

Hybrid inorganic-(bio)organic materials through molecular level modification with vapor-phase infiltration.

K.E. Gregorczyk¹, M. Garcia¹, I. Azpitarte¹, D. Pickup², C. Rogero², and M. Knez^{1,3}

¹CIC nanoGUNE, 20018 Donostia-San Sebastian, Spain

²Centro de Física de Materiales, Material Physics Center, 20018 Donostia-San Sebastian, Spain

³IKERBASQUE, Basque Foundation for Science, 48011 Bilbao, Spain

Polymeric materials of various types are anticipated being the most important building blocks for future applications. The reasons lie in their established processes for mass production in various shapes, mechanical flexibility for easy handling, compatibility for roll-to-roll production processes, versatility in functionalization, etc. While for many applications synthetic polymers are still without alternative, many approaches seek for a sustainable substitute, whenever suitability is given.

Cellulose represents the most abundant biopolymers on Earth and is the fundamental building block of plants and their subsequent products such as paper and cotton. Furthermore recent and significant interest has been expressed in using cellulose based materials in a wide variety of applications, in everything from supercapacitors, batteries, and solar cells, to advanced functional filters in waste water treatment, and even wearable electronics. Several techniques have been proposed for the functionalization of these next generation materials including, sol-gel, CVD, etc. However, one of the most promising techniques is atomic layer deposition (ALD). ALD is a similar, though chemically distinct, form of CVD that allows low temperature deposition, often below 100°C, monolayer material growth, and extreme conformality over even the most stringent geometries. A recent modification to ALD, termed vapor phase metal infiltration, allows for molecular scale modification of a variety of biological and synthetic substrates and scaffolds including; spider silk, collagen, porphyrins, and polytetrafluoroethylene (PTFE) towards an entirely new class of hybrid materials. As well as a more detailed understanding of the reaction between these organic substrates and the metal-organic precursors commonly used in standard ALD processes.

Here we report the modification of a variety of polymers, including spider silk, collagen, PTFE, Kevlar, cellulose and cotton with common ALD precursors, trimethyl aluminum and diethyl zinc. Our findings show that the precursors induce small, but important changes to the polymer upon chemical interaction and that each precursor has different potential reaction pathways. For characterization a variety of methods have been applied, including FTIR, XRD, NMR, XPS and Raman spectroscopy. We also discuss how these small molecular scale changes lead to large changes in the bulk mechanical properties of the substrates as studied through uniaxial tensile testing. These experiments point at the possibility of using this infiltration method to alter the properties of the materials by hybridizing inorganic ceramics with a polymeric substrate.