidone), Poly(4-vinylpyridine), and Polyacrylonitrile***, **Alexandra Wnuk**, Mark Losego, Typher Yom,* Georgia Institute of Technology

Vapor phase infiltration (VPI) of polymers to form organic-inorganic hybrid materials has been demonstrated to improve the material's chemical resistance to swelling and/or dissolution in organic solvents. Understanding the chemical stability of these hybrid organic-inorganic materials is important for developing new technologies, new membrane materials, and new photoresists. In this study, we examine the ability to use VPI of trimethylaluminum (TMA) and water (H2O) to alter the chemical stability of three different polymers: poly(vinylpyrrolidone) [PVP], poly(4-vinylpyridine) [P4VP], and polyacrylonitrile [PAN]. We find that all three of these polymers can be infiltrated with TMA, and we study their physicochemical structure and dissolution behavior after VPI at 70°C, 90°C, 120°C, and 150°C. For all polymers, the hybrids get thicker (swell) upon infiltration, indicative of inorganic loading into the film. This swollen thickness increases with VPI temperature, suggesting more inorganic loading at higher infiltration temperatures. This increased loading is further verified by combusting the hybrid at high temperatures (burn out) and measuring the residual inorganic layer's thickness. After burnout, the infiltrated P4VP and PAN had inorganic film thickness of 19.2% and 17.0%, respectively, of their original hybrid thickness compared to an inorganic burnout thickness of only 8.8% for PVP , suggesting significantly less inorganic loading in PVP than the other two polymers. When these hybrid materials are then tested for dissolution in solvents known to dissolve the parent polymer, infiltrated PVP films dissolve almost immediately, showing no change in dissolution behavior after VPI. In contrast, infiltrated P4VP shows resistance to dissolution at VPI temperatures of 120°C and 150°C, and infiltrated PAN shows resistance to dissolution at VPI temperatures of 90°C, 120°C, and 150°C. These differences suggest that inorganic loading is likely an important predictor for chemical stability in these systems, however we will also discuss chemical structure changes interrogated with infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) to provide more insights for how the chemical differences also contribute to chemical stability in these hybrid materials.

2:45pm **TF1-TuA-3 Understanding the Vapor Phase Infiltration of Trimethyl Aluminum (TMA) into Polyethylene Terephthalate (PET)***, **Mary Kate Broadway**, Mark Losego,* Georgia Institute of Technology

Vapor phase infiltration allows for the creation of hybrid organic-inorganic polymers through co-reaction with gas-phase small molecules. During VPI, polymers are isolated under vacuum and exposed to gas phase metal-organic precursors, which sorb into the bulk polymer and create hybrid materials possessing qualities of both the original polymer and the infiltrated inorganic. Despite the utility of VPI, well-defined reaction pathways, processing conditions, and resultant properties remain undefined for some of the most common commercial polymers. Herein, vapor phase infiltration of polyethylene terephthalate (PET) films via trimethlyl aluminum (TMA), in co-reaction with water, is explored as a function of both precursor dose time and subsequent isolation before introduction of water, in order to elucidate the process mechanisms. The rapid sorption of TMA is found to be followed by a slower, time-dependent desorption process that critically influences the resultant hybrid structure, chemical stability, and mechanical properties. In the case of inadequate desorption time, outdiffusing TMA reacts with subsequently dosed water vapor to form a brittle, aluminum oxide "coating" layer. If a longer desorption time is implemented between the TMA dose and water dose, then a homogeneous organic-inorganic hybrid can be achieved, resulting in the retainment of the PET film's optical clarity and observed increases in the strength and resilience of the resultant surface when subjected to strain or bending. Between these extremes, however, we observe unusual transitory behavior with some hybrid character, but susceptibility to brittle cracking when exposed to certain levels of strain. This talk will examine this transitory behavior, and provide insights into how the physicochemical structure is changing at different levels of infiltration. Overall, this work elucidates new understanding of balancing reagent dosage and purge time in controlling the VPI process for infiltration of PET polymers.

3:00pm **TF1-TuA-4 Vapor-Phase Synthesis and Process Optimization of Porphyrin-Based Covalent Organic Framework Thin Films***, **Mohammad Arham Khan**, Hamidreza Mohajeri Khorasani, Syed Ibrahim Gnani Peer Mohamed, Mona Bavarian, Siamak Nejati,* University of Nebraska-Lincoln, USA

Porphyrin based organic-inorganic hybrid thin films are promising for catalysis, energy conversion, sensing, biomedicine, and environmental applications because of their tunable structures, rich coordination chemistry, and programmable functionality. Among them, porphyrin-based covalent organic frameworks (POR-COFs) are especially attractive due to their intrinsic porosity, ordered structure, and potential for electroactive and optoelectronic applications. However, the poor solubility and limited processability of many two- and three-dimensional covalent frameworks limit their direct integration onto technologically relevant substrates. Here, we investigate vapor-phase growth of POR-COF thin films using 5,10,15,20-tetra(4-aminophenyl)porphyrin (TAPP) as the molecular precursor. Sequential delivery of precursor and oxidant species into the reaction chamber, followed by argon purge steps, enables solvent-free film formation and controlled integration onto surfaces. Temperature, pressure, and precursor exposure time are systematically varied to understand how vapor transport, precursor adsorption, and surface reaction kinetics influence nucleation, surface coverage, film thickness, and deposition rate. Film growth is studied using quartz crystal microbalance (QCM), spectroscopic ellipsometry, atomic force microscopy (AFM), scanning electron microscopy (SEM), and residual gas analysis (RGA). QCM monitors in situ mass uptake during exposure and purge cycles, while ellipsometry tracks thickness evolution under different growth conditions. RGA is used to monitor volatile fragments and reaction byproducts during precursor and oxidant exposure, providing mechanistic insight into oxidant-driven TAPP activation. AFM and SEM provide complementary information on surface morphology, film continuity, roughness, and uniformity. By correlating vapor-phase processing conditions with mass uptake, thickness evolution, and surface morphology, this work identifies growth conditions that promote uniform POR-COF film formation and provides insight into transport-limited and surface-reaction-limited growth regimes. Overall, this study demonstrates vapor-phase synthesis as a versatile strategy for integrating conjugated porous organic frameworks into functional thin-film architectures.

3:15pm **TF1-TuA-5 Enhancing Metalized Polymers Disassembly Using Plasma Polymer Films as a Sacrificial Interlayer**, ***Alexandre Culot***, *Dariane Fadoras, Robin Dantinne,* UMons, Belgium*; Damien Cossement,* Materia Nova Research Center, Belgium*; Jean-Marie Raquez, Damien Thiry,* UMons, Belgium

Metal coatings on polymers are widely used in industries such as electronics, automotive, and packaging for their conductivity, barrier properties, and aesthetics. While strong adhesion between the metallic layer and the polymer is typically beneficial, it poses a significant challenge for their recycling. The separation of such composites is the critical step, requiring costly and limiting methods (e.g., shredding, pyrolysis, dissolving), often resulting in disposal of such waste, causing considerable environmental impact.

In this context, this study explores the use of sacrificial plasma polymer films (PPF) as intermediate layers between metals and polymers to improve the recyclability of the composite. The PPF would ensure strong adhesion with the metallic layer (i.e., Al) while embrittling the coating when exposed to a stimulus (e.g., water immersion, heating).

The PPFs are synthesized from acrylic acid, known to generate PPFs with a high content of carboxylic acid groups, ensuring a strong interaction with aluminum coatings.[1] The analysis of the XPS data reveals a higher retention of the carboxylic group at low plasma power (P_{RF}). ToF-SIMS analysis further shows that, at low P_{RF}, the reduced ionic bombardment during deposition, combined with the higher oxygen content in the PPFs, results in lower cross-linking density compared to PPF deposited at high P_{RF}. Consequently, low P_{RF} PPFs can be readily delaminated upon immersion in water, making them particularly suitable as sacrificial interlayers. Finally, aluminum thin film deposited by magnetron sputtering adheres well to this interlayer while its subsequent removal is significantly facilitated by water exposure.

References:

[1] Friedrich, J. F. et al. Surface & Coatings Technology 2005, 200, 565-568.

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