FINAL REPORT

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"The Synthesis and Characterization of New Thermoplastic Fire Resistant Materials"

From:

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Introduction

Organic materials are widely utilized in aircraft interiors for various important applications, such as carpets, seats, bins, appliance housings, communication devices, etc. The relevance of fire-safe materials for the transportation industry has been widely acknowledged, but the relationship between the molecular structure of the materials and their behavior in fires has been poorly understood. Therefore, this research involved the synthesis, characterization, and processing of new materials that are essential for improving the fire performance of material systems

Research Objectives

This research explored the utilization of the phenyl or methylphosphine oxide moiety on the fire resistance of ductile thermoplastic high performance materials. The aryl phosphine oxide structure is readily incorporated into engineering thermoplastic backbones in controlled concentrations. It is hydrolytically stable, but allows for the transformation into a very high char residue after burning, which prevents ignition and inhibits continued burning. An emphasis was placed on the synthesis of arylene ether ketone copolymers containing systematically varied concentrations of triphenyl phosphine and diphenyl methyl phosphine oxide residues. We also synthesized wholly aromatic polyimides and polybenzoxazoles that contained the phosphine oxide structure. Dynamic TGA traces showed remarkably high char yield in air.

Molecular characterization was also an important component of this project, and including assessing molecular weight, chemical composition, and copolymer molecular structure, morphological behavior, with an emphasis on thermal analysis and dynamic mechanical behavior. Fire testing data was generated in conjunction with government colleagues at NIST, and with industrial colleagues at the DuPont and Phillips Petroleum Laboratories.

The goal of this researched included the demonstration that melt processable, high performance fire safe material systems could be generated that would be amenable to standard important fabrication techniques, such as injection molding, extrusion, and fiber spinning. Our laboratory utilized a Custom Scientific film extruder to demonstrate that film or tape could be prepared in an analogous way to tat sought by commercial producers. Parallel plate rheology was also utilized to demonstrate that melt stable systems based on the high performance materials, such as the poly(ether ketone)s, polyimides, and polyphenylene sulfides, could, in fact, be prepared. Variations in calculated molecular weight using the Caruthers equation was correlated with apparent melt viscosities.

Detailed Summary

Phosphorus containing monomers, bis(3-aminophenyl)methyl phosphine oxide (m-DAMPO) and bis(3-aminophenyl)phenyl phosphine oxide (m-DAPPO), were synthesized and incorporated into a thermoplastic poly(arylene ether imide) based upon 2,2'-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride and 1,3-phenylene diamine, in order to study their influence on flame resistance. DAMPO or DAPPO were quantitatively incorporated in concentrations of 25, 50, 75 and 100 mole percent and molecular weight of 20K. The resulting copolymers demonstrated a significant increase in char yield in air as a function of the phosphine oxide content, thus suggesting improved fire resistance. In addition, a series of high molecular weight triphenyl phosphine oxide and/or diphenyl ketone containing PPSS copolymers were synthesized from the bis-(4-mercaptophenyl) sulfone by reaction with 4,4'-dichlorodiphenyl sulfone, bis-(4-fluorophenyl) phenyl phosphine oxide, and 4,4'-difluorobenzophenone in DMAc in the presence of K_2CO_3 at 160°C. The new phosphine oxide containing PPSS copolymers were completely amorphous, showed improved solubility in common organic solvents and exhibited very high char yields in air at 750°C. Surface (XPS) analysis results shows that the phosphorus moieties in the polymer backbone formed phosphate-like layers on the polymer surface, protecting the inner materials from further decomposition in air at high temperatures. TGA and micro cone calorimetry analyses showed that the semi-crystalline materials with high ketone content had much higher char yields and significantly lower heat release rate and total heat release, compared to the poly(phenylene sulfide sulfone) and poly(phenylene sulfide) controls.

Overall Results

This research involved the synthesis of either aromatic diamine monomers containing the phenylphosphine oxide structure for polyimides, or the activated aromatic halide containing the phenyl or methyl phosphine oxide connecting link for poly(arylene ether)s or poly(arylene sulfide)s. The resulting thermoplastic poly(ether imide)s and thermoplastic poly(phenylene sulfide sulfone) copolymers had similar, if not better properties, than the control commercially available materials. They provided equal or better reduced heat release rates relative to their commercial counterparts and in traditional tests they self-extinguish more rapidly. In addition, these thermoplastic systems displayed good thermooxidative and tensile properties.

Publications resulting from USDOT/FAA Award Number 95-G-051
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