

Fire-Resistant Elastomers

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May 2002

DOT/FAA/AR-TN01/104

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1. Report No. DOT/FAA/AR-TN01/104		2. Government Accession No.		3. Recipient's Catalog No.	
4. Title and Subtitle FIRE-RESISTANT ELASTOMERS				5. Report Date May 2002	
				6. Performing Organization Code	
7. Author(s) Richard E. Lyon				8. Performing Organization Report No.	
9. Performing Organization Name and Address Federal Aviation Administration William J. Hughes Technical Center Airport and Aircraft Safety Research and Development Division Fire Safety Branch Atlantic City International Airport, NJ 08405				10. Work Unit No. (TRAIS)	
				11. Contract or Grant No.	
12. Sponsoring Agency Name and Address U.S. Department of Transportation Federal Aviation Administration Office of Aviation Research Washington, DC 20591				13. Type of Report and Period Covered Technical Note	
				14. Sponsoring Agency Code AIR-120	
15. Supplementary Notes					
16. Abstract Molecular design of semi-inorganic rubbers has yielded flexible polysilphenylene-siloxane and polyphosphazene elastomers having the fire resistance of rigid, high-temperature engineering plastics (e.g., polyaramids, polyetherketones, and polyarylsulfones) based on the results of microscale combustibility data. In flaming combustion, a commercially viable polyphosphazene exhibited a 75% reduction in heat release rate compared to the polyurethane rubber currently used in fire-blocked foam aircraft seat cushions. A comparable reduction in heat release rate is obtained at lower cost by adding expandable graphite flakes to the polyurethane formulation. The graphite flakes exfoliate during heating to produce a 2000% volumetric expansion of the burned rubber which shields and insulates the underlying material from the heat source and lowers the heat release rate significantly. Future work will explore the use of relatively low-cost expandable graphite technology in semi-inorganic rubber to obtain a fireproof (zero heat release rate) seat cushion foam.					
17. Key Words Fire, Heat release, Elastomer, Rubber, Seat cushion, Graphite, Polymer, Silphenylene, Siloxane			18. Distribution Statement This document is available to the public through the National Technical Information Service (NTIS), Springfield, Virginia 22161.		
19. Security Classif. (of this report) Unclassified		20. Security Classif. (of this page) Unclassified		21. No. of Pages 22	22. Price

ACKNOWLEDGEMENTS

The Federal Aviation Administration is grateful to Harry Allcock of the Pennsylvania State University for providing the polyphosphazenes, to Bill MacKnight and Simon Kantor of the University of Massachusetts for the polysilphenylene-siloxanes, and to Kay-Metzeler for supplying the polyurethane with and without expandable graphite. Certain commercial equipment, instruments, materials, or companies are identified in this report in order to adequately specify the experimental procedure. This in no way implies endorsement or recommendation by the Federal Aviation Administration.

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EXECUTIVE SUMMARY

Molecular design of semi-inorganic rubbers has yielded flexible polysilphenylene-siloxane and polyphosphazene elastomers having the fire resistance of rigid, high-temperature engineering plastics (e.g., polyaramids, polyetherketones, and polyarylsulfones). In flaming combustion, a commercially-viable polyphosphazene exhibited a 75% reduction in heat release rate compared to the polyurethane rubber currently used in fire-blocked foam aircraft seat cushions. A comparable reduction in heat release rate is obtained at lower cost by adding expandable graphite flakes to the polyurethane formulation. The graphite flakes exfoliate during heating to produce a 2000% volumetric expansion of the burned rubber—a process that shields and insulates the underlying material from the heat source and lowers the heat release rate significantly. Adding expandable graphite flakes to the polyphosphazene reduced its flaming heat release rate to 6% of the standard polyurethane (i.e., an order of magnitude reduction in fire hazard) and to 40% of the graphite modified polyurethane.

BACKGROUND

Commercial transport category aircraft contain about two tons of flammable rubber (elastomers) as seat cushions, pillows, and flexible sealants [1]. Polyurethane rubber foam seat cushions are favored for their durability and shape recovery, but they are among the primary contributors to the fire hazard in aircraft interiors [2 and 3] as shown in the full-scale fire test of figure 1. In 1987, the Federal Aviation Administration (FAA) imposed Federal Airworthiness Regulation (FAR) 25.853c on the flammability of aircraft seat cushions to delay their involvement in cabin fires [4 and 5]. The oil burner test for flammability of seat cushions involves subjecting a fully constructed seat cushion (e.g., figure 2) to an oil burner flame for 2 minutes (see figure 3) and recording the mass loss of the cushion and the burn length. The FAA requirements are that the burn length of the cushion should not exceed 43 cm (17 inches) and the mass loss should not exceed 10 percent of the original weight.

Manufacturers responded to these regulations by wrapping the polyurethane seat cushion in a fire-resistant barrier fabric [3 and 5] (see figure 2). Seat fire blocking allowed manufacturers to pass the 2-minute FAA certification test but the polyurethane foam burns vigorously when the fire-blocking layer is consumed (see figure 1). More recently, combustion-modified polyurethane foam rubber has been developed [6], some of which passes the FAA seat cushion flammability test without the need for a fire-blocking layer [7 and 8]. These second-generation aircraft seat cushions are made fire resistant by combining the polyurethane foam with a halogen-containing rubber [7] or by the addition of flame-retardant chemicals and expandable graphite flakes to the polyurethane [8].



FIGURE 1. FULL-SCALE FIRE TEST SHOWING SEAT CUSHION INVOLVEMENT



FIGURE 2. AIRCRAFT SEAT CUSHION INCLUDING COVER FABRIC, FIRE-BLOCKING LAYER, AND POLYURETHANE FOAM CUSHION

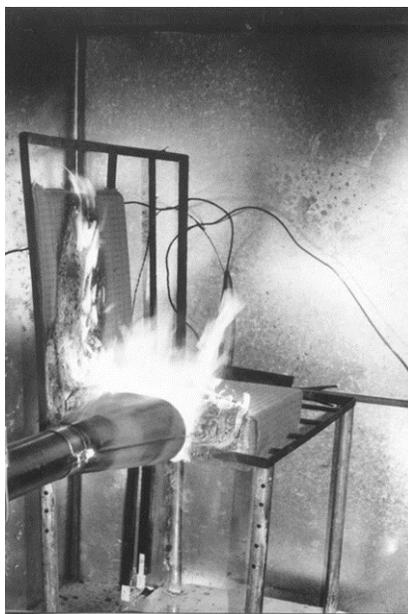
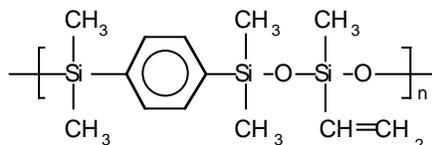


FIGURE 3. FAA SEAT CUSHION FLAMMABILITY TEST FAR 25.853c

The flammability of foamed rubber depends on the chemical composition of the polymer from which it is made. Hydrocarbon rubbers, such as polyurethane, styrene-butadiene (SBR), polyisoprene, and rubbers from ethylene-propylene-diene monomers (EPDM) are the most flammable because they ignite easily and have high-fuel value and heat release. Replacing carbon and hydrogen atoms in the polymer with inorganic atoms, such as chlorine, silicon, nitrogen, sulfur, or phosphorus, results in a polymer with reduced flammability because of increased heat resistance and lower fuel value. The Fire-Resistant Materials research program is focusing on semi-inorganic rubbers for seat cushions.

Silphenylene-siloxane elastomers [9 and 10] with a phenyl-silicon-oxygen backbone were synthesized, which can be cross-linked through pendant vinyl groups and are extremely heat resistant [10-12]. The silphenylene whose chemical structure is shown below contains only 30% combustible material and can withstand short temperature exposures of 600°C (1100°F).

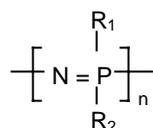


The motivation to investigate flame-retardant elastomers based on silphenylene and siloxane with vinyl groups is the following: (1) the presence of silphenylene in the polymer backbone inhibits the formation of 5- and 6-membered cyclic siloxane oligomers, which are thermodynamically favored at temperatures above 300°C so that thermal decomposition is delayed to temperatures above 500°C. Increasing the thermal decomposition temperature increases the amount of heat needed to cause ignition and reduces the fuel generation rate; (2) the incorporation of vinyl groups on the siloxane allows the polymer to be cured by addition of a multifunctional Si-H

compound under catalysis with a variety of platinum complexes. The hydrosilylation reaction of the double bonds with the Si-H cross-linker then generates a network structure. Depending upon the ratio of cross-linker to vinyl groups, the cross-link density of such a system can be controlled over a broad range. Materials can thus be obtained with properties ranging from a slightly cross-linked elastomer to a highly cross-linked rigid resin. A rubbery polymer results when only a small amount of the vinyl groups present in a high-vinyl content-polymer are cross-linked by hydrosilylation, leaving the bulk of the vinyl groups available to thermally cross-link at fire temperatures. The resulting resin is rubbery and has high char yield in a fire and good flame retardancy.

A series of strictly alternating vinyl substituted (i.e., cross-linkable) silphenylene-siloxane copolymer elastomers with systematically varying vinyl content were synthesized and characterized [10-12]. The polymers are completely amorphous gums with glass transition temperatures ranging from -86° to -59°C as a function of vinyl content and volume fraction of highly mobile siloxane units. The materials degrade thermally above 500°C . As the vinyl content increases, both the onset temperature of major degradation and the char yield at 900°C shift to higher values. One of the polymers has an extremely high degradation temperature of over 600°C and a char yield of almost 70 percent in air, which makes it a promising candidate for potential applications as a flame-retardant elastomer. The reason for the remarkable thermal stability is ascribed to the interruption of the siloxane backbone sequence with the silphenylene moiety and cross-linking reaction of the vinyl groups which occurs slightly below the onset of siloxane redistribution reactions around 300°C .

Polyphosphazenes are semi-inorganic rubbers based on a phosphorus-nitrogen backbone



where R_1 and R_2 may be the same or different chemical groups which allow the material to be dissolved or cross-linked. Polyphosphazenes are intrinsically fire-resistant materials [13] which impart fire resistance to flammable materials when blended [14 and 15]. Foamed polyphosphazene rubber (EYPEL-A, Ethyl Corporation) was used by the U.S. Navy for fire-resistant helicopter seating until 1993 when production was discontinued because the process to make the material was too expensive. The FAA is funding research to develop polyphosphazene blends and interpenetrating networks with polyurethane [16]; new cyclophosphazene derivatives for use as flame retardants [17 and 18]; a new low-cost, low-temperature cationic polymerization route to polyphosphazenes and phosphazene copolymers which eliminates a costly intermediate from the process and allows control over the molecular weight of the polymer [19-23]; and phosphazene derivatives of combustible polymers [24-29].

In particular, phosphazene high polymers with side groups $\text{R} = -\text{OC}_6\text{H}_4\text{COOH}$ were incorporated chemically into a standard (Bayer) expanded polyurethane foam formulation at levels of 20% polyphosphazene (2% phosphorus) or higher. The resultant phosphazene-urethane interpenetrating network (IPN) is self-extinguishing in horizontal burn test [16]. Polyphosphazenes with $\text{OC}_6\text{H}_4\text{OP}(\text{O})(\text{OR})_2$ ($\text{R} = \text{ethyl or phenyl}$) side groups and the

corresponding small-molecule cyclic trimers were synthesized and the phosphorylated polymers showed 40%-50% char yields and resistance to combustion. The small-molecule cyclic trimers can be used as fire-retardant additives for polystyrene [17 and 18]. Linear polyphosphazenes and cyclic phosphazene side units were incorporated into hydrocarbon polymers such as polynorbornenes. Polynorbornenes are extremely flammable. However, by linking norbornene monomer molecules to phosphazene rings or chains, followed by ring-opening-metathesis polymerization of the norbornene, a broad series of polymers have been produced that have fire resistance. Moreover, the macromonomers can be copolymerized with norbornene or its derivatives to dilute the phosphazene component along the polymer chain. These polymers are candidates for blending with a wide range of classical organic polymers to generate fire resistance. Note that, because the phosphazene components are covalently linked to the organic polymer, they cannot diffuse from the system, whatever their molecular size [24]. Fire-retardant phosphazene units were incorporated into flammable organic polymers using an azide coupling process in which styryldiphenylphosphine is homopolymerized or copolymerized with styrene or methyl methacrylate. A monoazido cyclic phosphazene is then coupled to the pendent phosphine groups to give an organic polymer with cyclic phosphazene units as side groups. The copolymers with styrene showed markedly enhanced fire resistance at the 10% incorporation level with limiting oxygen index values of 28%-33% v/v oxygen. Polymer blends also showed good promise for fire-resistant materials [25-28]. Fire-retardant phosphazenes were incorporated into organic polymers by the formation of cycloliner polymers in which small-molecule phosphazene rings are joined together by organic chains. This was accomplished through acyclic diene metathesis (ADMET) polymerization of cyclophosphazenes with two olefinic side chains. The process gives polymers with high loadings of phosphorus and nitrogen in which the separation between the phosphazene rings along the chain can be varied easily. These polymers appear to be excellent candidates for blending with classical hydrocarbon polymers such as polyolefins [29].

A new method for the synthesis of polyphosphazenes using a living cationic polymerization of phosphoranimine monomers was discovered [19-23]. This process allows the molecular weight of the polymers to be controlled by the initiator to monomer ratio, gives narrow-molecular weight distributions, and provides access to the first phosphazene block copolymers. The most important fire-related aspect is the ability to produce block copolymers between polyphosphazenes and classical organic polymers such as polystyrene or polyethylene oxide. This opens up a method for the preparation of polymers that will be compatible with flammable organic polymers and will facilitate the incorporation of the fire-retardant phosphazene component into compatible blends or IPNs.

The objective, as with all the synthetic polymer chemistry described above, is to find ways to reduce the cost of fire-resistant elastomers and optimize their physical properties. This report summarizes the fire and flammability results of the poly(silphenylene-siloxane) and polyphosphazene elastomers and compares them to the state-of-the art polyurethane, which is foamed to make fire-blocked seat cushions or modified with expandable graphite flakes to make intrinsically fire-resistant aircraft seat cushions.

MATERIALS

POLYURETHANES.

A commercial supplier of combustion-modified aircraft seat cushion foams provided 4 ±1-mm-thick, full-density sheets of the standard seat cushion polyurethane (without the added water and excess isocyanate to prevent foaming). A standard polyurethane rubber containing 20% w/w expandable graphite was also provided.

POLYSILPHENYLENES.

Research quantities (grams) of vinyl-substituted silphenylene-siloxane polymers of high molecular weight were synthesized as described in references 11, 12, and 13. Because of the high cost of the starting materials, quantities sufficient for fire calorimetry testing (kilograms) were not synthesized.

POLYPHOSPHAZENES.

The polyphosphazenes in this report were synthesized by bulk thermal ring opening polymerization of hexachlorocyclophosphazene to form high molecular weight polydichlorophosphazene [30], followed by substitution of chlorine atoms with alkoxy and aryloxy pendant groups from the sodium salts of the corresponding alcohol. Samples of the phenoxy-paraethylphenoxy polyphosphazene (PN-A), formerly known commercially as EYPEL-A, were synthesized and cast as 4 ±1 mm-thick full-density sheets. Some samples were lightly cross-linked through a few ortho-allylphenoxy substituents using benzoyl- or dicumylperoxide. A sample of PN-A polyphosphazene rubber containing 20% w/w expandable graphite was also provided.

METHODS

The following methods were used to evaluate the combustibility and fire behavior of the polysilphenylene and polyphosphazene elastomers.

MICROSCALE COMBUSTION CALORIMETRY.

The heat release capacity [31] is a quantitative measure of the dynamic combustion potential of a material and is a good predictor of fire and flame test performance. The heat release capacity was measured in a pyrolysis-combustion flow calorimeter (PCFC) [32 and 33]. The PCFC is a thermoanalytical technique that reproduces the separate processes of fuel generation and combustion as they occur at the material surface in a fire. In the test, a 1 milligram sample is placed inside a quartz capillary tube and heated to 900°C in an inert gas stream (nitrogen) at a constant heating rate of ≤ 5 K/s. The fuel gases are swept from the pyrolyzer by the nitrogen purge gas, mixed with excess oxygen, and enter a tubular furnace at 900°C where complete oxidation of the fuel occurs. The (nonflaming) combustion products water, carbon dioxide, and possibly acid gases are removed from the gas stream by Ascarite™ and Drierite™ scrubbers, and the mass flowrate and oxygen concentration are measured and used to calculate the heat release rate of the sample from the oxygen consumption [34]. Dividing the maximum value of the heat

release rate (W) by the initial sample mass (g) and heating rate (K/s) gives the heat release capacity of the sample in units of J/g-K.

FIRE CALORIMETRY.

A fire calorimeter (Cone2, Atlas Electric Devices) operating on the oxygen consumption principle was used to measure the mass loss rate, smoke generation, heat release rate, and total heat release of materials in forced flaming combustion at a cold-wall external radiant heat flux of 50 kW/m², according to a standard method [35]. Duplicate samples of each formulation having approximate dimensions of 10 by 10 by 0.4 ±0.1 cm were cut from full-density rubber sheets and tested for heat release rate, total heat release, smoke, and carbon dioxide/carbon monoxide yield.

RESULTS

MICROSCALE COMBUSTIBILITY.

The heat release capacity, η_c , the total heat of combustion of the fuel gases per unit mass of original polymer, h_c , and the char yield, μ , from pyrolysis combustion flow calorimetry are listed in tables 1, 2, and 3 for the polyurethane rubber, polysilphenylene-siloxanes, and the polyphosphazenes, respectively. The heat release capacity is the molecular-level response of a polymer to an imposed heat flux (heating rate) and is proportional to the heat release rate in steady-flaming combustion. Consequently, low values of η_c are indicative of low flammability in the FAA seat cushion test and low full-scale fire hazard.

TABLE 1. MICROSCALE COMBUSTIBILITY DATA FOR POLYURETHANES

POLYURETHANE	η_c (J/g-K)	Total Heat (kJ/g)	μ (%)
Polyurethane rubber with expandable graphite	431	19.8	13
Polyurethane rubber	607	24.3	1.5

TABLE 2. MICROSCALE COMBUSTIBILITY DATA FOR POLYSIPHENYLENE SILOXANES

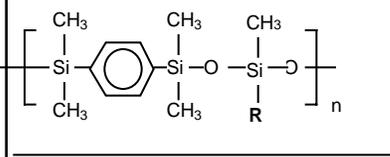
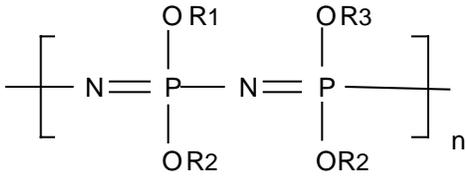
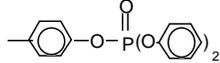
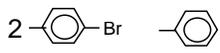
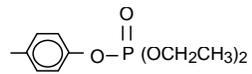
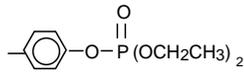
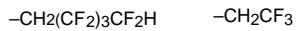
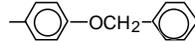
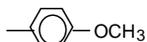
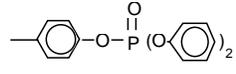
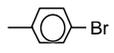
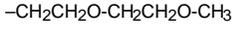
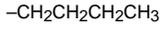
	η_c (J/g-K)	Total Heat (kJ/g)	μ (%)
R = -CH=CH ₂	71	12.7	48
R = 9/9/2, -CH ₃ /  / -CH=CH ₂	112	15.4	31
R = 4/1, -CH ₃ / -CH=CH ₂	134	19.1	27
R = 9/1, -CH ₃ / -CH=CH ₂	139	18.9	21
R = CH ₃	159	20.1	12
R = 	175	19.9	19

Figure 4 is a plot of the heat release capacity of commercial polymers versus their price in bulk, showing the proportionality between fire safety and materials cost. Superimposed on this set of data are the range of heat release capacities in tables 2 and 3 for the polysilphenylene-siloxane and the polyphosphazene elastomers, respectively. It is observed that, depending on the fuel value of the backbone substituent, the research elastomers span the range from highly flammable commodity polymers, like polyurethane, nylon, and epoxy, to low-flammability, heat-resistant engineering plastics like polyetherimide (PEI) and polyetherketoneketone (PEEK). The polyurethane elastomer used in fire-blocked seat cushions is the current (2001) baseline material and the FAA research milestones of a 50% reduction in heat release capacity by 2001, and order of magnitude reduction in heat release rate by 2005, are indicated.

TABLE 3. MICROSCALE COMBUSTIBILITY DATA FOR POLYPHOSHAZENES

	η_c (J/g-K)	Total Heat (kJ/g)	μ (%)
	62	9.5	41
	88	13.9	31
	88	12.5	43
	93	11.0	43
	98	7.8	1
EYPEL-A 	100	9.1	45
	135	19.7	41
	163	16.3	39
	166	9.6	0
	169	19.5	25
	279	15.1	17
	359	22.5	20
	418	25.9	9
	758	30.5	18

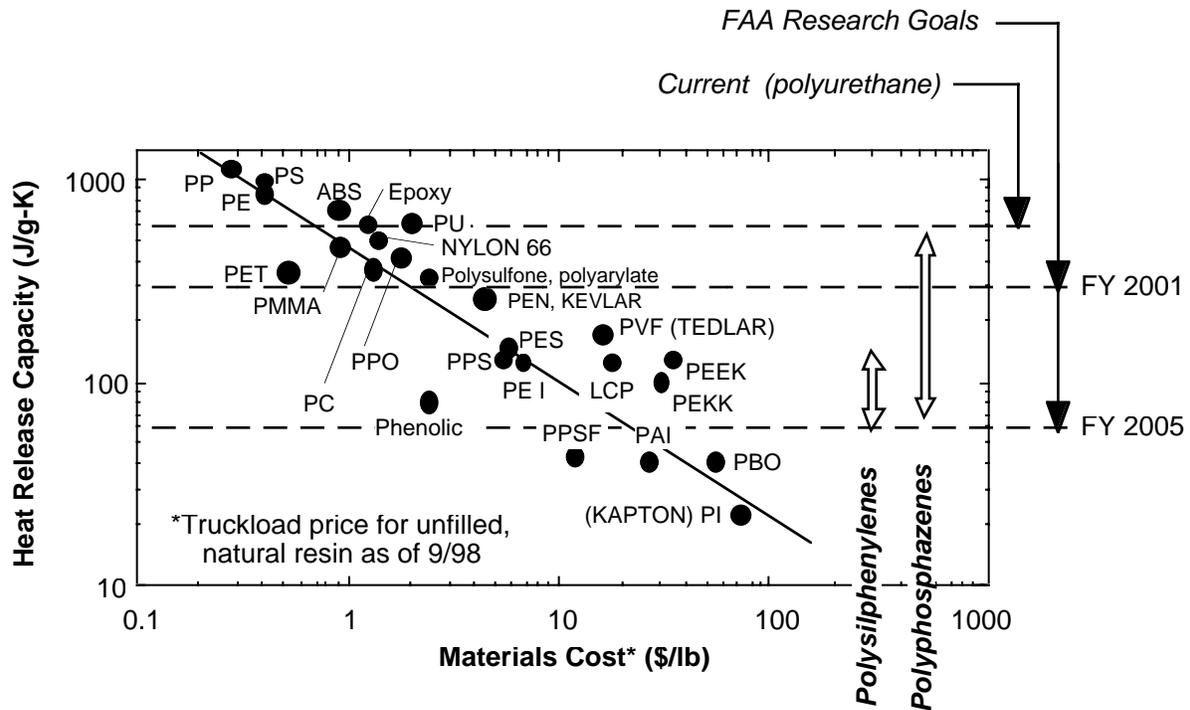


FIGURE 4. HEAT RELEASE CAPACITY OF COMMERCIAL POLYMERS IN COMPARISON TO POLYSILPHENYLENE-SILOXANE AND POLYPHOSPHAZENE ELASTOMERS

FIRE RESPONSE.

Coupon-level flaming combustion parameters are listed in table 4 for a polyurethane elastomer currently used in aircraft seat cushions with a fire-blocking layer, the same polyurethane elastomer formulated with expandable graphite to pass the FAA seat cushion test, the PN-A polyphosphazene, and the PN-A polyphosphazene formulated with 20 weight percent expandable graphite. The time-to-sustained ignition reported in table 4 is the measured time for the surface to maintain flaming combustion in the absence of the spark igniter. The total heat released is the time integral of the areal heat release rate over the test duration. The specific extinction coefficient is an average obscuration value per unit mass of combusted material computed over the test duration and duct cross-section from the attenuation of the laser beam and the instantaneous mass loss rate. Carbon dioxide/carbon monoxide (CO_2/CO) yields are the test averages obtained from on-line infrared analyzers and the instantaneous mass loss rate. All of the other 16 gases analyzed were below the limit of detection.

TABLE 4. FIRE RESPONSE PARAMETERS OF SELECTED ELASTOMERS

Fire Parameter	Polyurethane	Polyurethane With Expandable Graphite	Polyphosphazene	Polyphosphazene With Expandable Graphite
Time to Ignition (s)	16	13	16	13
Peak Heat Release Rate (kW/m ²)	1122	155	295	63
Total Heat Released (MJ/m ²)	88	69	53	25
Average Mass Loss Rate (kg/m ² -s)	0.032	0.005	0.012	0.003
Average Effective Heat of Combustion (MJ/kg)	24	23	15	12
Flaming Combustion Efficiency	0.98	0.99	0.91	0.85
Avg. Specific Extinction Area of Smoke (m ² /kg)	307	91	1161	659
Average Combustion Gas Yields (kg/kg)				
Carbon dioxide	2.02 ±0.44	1.58 ±0.28	0.66 ±0.17	1.47
Water	0.82	0.52	0.24	0.62
Carbon monoxide	0.03 ±0.01	0.04 ±0.03	0.14 ±0.00	0.20
Hydrogen chloride	Not detected	Not detected	0.002	0.003
Nitric oxide	0.011	0.003	0.002	Not detected
Hydrogen cyanide	0.001	0.001	0.004	0.004
Ethylene	Not detected	Not detected	0.004	0.001

Figure 5 shows heat release rate data for 4 ±1-mm-thick sheets of polyurethane, polyurethane formulated with expandable graphite, PN-A polyphosphazene, and PN-A polyphosphazene formulated with 20% w/w graphite tested at 50 kW/m² incident radiant heat flux in the cone calorimeter. The addition of the expandable graphite to the polyurethane and polyphosphazene elastomers reduces their peak heat release rates by 5-7 times. The PN-A polyphosphazene containing expandable graphite exhibits a heat release rate 18 times lower than the standard polyurethane rubber and approximates that of heat resistant engineering plastics such as polyetherimide and polyphenylsulfone. The flaming combustion efficiencies in the last row were calculated from the ratio of the net effective heat of flaming combustion from fire calorimetry (table 4) divided by the net heat of complete combustion of the pyrolysis gases from pyrolysis-combustion flow calorimetry (tables 1-3).

Figure 6 shows the postfire test sample residues for the polyphosphazene and polyurethane with and without expandable graphite. It is seen that the polyurethane rubber is completely consumed in the fire test, leaving only the aluminum foil sample-backing in the test fixture. In contrast, the polyphosphazene leaves a considerable char residue. The polyurethane and polyphosphazene formulated with the expandable graphite leave a light friable char on the order of 20-50 times the original sample volume that insulates the underlying polymer during the test and results in a 5-7X lower peak heat release rate (see table 4).

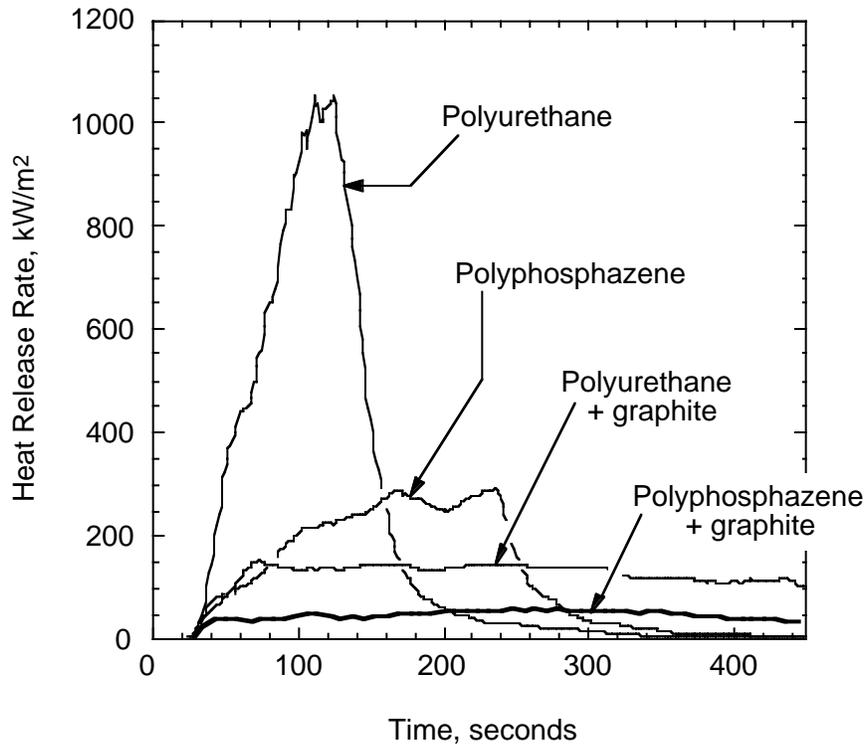


FIGURE 5. FLAMING HEAT RELEASE RATE DATA FOR POLYURETHANE AND POLYPHOSPHAZENE WITH AND WITHOUT EXPANDABLE GRAPHITE

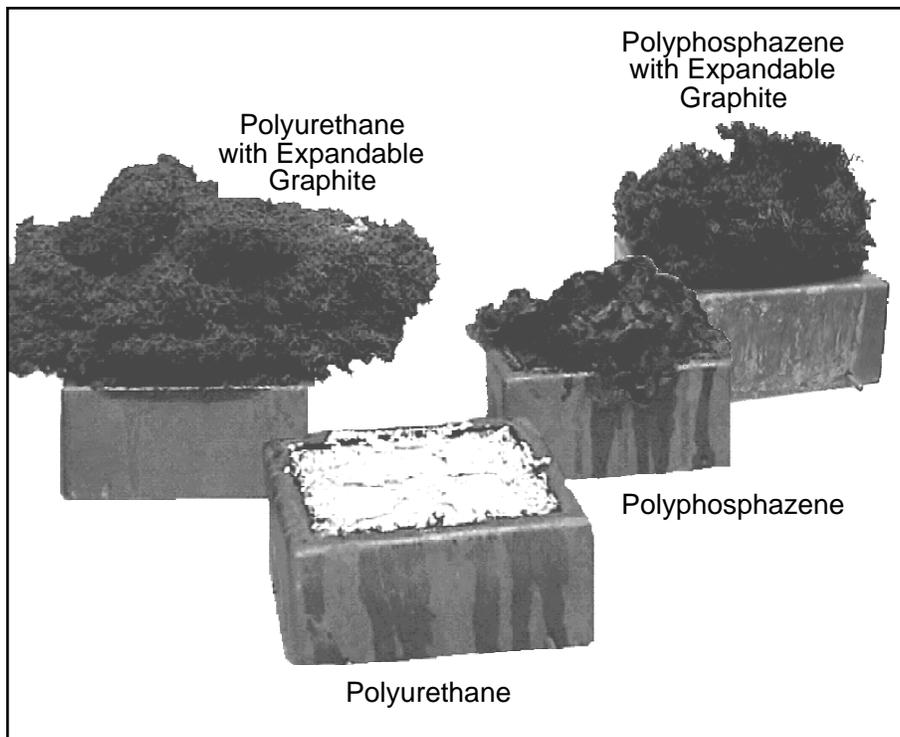


FIGURE 6. POSTFIRE TEST PHOTOGRAPH OF POLYURETHANE AND POLYPHOSPHAZENE WITH AND WITHOUT EXPANDABLE GRAPHITE

DISCUSSION

The heat release rate of an unmodified polyphosphazene elastomer in flaming combustion is 75% lower than the current unmodified aircraft polyurethane elastomer used in fire-blocked seat cushions. Further reduction in heat release rate is expected for halogen-containing polyphosphazenes and halogen-free polysilphenylene-siloxane elastomers based on microscale combustibility data. The flaming combustion efficiency of the polyphosphazene samples is slightly lower than for the polyurethanes (90% versus 99%), probably due to the presence of phosphorus in the polyphosphazene combustion gases. Incomplete combustion results in the higher smoke obscuration, CO/CO₂ ratio, and HCN levels observed for the polyphosphazene compared to the polyurethanes. However, because the mass loss rate is lower for the polyphosphazene samples, the smoke-generation rate (average specific extinction area multiplied by average mass loss rate) differs by less than a factor of 2 between the pure polymers and a factor of 4 for the graphite modified polymers. The low-combustion efficiencies of the polyphosphazene samples are consistent with the proposed mechanism of the flame-retardant action of other organophosphorus compounds, such as phosphines and phosphine-oxides, where phosphorus is in a low-oxidation state. Flame retardancy in phosphine oxide-containing polymers has been ascribed primarily to gas phase combustion inhibition via hydrogen scavenging by a volatile P=O species, regardless of whether the phosphorus is present as an additive [36] or as a backbone structural unit in the polymer [37].

The polyphosphazene and polyurethane elastomers formulated with expandable graphite flakes have heat release rates which are 5 and 7 times (5-7X) lower, respectively, than the unmodified materials. The addition of graphite flakes is, thus, a very cost-effective strategy for imparting fire resistance to combustible elastomers. The use of expandable graphite in the more fire-resistant polyphosphazenes or polysilphenylene-siloxane elastomers at comparable efficiency would provide a 20-30X reduction in heat release rate compared to the polyurethane rubber currently used in fire-blocked seat cushions and would provide a factor of 4 reduction in heat release rate compared to graphite-modified polyurethane foamed rubber.

CONCLUSIONS

Molecular design of polysilphenylene-siloxane and polyphosphazene has yielded flexible elastomers having the fire resistance of high-temperature, engineering plastics (e.g., polyetherimides, polyetherketones, and polyphenylsulfones) based on the results of microscale combustibility data. In flaming combustion, a polyphosphazene exhibited a 75% reduction in heat release rate compared to the polyurethane currently used in fire-blocked foam seat cushions. The addition of expandable graphite to polyurethane rubber produces a material with a heat release rate comparable to the pure polyphosphazene but at significantly lower cost. The addition of expandable graphite to polyphosphazene reduces its peak heat release rate by 80% to a level which is less than half of the value for combustion modified polyurethane currently used in aircraft seat cushions without a fire-blocking layer.

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