Emerging Materials
Room Grand Ballroom A-C - Session EM2-WeM
Organic-Inorganic Hybrid Materials

Moderators: Gregory N. Parsons, North Carolina State University, Jonas Sundqvist, Fraunhofer Institute for Ceramic Technologies and Systems IKTS

10:45am **EM2-WeM-12 Vapor Phase Infiltration: A Route for Making Insulating Polymer Fibers Conductive***, **Mato Knez**,* CIC nanoGUNE, Spain*; I Azpitarte,* CTECHnano, Spain

Future technological devices rely in large parts on flexible functional materials. Polymers play an important role for this approach as the combination of low weight and mechanical flexibility makes them unavoidable within this technological concept. However, for a variety of technological approaches, not only the mechanical properties, but also electronic properties of polymers need to satisfy the technological needs.

A promising strategy to implement conductivity into polymer fibers is based on vapor phase infiltration (VPI), if it was successfully applied for an infiltration of a conductive or semiconducting material. VPI is a modification of Atomic Layer Deposition (ALD) which allows synthesis of hybrid materials by infiltration of inorganic materials into organic substrate. With this technique diffusion of precursors into polymeric materials from the gas phase is enforced and yields new composites with inorganic moieties coordinated or covalently linked with the polymeric matrix.

Fibers of poly(p-benzamides), for example Kevlar®, are known since decades and are of great commercial importance primarily because of their exceptional mechanical strength and flexibility as well as an established industrial fabrication process. The polymer gains its mechanical properties through the high molecular order and the intermolecular hydrogen bonds, which in turn makes it very complex to introduce further functionalities into the material. This seriously limits the application range. For example, Kevlar is an electrical insulator and as such by default not suitable as active component in wearable electronic applications.

The present work shows a VPI-based approach towards functionalization of Kevlar fibers in two aspects. In the first instance, electrical conductivity of the intrinsically insulating fibers was induced. This was performed by infiltration of conductive metal oxides. In the second instance the resulting hybrid polymer-inorganic fibers became photocatalytically active upon irradiation with visible light. The photocatalytic effect relies on the insertion of ZnO into the fiber matrix and the chemical interaction between the inorganic and polymeric phase, which eventually result in back-doping of the ZnO with nitrogen hand in hand with the alteration of the electronic structure of the polymeric chain.

11:00am **EM2-WeM-13 Vapor Phase Infiltration of Metal Oxides into Microporous Polymers for Organic Solvent Separation Membranes***, **Emily McGuinness**, F Zhang, Y Ma, R Lively, M Losego,* Georgia Institute of Technology

Membrane-based organic solvent separations promise a low-energy alternative to traditional thermal separations but require advanced materials that operate reliably in chemically aggressive environments. While inorganic membranes can withstand demanding conditions, they are costly and difficult to scale. Polymeric membranes, such as polymers of intrinsic microporosity, are easily manufactured into form factors consistent with large-scale separations (e.g., hollow fibers), but perform poorly in aggressive solvents. Here, a new post-fabrication membrane modification technique, vapor phase infiltration (VPI) is reported that infuses polymer of intrinsic microporosity 1 (PIM-1) with inorganic constituents to improve stability while generally maintaining the polymer's macroscale form factor and microporous internal structure **(Figure 1)**. The atomic-scale metal oxide networks within these hybrid membranes protect PIM-1 from swelling or dissolving in organic solvents including: tetrahydrofuran, dichloromethane, and chloroform **(Figure 2a)**. This atomic-scale metal oxide network further decreases the molecular weight cutoff (MWCO; the smallest molecular weight the membrane "successfully" rejects) in n-heptane and toluene from a MWCO of about 600 g/mol for pristine PIM-1 thin film composite membranes to 204 g/mol for hybrid AlOx/PIM-1 membranes **(Figure 2b)**. The hybrid membranes further retain this MWCO and high levels of rejection (>95%) in solvents that traditionally swell or even dissolve pristine PIM-1 (such as ethanol and tetrahydrofuran). The decrease in MWCO and increase in stability of AlOx/PIM-1 hybrid membranes allows them to perform separations not only between solutes and solvents, but also separations of more challenging systems such as those comprising multiple solvents. For example, the hybrid AlOx/PIM-1 membranes are capable of enriching the toluene concentration in a mixture of 90 wt% toluene, 5 wt% 1,3,5-triisopropylbenzene, and 5 wt% 1,3-diisopropylbenzene from 90.0 wt% to 97.8 ± 0.3 wt%. In this talk, we will discuss the chemical mechanisms of the infiltration process that we believe create the hybrid structures necessary to support this enhanced stability and separation performance.

11:15am **EM2-WeM-14 ZnO-Infiltrated Hybrid Polymer Thin Films with Enhanced Gravimetric Water and Oxygen Vapor Sensing Properties***, E Muckley, L Collins, A Ievlev,* Oak Ridge National Laboratory*; X Ye, K Kisslinger,* Brookhaven National Laboratory*; B Sumpter, N Lavrik,* Oak Ridge National Laboratory*; **Chang-Yong Nam**,* Brookhaven National Laboratory*; I Ivanov,* Oak Ridge National Laboratory

Organic-inorganic hybrids generated by infiltration synthesis, a hybridization technique derived from atomic layer deposition (ALD), can feature various unique materials properties and functionalities not observed in conventional materials. In this work, we discover that the ZnO-infiltrated polymer hybrid nanocomposite thin film exhibits remarkably enhanced light-activated gravimetric gas vapor sensing properties. The hybrid nanocomposite thin film prepared by infiltrating molecular ZnO in SU-8, a common negative-tone, epoxy-based polymer resist, features up to 20-fold greater gravimetric responses to oxygen and water vapors compared with control ZnO or SU-8 thin films in a dark environment. Additional 50 – 500% enhanced responses are detected under ultraviolet (UV) irradiation. Experimental interrogation shows that the increased gravimetric response of the hybrid film is attributed not only to the higher analyte accessibility to active ZnO sites in the matrix but also to the reversible, light-induced increase of surface potential and adsorption energy. Density function theory calculations suggest that the UV enhancement is caused by the light-induced, reversible generation of hydrophilic fluoroantimonic acid from the photoacid generator (PAG) residual in the SU-8 film matrix. A gravimetric sensor based on the ZnO-infiltrated SU-8 hybrid finally enables 96% accurate classification of water and oxygen environments with sub-10 mTorr detection limits. The results highlight the utility of infiltration synthesis for advancing sensor technologies.

11:30am **EM2-WeM-15 Physically Interpenetrated Organic-Inorganic Sub-Surface Layers Created via Vapor Phase Infiltration for Improved Film Adhesion***, **Mark Losego**, S Dwarakanath, R Tummala,* Georgia Institute of Technology

Like atomic layer deposition (ALD), vapor phase infiltration (VPI) uses sequential pulsing of gaseous precursors to chemically modify a substrate. In VPI, these precursors sorb into the subsurface (bulk) of the polymer substrate, eventually becoming entrapped and forming a new organic-inorganic hybrid material. We have been studying the effects of just a few (< 5) VPI exposure cycles on the structure and properties of various polymeric materials and often find that significant inorganic loading can be achieved through a single exposure step (from 2 wt% to up to 20 wt%). Beyond loading, the chemical structure of these materials is still not well understood. While in some cases, chemical bonding between the organic and inorganic components is evident, often we do not observe any chemical changes. For these materials, we believe the metal-organic precursor is forming an adduct to one of the polymer's functional groups, but upon exposure to a co-reactant (e.g., H_2O or O_2), the metal oxide cluster product becomes detached from the polymer. The resulting physically intertwined network of organic and inorganic constituents offers a unique hybrid structure with new property space to explore. This talk will focus on one such system, a redistribution layer (RDL) polymer used for electronic packaging infiltrated with AlO_x. We have found VPI of this RDL polymer can improve adhesion strength to metallic electrode layers by 3x (~200 g/cm for untreated versus ~600 g/cm treated). At failure, these infiltrated interfaces show bulk polymer fracture, indicating the polymer fails before the interface. Extensive spectroscopic investigations show no indication of change to the RDL polymer chemistry, suggesting that the inorganic is physically interpenetrated with the polymer chains creating a "root system" that improves adhesion through physical entanglement. Optimization of the VPI process temperature for adhesion will be discussed. Low process temperatures impede sufficient diffusion depth of the inorganic, while high process temperature preclude sufficient inorganic loading because sorption is thermodynamically limited.

11:45am **EM2-WeM-16 Inorganic-Organic Thin Film Layer-Structures and Thermal Conductivity***, **Fabian Krahl,*** Aalto University, Finland*; A Giri, P Hopkins,* University of Virginia*; M Karppinen,* Aalto University, Finland

We utilize a combined atomic/molecular layer deposition approach to engineer layered ZnO-benzene structures that are meant to show precisely tailorable thermal conductivity values. We deposit a wide range of different layer sequences from regular superlattices to linear gradients (a linear increase in the space between benzene layers) and even more complex layering structures (see attached picture).

In superlattice structures with 12 benzene layers the thermal conductivity is effectively suppressed by decreasing the thermal conductivity from around 54 W $m^{-1}K^{-1}$ in pure ZnO down to values of around 4 W m^{-1} K^{-1}[1,2]. The thermal conductivity in the ZnO-benzene system is most probably suppressed by scattering the phonons that are responsible for the heat conduction in ZnO [2,3]. We are investigating deviations from the superlattice structure and reported our first findings last year [4], more samples are currently measured. We want to understand the connection between the films thermal conductivity and their internal structure to design materials with a high electrical but low thermal conductivity which would be of tremendous use for thermoelectric devices.

References

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