

Infiltration, Imidization, and Cross-Linking of Polyimides in Molecular-Scale Confinement

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Abstract:

Nanocomposite materials with a polymeric phase have novel properties—including exceptional toughness, strength, and low density—making them desirable for a variety of applications. Previous studies have shown that when the polymer within the nanocomposite material is confined to molecular-scale dimensions, polymer and nanocomposite properties are dramatically altered. In this work, we studied the effect of molecular-scale confinement on the synthesis and toughness of a nanocomposite material composed of polyimide in a nanoporous matrix. We optimized the properties of this composite material by varying the processing time and temperature. The extent of polymer infiltration, the ring-closing imidization reaction, and cross-linking of the polymer were studied. Finally, we measured the toughness of the composite material and found it to be increased by 87% as compared to the empty matrix. This work led to a better understanding of the effect of nanometer-scale confinement on the toughness of nanocomposite materials.

Introduction:

Composite materials combine dissimilar materials to produce improved properties, including low density and increased toughness and strength. One method of composite material synthesis involves infiltrating a polymer into the interconnected pore structure of a stiff inorganic matrix, which induces confinement of the polymer phase. In this work, we synthesized nanocomposite materials with polymers confined at molecular length-scales in order to test the limits of toughening with polymers in extreme confinement. The materials were created through a unique backfilling approach in which polymers are infiltrated into the pores of a nanoporous glass scaffold. This synthesis technique leads to uniform mixing of the two phases at small length-scales and produces uniform, high-quality films over large areas.

The confining matrix for this work was ethylene oxycarbosilane (Et-OCS), a porous organosilicate with a porosity volume of 47% and interconnected pores roughly 7 nm in diameter. Polyimide was chosen for the polymer phase in this work, as its ability to withstand high temperatures makes it ideal for future applications as a material for high-performance aerospace applications. Our objective for this work was to optimize the processing conditions for the Et-OCS/polyimide nanocomposite material and to test its mechanical properties.

Experimental:

The porous Et-OCS matrix was synthesized as a ~ 600 nm film on a silicon wafer and then cut into 1 × 1 cm² samples [1]. Each sample was then spin-coated with a thin film (~ 300 nm) of polyamic ethyl ester, a polyimide precursor manufactured by the U.S. Air Force. The sample was then cured under an inert atmosphere in a Yield Engineering Systems oven (Figure 1).

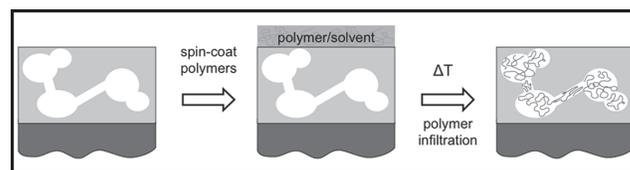


Figure 1: Infiltration strategy for Et-OCS/polyimide nanocomposite material.

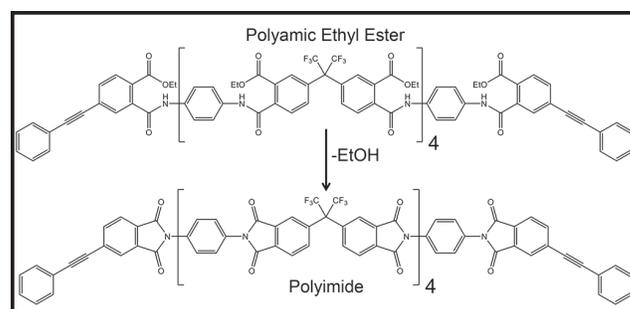


Figure 2: Imidization of polyamic ethyl ester to form polyimide.

During this high-temperature curing process, a number of changes can occur within the sample, all of which can affect the properties of the final product. First, the polymer infiltrates the pores of the matrix. Additionally, the polymer itself undergoes reactions in confinement: a ring can close in the polyamic ethyl ester structure, forming polyimide (Figure 2) and possible side products, and cross-linking can occur at the alkyne end-groups of the polymer chains. Infiltration of the polymer was monitored using depth profiling x-ray photoelectron spectroscopy (XPS). Chemical changes within the polymer structure were monitored using Fourier transform infrared spectroscopy (FTIR).

FTIR peaks for the various polymer species in the sample were then assigned and used to elucidate an imidization reaction mechanism for this process [2]. From the XPS and FTIR data, an ideal curing profile was selected to make nanocomposite samples with the maximum degree of infiltration, the largest amount of desired polyimide product, and the desired density of cross-linking. Finally, toughness of samples was assessed by making double cantilever beam (DCB) specimens containing the nanocomposite material of interest between two silicon beams (Figure 3). These specimens allowed us to measure the energy required to propagate a crack through the nanocomposite film, providing a quantitative measure of toughness.

Results and Discussion:

We found that imidization was most successful (gave the greatest ratio of desired product to side product) when the samples were cured at higher temperatures (>300°C) for one hour. We also observed that infiltration was most complete when the samples were cured at a lower

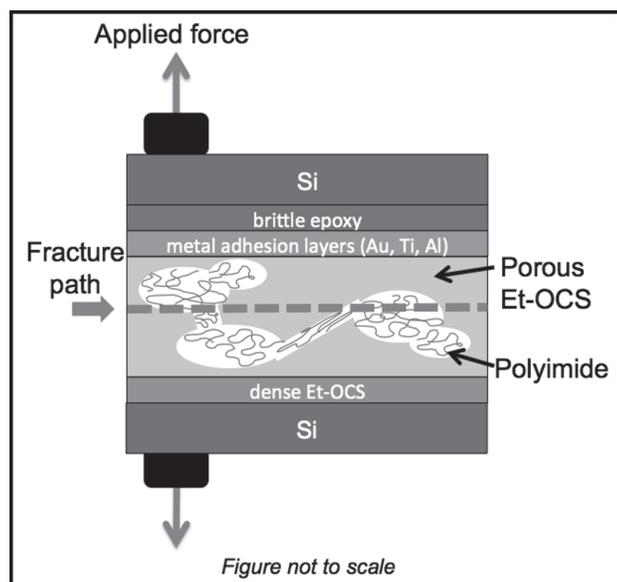


Figure 3: A schematic of a double cantilever beam specimen.

temperature (<200°C) for four hours. Cross-linking did not occur until the cure temperature reached 360°C.

In order to synthesize a sample with optimized degrees of imidization, infiltration, and cross-linking, we chose a cure profile of 170°C for four hours to allow the polymer to infiltrate the pores and begin imidizing, followed by an hour-long period of increased temperature (370°C) in order to complete imidization and cross-link the confined polymer chains. Then, we measured the fracture energy of two nanocomposite films: one consisting of an Et-OCS matrix containing no polymer in the pores, and one containing polyimide processed according to the optimized curing conditions described above.

The sample with no polyimide in the pores had a cohesive fracture energy of 2.3 J/m², a low toughness that is common for nanoporous glasses. The sample with cross-linked polyimide in the pores exhibited increased cohesive fracture energy of 4.3 J/m², an 87% increase

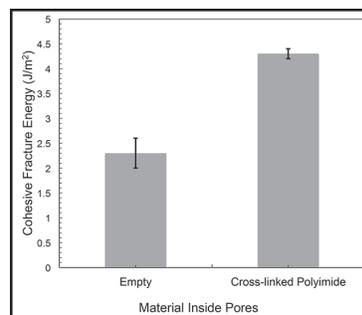


Figure 4: Cohesive fracture energy, a measure of toughness, increases when the pores of a nanoporous glass are filled with cross-linked polyimide.

in toughness compared to the unfilled film (Figure 4). Therefore, the objective of this project was met: we synthesized a novel nanocomposite material, tested its mechanical properties, and found it to be tougher than the empty matrix.

Future Work:

Future work will focus on further mechanical testing of samples containing polyimide with various degrees of cross-linking, investigating thermal stability of the nanocomposite material, and investigating other polyimides for filling the pores of the Et-OCS matrix.

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