Polyphosphazenes: Flame-Retardants for Aircraft Applications

H. R. Allcock and M. M. Coleman Departments of Chemistry and Materials Science and Engineering The Pennsylvania State University, University Park, PA 16802

Research Objective

To develop new fire-retardant polymers that can be incorporated into blends, IPN's and composites with existing commodity polymers to improve their fire resistance when used in aircraft applications.

Approach: The polymers being developed are based on the inherently fire-retardant polyphosphazene platform, in which the phosphorus-nitrogen polymer backbone confers fire-resistance not only on the phosphazene but also on the second (organic) polymer component in the mixture. In this way, the valuable properties of the polyphosphazene can be transposed to the composite as a whole, while retaining the low cost and processing advantages of the commodity material. Three approaches are being examined. First, new methods for the synthesis of polyphosphazenes are being developed that are expected to give greater control over the polymer chain length and polymer architecture, and to lower the costs for the large-scale production of polyphosphazenes. Second, a range of different polyphosphazenes, with different side groups, are being synthesized and examined to determine their behavior under combustion conditions. Third, these same polymers are being incorporated into polymer blends with classical polymers that are currently used in the interiors of commercial aircraft, and their combustion behavior is monitored. As part of this aspect, fundamental studies are being conducted on the compatibility of the different polyphosphazenes with other polymers to determine the ways in which different polymer side groups influence polymer-polymer interactions in blends and IPN's. Infrared spectroscopy is used as one method to determine the miscibility of polymer blends.

Accomplishment Description: A new method for the synthesis or polyphosphazenes has been developed. This involves the room temperature, cationic living condensation polymerization of a phosphoranimine, $Me_3SiN=PCl_3$, to give polymers with controlled chain lengths, end group control, and access to phosphazene-organic block copolymers. The availability of block copolymers produced in this way is a major breakthrough in this field that is expected to facilitate the development of new polymers that are compatible with conventional organic polymer systems. It should also lead eventually to a reduction in the costs of the polymers. In addition more than 20 new types of polyphosphazenes have been synthesized, with different side chains and different ratios of two or more different side groups. These polymers are being subjected to molecular and materials characterization studies, and have been evaluated by thermal analysis, horizontal flame tests, standard oxygen index burning tests, and by pyrolysis-combustion flow calorimetry (by Dr. R. Lyon, FAA). Overall, these polymers show superior resistance to combustion compared to most organic polymers. One

polyphosphazene $[NP(OC_6H_4COOH)_2]_n$ has been incorporated into IPN's with polyurethanes and has shown flame retardant properties when present at¹ 15-20% concentration levels. Good progress has also been made in the study of polymer compatibilities via infrared analysis of polymer interaction parameters. In Figure 1, the carbonyl stretching region of several blends are shown. From these spectra we are able to determine that the *bis*ethoxy and the *bis*propoxy polyphosphazenes are miscible, while the *bis*butoxy and the *bis*pentoxy polyphosphazenes are not. Similarly, poly(vinyl methyl ether) and poly(vinyl ethyl ether) are miscible with BMAVPh{74}, but the higher homologues are not. Experimental miscibility data such as these are being used to evaluate parameters that can be utilized to predict the phase behavior of a wide variety of polyphosphazene blend systems that have potential as flame retardant materials.

Significance: We are making good progress toward the design and synthesis of new polymers that will significantly improve the fire resistance of the materials used in the interiors of commercial aircraft. The major significance is our ability to custom design different polyphosphazenes to form blends or IPN's with widely used commodity petrochemical-based organic polymers.

Expected Results: As this research progresses we anticipate an improvement in our ability to design polyphosphazenes with specific combinations of properties (eg. elasticity and compatibility coupled with flame retardance) and to produce polymer blends and IPN's of these polymers with the materials currently used in aircraft construction. A reduction in the costs of these polymers and the ease of scale-up are other important objectives.

References:

Reed, C. S.; Taylor, J. P.; Guigley, K. S.; Coleman, M. M.; and Allcock, H. R. "Polyurethane/Poly[bis(carboxylatophenoxy)phosphazene] Blends and their Potential as Flame-Retardant Materials." <u>Polymer and</u> <u>Engineering Science</u>, in press, 1999.

Taylor, J. P. and Allcock, H. R. "Phosphorylation of Phosphazenes and its Effects on Thermal Properties and Fire Retardant Behavior". <u>Polymer Engineering and Science</u>, submitted, 1999.

Point of Contact: Dr. Richard Lyon, Manager, Fire Research Program, Fire Safety Section AAR-422/Building 277 FAA W. J Hughes Technical Center, Atlantic City International Airport, NJ 08405, rlyon@admin.tc.faa.gov, Tel/Fax (609) 485-6076 / 6909.

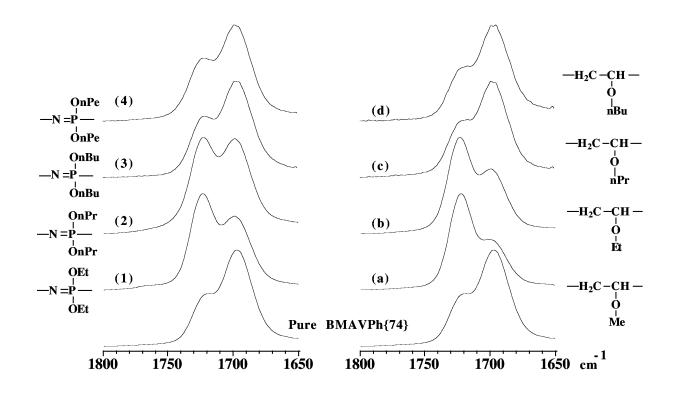


Figure 1. Left: Infrared spectra of 50:50wtblends of poly n-alkoxy phosphanzenes with poly (butyl methacrylate-co-vinyl phenol) containing 74 mol% VPh (BMAVPh{74}). Right: Analogous blends with poly (vinyl alkyl ethers).