

RESEARCH CLUSTER F: Fire-Safe Polymers & Polymer Composites

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Cluster F research centers on the synthesis and characterization of polymer materials that combine key properties of mechanical performance with low flammability. Application areas for these materials range from transportation interior (aircraft, trains, ships, etc.) to polymers used in microelectronics packaging. Collaborative activity of Cluster F researchers is geared towards improved understanding of anti-flammable materials by considering the chemistry, engineering, characterization, and theoretical components of the research. The elimination of additives, such as halogens, needed to obtain non-flammable properties is a major driver of the research.

Overview. Fire in enclosed and inescapable areas, such as aircraft cabins, submarines, ships, subways and hotels represents a serious threat to human life. While lightweight, high performance polymers offer many performance advantages, their inherent flammability is a drawback that must be addressed through fundamental and applied research. In 1996, the University of Massachusetts Amherst, in conjunction with the Federal Aviation Administration and industrial partners, initiated a multi-investigator program towards novel, fire-safe materials. The program, part of the FAA's Fire-Resistant Materials Program, strives to eliminate burning cabin materials as a cause of fatalities in aircraft accidents. This requires substantial reduction in cabin fire hazards that cannot be achieved with currently used materials. UMass Amherst research activities focuses on new fire-resistant polymers and polymer/inorganic composites that have high thermal stability, extremely low combustion heat-release rates, low total heats of combustion, and high char formation. Novel synthesis, materials modification, modeling, analytical tools, and testing methodologies are all key elements of the Cluster.

Synthetic Efforts in Cluster F center on producing polymers and nanocomposites that, upon burning, char quickly as a fire-extinguishing mechanism. Polyimides and bisphenol C-containing polyarylates and polycarbonates have proven particularly attractive in this regard, as have nanocomposites composed of clay-based epoxy resins, and POSS-polymer hybrid materials. New synthetic efforts have discovered monomer and polymer designs that mimic the anti-flammable properties of halogenated polymers, but that are halogen-free. For example, Cluster F researchers led the discovery of deoxybenzoin-based monomers for the preparation of non-flammable polyarylates, polyphosphonates, polyurethanes, and epoxy polymers. In addition, nanocomposite research (*i.e.*, with carbon nanotubes and graphene) reveal many positive attributes towards reducing polymer flammability.

Characterization. *Microscale Calorimetry and Combustion Analysis.* New experimental techniques, especially pyrolysis GC/MS, simultaneous thermal analysis (STA), and pyrolysis-combustion flow calorimetry (PCFC) characterize the flammability and thermal decomposition behavior of polymers synthesized in Cluster F. Unlike conventional flammability measurements, these experiments require only milligram-scale samples. For example, the PCFC method, originally developed by FAA researchers, is rapid and quantitative, and provides information equivalent to the Cone Calorimeter, which requires hundred-gram samples, and operates on the same oxygen-consumption principle. Heat release rate, total heat of combustion, and char yield, the most important parameters of materials thermal performance, are obtained directly from PCFC. The STA, which can perform simultaneous TGA and DSC to temperatures of 1200 deg C, is an important method to study thermal reactions in the condensed phase. It quantifies the heat associated with thermal stability, the decomposition process, and the rate of decomposition. Pyrolysis GC/MS is a simple, rapid and sensitive method for characterization of volatiles produced during polymer decomposition. By quantifying the decomposition products as a



Pyrolysis GC/MS (50~100ug)



STA (TGA/DSC) (10mg)



Pyrolysis-combustion flow calorimeter (PCFC) (1mg)

Thermal decomposition and flammability testing using milligram samples

function of temperature and heating rate, decomposition mechanisms can be elucidated, and heats of combustion calculated. These methods screen small samples of newly synthesized materials to guide further synthetic efforts. Numerical and analytical modeling has also been applied to understand mechanisms of polymer combustion and fire resistance. To date, several new classes of materials synthesized in the Cluster meet FAA objectives in terms of flammability, and afford some of the lowest measured heat release rates of any hydrocarbon polymers ever made.

Research topics include:

- *Synthesis of Low Heat Release, High-char Thermoplastic and Thermoset Polymers* - Bryan Coughlin and Todd Emrick
- *Development of Non-halogenated Polymer Materials* - Todd Emrick and Bryan Coughlin
- *Thermal and Mechanical Properties and Processing of Flame Retardant Precursor Polymers* – Alan Lesser and Todd Emrick
- *Thermomechanical Stability of Resins and Composites* - Alan Lesser
- *Microscale Combustion Calorimetry for Determining Flammability Parameters of Materials* - Richard Lyon (FAA) and Alan Lesser

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