Multifunctional Polymers via Incorporation of Ionic Groups at Molecular and Mesoscopic Length Scales

Mohamed Aflal Mohamed Rahmathullah

Giuseppe Palmese, Ph.D. Co-Advisor: Yossef A. Elabd, Ph.D.

Multifunctional polymer systems with specific functionality and strength are developed by integrating diverse polymers into physically and chemically compatible composite structures. The concept has been achieved repeatedly in nature in examples such as the human skin or stimuli-responsive plants, where sensory or actuating mechanisms are part of a structurally sound system. Similar ideas can be extended to polymeric materials by incorporating hydrophilic ionic groups within hydrophobic nonionic polymers to achieve desired functionality and mechanical strength respectively. This notion has been the focus of this work that is broadly categorized into investigations at the molecular and mesoscopic length scales.

At the molecular scale, three strategies were investigated for thermoset functionalization. First, ionic groups were grafted on nanoporous and hydrophobic epoxy-amine thermosets via sulfonation. Second, copolymerization of hydrophobic diglycidyl ether of bisphenol A vinyl ester (VE) and hydrophilic 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS) was investigated. Reactivity ratios were used to determine the distribution of VE and AMPS in a copolymer network based on the Mayo-Lewis terminal model. Links between structure and properties such as water uptake, proton conductivity, and proton mobility were elucidated. Fuel cell performance was evaluated and compared to Nafion® 117. Third, functionalized epoxy thermosets were prepared by the encapsulation of reactive or non-reactive ionic liquids. 1-ethyl 3-methyl imidazolium dicyanamide exhibited thermally latent cure behavior and tunable network hydrophilicity, modulus, and glass transition temperatures.

At the mesoscopic length scale, two strategies were investigated in developing polymer-polymer composites. First, fiber-thermoplastic matrix composites were developed as selective permeation membranes and proton conductive membranes. This was achieved by encapsulating, within a thermoplastic matrix, either hydrophobic fibers with grafted ionic groups or hydrophilic fibers. A combination of microscopy, permeability measurements and proton conductivity were used to assess composite performance. Correlations between the spatial location of ionic groups and proton mobility were developed and extended to understand the effects of polymer structure. Second, ionomer-thermoset composites were developed as potential self-healing materials designed to combine crack-repair characteristics of the ionomer with the mechanical strength of the thermoset. Since an unmodified epoxy-amine thermoset also exhibits significant healing, a fundamental understanding on the crack-healing behavior of epoxy-amine thermosets was developed.