Flame Resistant Polymers from Natural Resources
Dept. of Materials Science and Engineering
University of Michigan, Ann Arbor, MI 48109-2136

Research Objective: To develop routes to simple, low cost Al and Si containing metalloorganic monomers and polymers starting directly from Al(OH)₃ and SiO₂ (e.g. rice hull ash) that offer potential as novel flame resistant materials.

Approach: We recently demonstrated that SiO₂ and Al(OH)₃ react with triethanolamine in ethylene glycol solvent, to form air and moisture stable silatrane and alumatrane complexes, NCH₂CH₂O)₃SiOCH₂CH₂OH and NCH₂CH₂O)₃Al with essentially quantitative yields. We can also synthesize the cubic octasilsesquioxane, (HMe₂SiOSiO₁.₅)₈, from rice hull ash in > 90% yields and modify it by hydrosilylation. We then sought to functionalize these compounds with various polymerizable groups to develop novel, processable polymers. Our goal is to synthesize and process low cost polymers that offer mechanical/insulating properties of potential use in aircraft interiors.

Accomplishment Description: We have developed polymerizable silatrane glycol, NCH₂CH₂O)₃SiOCH₂CH₂OH, derivatives by replacing the OCH₂CH₂OH group with acetate to form NCH₂CH₂O)₃SiOAc which in turn provides access to: NCH₂CH₂O)₃SiOR where R = methacrylate, allyl, ethylamine, 2-chloroethane, etc. We are currently preparing polymeric derivatives. We also synthesized (RMe₂SiOSiO₁.₅)₈ (R = 3-propanol, ethylcyclohexene epoxide, ethylcyclohexene, etc) and are exploring methods of homopolymerizing and copolymerizing them to making hybrid composites with architectural features controlled at the nanometer length scales—nanocomposites. We scaled up syntheses to 100 g scales to make mechanical test samples, which were tested for tensile strength and fracture toughness. We find that by controlling length scales we can make nanocomposite materials: (1) stable to temperatures of >400°C, (2) nanoporous for insulation, (3) and that offer better mechanical properties than common epoxy resins, with improved resistance to oxidation.

Significance: The work done with cubic silesquioxanes allowed formulation of new principles for the design and synthesis of discontinuous, hybrid nanocomposites wherein the length scales are completely defined. Syntheses provide nanocomposites consisting entirely of interphase or with controlled microporosity. We are able to test the fundamental principles that relate interfacial organic architectures with mechanical properties in nanocomposite materials. Furthermore, we can probe the effects of architectural changes in organic segments linking inorganic segments, on physical properties. In principle, we can totally delineate how interfacial interactions work, design nanocomposites for specific applications and identify the source of novel properties that arise when very different materials are combined at the nanoscale. This is potentially a revolutionary approach to the design of nanocomposite materials in general (ref. 1).
**Expected Results:** We were hoping to compare and contrast the effects of using cubic silesquioxanes in epoxy resins on the mechanical properties of these resins. For example, Figure 1 shows the reaction of an octaglycidal epoxy cube with dianilinomethane, MDA. Figure 2 shows the anticipated reaction, wherein it is implied that each nitrogen on the MDA reacts with only one epoxide group.

![Figure 1](image1.png)

**Figure 1**

![Figure 2](image2.png)

**Figure 2**

Figure 3 shows a plot of the elastic modulus as a function of added MDA. The modulus peaks at exactly the 1:1 ratio. Likewise, the fracture toughness shown in Figure 4 also peaks at the same ratio. This strongly suggests that each MDA bridges between two cubes when the mechanical properties are greatest. Furthermore, the peak elastic modulus is the same or slightly less than that obtained using the diglycidyl ether of bisphenol A, DGEBA—see 0% line for modulus. Finally, the fracture toughness is >30% higher than the DGEBA/MDA epoxy resin, see 0% line for Kic in Figure 4. This strongly suggests that designed nanocomposites can provide unusual and superior properties. Flame resistance studies are to be done at FAA.

Point of Contact: Dr. R. M. Laine, Dept. of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109-2136. (734) 764-6203, FAX 763-4788, email: talsdad@umich.edu

Figure 3. Elastic Modulus of Epoxy Resin Made with Octaglycidyl Octasilsesquioxane (OG) and Dianilinomethane (MDA).
Data point at 0 mole fraction OG is for DGEBA/MDA prepared under the same conditions, cured 150°C/4 h.

**Figure 4. Fracture Toughness of OG/MDA Epoxy**  Data point at 0 MF OG is for DGEBA/MDA