

VAPOR PHASE INFILTRATION FOR TRANSFORMING POLYMERS INTO ORGANIC-INORGANIC HYBRID MATERIALS: PROCESSING SCIENCE, STRUCTURAL COMPLEXITY, AND EMERGING APPLICATIONS

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Vapor phase infiltration (VPI) exposes polymers to gaseous metalorganic molecules that sorb, diffuse, and become entrapped in the bulk polymer, transforming it into a complex organic-inorganic hybrid material.¹ This process is pictured in Figure 1. While VPI's gaseous dosing sequences may appear similar to other vapor deposition techniques (e.g., atomic layer deposition) the set of atomic scale processes occurring during synthesis constitute a fundamentally different process that results in not just a simple coating on the polymer but rather a complete alteration of the polymer's bulk chemistry.

This talk will discuss our development of a thermodynamic and kinetics framework for understanding the VPI materials synthesis process² and how different mechanisms of entrapment can create either three-dimensionally, covalently bonded organic-inorganic networks or, perhaps more interesting, segregated organic and inorganic networks that interpenetrate at the atomic scale but do not form primary bonds with each other. These unusual structures challenge our definition of concepts like "phases" and "interfaces" that we typically use to describe the physiochemical structure of most materials. In this talk, we will ask the audience to consider if the language we use to classify hybrid materials and nanocomposites is appropriate and sufficient.

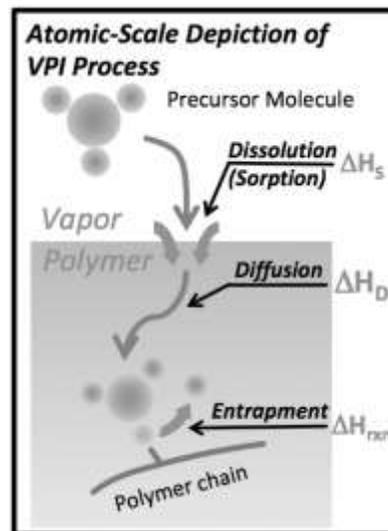


Figure 1 – Depiction of the atomic scale processes important in VPI.

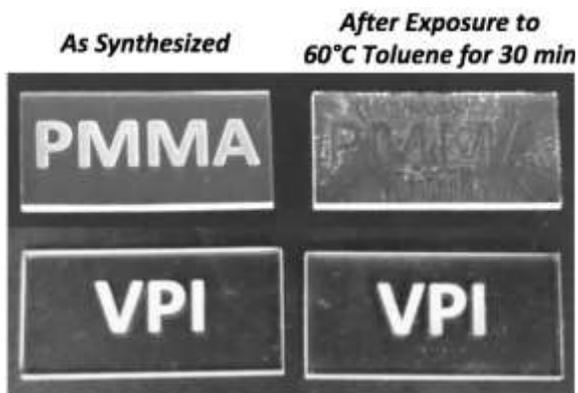


Figure 2 – Photographs of PMMA and VPI treated PMMA (1 exposure cycle to trimethyl - aluminum and water) before and after exposure to hot toluene for 30 min.

This atomic scale intermixing of organic and inorganic constituents generates new physiochemical properties in the material, including a resistance to dissolution or swelling in organic solvents. In certain cases, it is sufficient to infiltrate just a few microns into the subsurface of a polymer to protect the entire polymer (See Figure 2). In other cases, like membranes, we transform the entire material so that it can operate in otherwise "extreme" conditions with little change in performance. Interestingly, the swelling and dissolution behaviors of hybrids with bound and unbound organic-inorganic constituents can vary and appear to depend more upon this bonding environment than the inorganic loading fraction. Perhaps most importantly, many of these modifications can be accomplished with a single exposure to the metalorganic vapors, implying the process can be readily scaled for manufacturing.

¹ C. Z. Leng, M. D. Losego, "Vapor phase infiltration (VPI) for transforming polymers into organic-inorganic hybrid materials: a critical review of current progress and future challenges." *Mater. Horiz.* 4 747 (2017).

² C. Z. Leng, M. D. Losego, "A physiochemical processing kinetics model for the vapor phase infiltration of polymers: measuring the energetics of precursor-polymer sorption, diffusion, and reaction." *Phys. Chem. Chem. Phys.* 20 21506 (2018)