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### Title

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## JOURNAL ARTICLE

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# Ignition of Combustion Modified Polyurethane Foam

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**ABSTRACT:** Results are presented from an experimental study on the ignition of the combustion modified (fire retarded) polyurethane foam Pyrell<sup>®</sup> (35.3 kg/m<sup>3</sup> and 64.0 kg/m<sup>3</sup>) in elevated oxygen concentrations, ranging from 30% to 60%. The samples are exposed to an external flow and variable radiant heat flux on one face, and insulated on the other faces. The experiments show that Pyrell undergoes a weak smoldering reaction that requires significant assistance in the form of external heat input in order to propagate. The results also show that given sufficient oxygen and radiant heat flux, the smoldering reaction can produce enough volatile fuel and heat to trigger a gas phase ignition, i.e. a transition from smoldering to flaming, in pores in the char region. The experiments also indicate that high-density Pyrell is more ignitable than low-density Pyrell, which could be explained by the greater solid surface area for smoldering reactions to take place.

**KEYWORDS:** combustion modified, fire retarded, polyurethane foam, oxygen enriched, smoldering, transition to flaming, ignition, spacecraft, fire.

## Introduction

The potential danger of a fire aboard spacecraft warrants extreme care in the design and selection of spacecraft materials. In particular, cushioning materials present a fire safety risk because foams tend to be susceptible to smoldering and transition to flaming. Smoldering, which generally occurs in porous materials, is defined as a slow, low-temperature, flameless, heterogeneous form of combustion, in which oxygen directly attacks the surface of a condensed-phase fuel. Smoldering is hazardous because it provides a pathway to flaming that can be initiated by sources much too weak to directly produce a flame [1]. The transition to flaming results in a fast, highly exothermic, gas phase reaction with potentially catastrophic consequences. The danger of smoldering is clearly observable by the fact that 40% of household fire deaths in the United States are caused by smolder-originated fires [2]. In addition, there have been reports of minor incidents of overheated and charred cables and electrical components on Space Shuttle flights [3] and a fire caused by a solid fuel oxygen generator on the Mir Space Station in 1997 [4]. Currently, there is insufficient knowledge about the behavior of smoldering and the transition to flaming in the absence of buoyancy encountered in microgravity conditions aboard spacecraft. The present work is part of a NASA funded project to study the transition

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from smolder to flaming of polyurethane foam in environmental conditions encountered in spacecraft facilities, i.e., microgravity, and low velocity and variable oxygen concentration oxidizer-flows.

Pyrell<sup>®4</sup>, a combustion modified (fire retarded) polyurethane foam, is one of the allowed materials for equipment stowage protection in the NASA Space Shuttles and the International Space Station because it performs very well in terms of fire resistance in environments with 21% oxygen [5]. However, for future extended space flights, NASA is considering using higher spacecraft oxygen concentrations in order to lower the total pressure (by reducing the nitrogen partial pressure) [6]. The benefits of reducing the total cabin pressure include minimizing weight and facilitating extra vehicular activity (EVA) by reducing the decompression sickness risk. According to a recent NASA report [7], the tentative upper bound for future spacecraft cabin oxygen concentration is 30%, but higher concentrations have been used in the past, such as 70% oxygen in Skylab. The current NASA committee on this topic, the Exploration Atmospheres Working Group, of which two authors of this paper are members, is currently considering environments of up to 36% oxygen for future spacecraft. In practice, there are fluctuations around the nominal oxygen concentration; for the Mars mission the control range is expected to be +/- 2%. Clearly, the flammability of Pyrell in elevated oxygen concentrations must be examined. The present study investigates smoldering and transition to flaming in Pyrell in enriched oxygen environments.

It is well known that non-fired retarded (NFR) polyurethane foam is susceptible to smoldering and transition to flaming [1,8,9]. In particular, Bar-Ilan et al. conducted a study on forward smoldering and transition to flaming in NFR flexible polyurethane foam of density 26.5 kg/m<sup>3</sup>, using the same experimental apparatus as that in the present study. It was found that the smoldering reactions, including strong secondary char oxidation, were responsible for triggering the transition to flaming, by supplying heat and vaporized fuel to the gaseous mixtures within the char region [9].

There have been numerous studies performed on fire retarded (FR) flexible polyurethane foam. Rogers performed one of the first studies on the effects of a variety of commercial fire retardants on flexible polyurethane foam, and found that some fire retardants suppressed smoldering while others enhanced smoldering, but did not offer explanations for the differences [10].

Chao and Wang performed several studies on both FR and NFR flexible polyurethane foams, and observed behaviors in their FR foam different from those of Pyrell. Using time-of-flight secondary ion mass spectroscopy and a colorimetric method, they found that the FR foam had 0.08% phosphorus and 1.4% bromine additives by weight. By thermogravimetric analysis (TGA) they found that the fire retardant additives decreased the thermal stability and increased the char formation in the temperature range 300-400°C [11], which is the typical smolder temperature range in polyurethane foam. In another set of experiments, Chao et al. showed that their FR foam samples of 150 x 150 mm cross section can undergo self-sustained smolder in air [12]. Finally, Chao and Wang conducted a study on smoldering and transition to flaming in both FR and NFR foam, and found that the fire retardants can make the transition more likely. They suggested that the increased char formation in the FR foam provides more fuel for secondary

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<sup>4</sup> Pyrell<sup>®</sup> is a registered trademark of Foamex International, Inc., Linwood, PA, USA. Commercial trade names are used for certain products in this report for identification purposes. This use does not constitute an endorsement by UC Berkeley or the US Government.

char oxidation, which produces the heat to trigger the gas phase ignition of the flammable smolder gases [13].

To date, there has been very little work published on the flammability of Pyrell foam. Hshieh et al. showed that in 30% oxygen and 70.3 kPa, Pyrell fails the NASA Upward Flame Propagation Test (NASA STD-6001 Test 1) because the flame spreads up the entire sample length. Hshieh et al. also subjected Pyrell to cone calorimeter experiments in 21% oxygen, and found that the minimum heat flux for ignition (by spark igniter) was  $27 \text{ kW/m}^3$ . When exposed to a radiant heat flux of  $26 \text{ kW/m}^3$  for 10 minutes in the cone calorimeter, Pyrell smoldered, but the smolder reaction quickly extinguished upon removal of the external heat source [5].

Levchik and Weil compiled a review of the many types of fire retardants currently used in flexible polyurethane foams [14]. The most common fire retardants are phosphorus-containing additives and halogen-phosphorus-containing additives. The most widely used commercial fire retardant is the halogen-phosphorus-containing compound TDCPP, which acts in both the condensed and vapor phases. In the solid phase, a phosphorus-containing carbonaceous layer grows between the flame and the pyrolysis zone, and acts as a barrier for the transfer of heat and fuel [15]. In the gas phase, the vaporized TDCPP dilutes the fuel vapors sufficiently to reduce the flame-propagation velocity to below that at which they stream out of the pyrolysis zone [16]. Halogen-phosphorus-containing additives also inhibit flaming by radical scavenging: the decomposition of halogen-phosphorus additives produces both halogen radicals and phosphorus compound radicals that scavenge  $\text{OH}^*$  and  $\text{H}^*$  radicals, which can otherwise react in highly exothermic flaming [17]. Jayakody et al. tested a wide variety of commercial fire retardants in polyurethane foam using a cone calorimeter, and found that TDCPP was the most effective and reduced the peak heat release rate by 21% [18].

Another common fire retardant, melamine, is usually synergistic with phosphorus or halogen-phosphorus additives, and is especially useful in suppressing smoldering [14]. Bastin et al. suggested that the synergistic effect is that the TDCPP generates phosphoric acid, which promotes the conversion of melamine into thermally stable network structures such as melam, melem, and melone [19]. Dick et al. used  $^1\text{H}$  NMR spectroscopy to find that the melamine additive acts in the condensed phase by promoting the formation of a rigid char at temperatures above  $400^\circ\text{C}$  [20]. Melamine is also believed to act as a heat sink, and the nitrogen content of melamine may partly end up as nitrogen gas, providing a heat sink and diluent in the gas phase [21]. In addition, the melamine is believed to react with the evolved toluene diisocyanate fraction arising from the decomposition of polyurethane, to form a polymeric structure that reduces the smoke and CO release [21].

## Experiment

### *Experiment Concept*

The foam sample is a vertically-oriented rectangular prism with a square cross-section, insulated on three of its surfaces and with the fourth, free surface, exposed to an upward forced convective oxidizer flow parallel to the surface. The experimental apparatus is very similar to that used by Bar-Ilan et al. for non-fire retarded polyurethane foam experiments [9], and a schematic is shown in (Fig. 1).

Because the microgravity experiments were planned for the International Space Station, the foam samples had to be limited in size for safety and launch mass reasons, to 50 mm x 50

mm cross section and 125 mm long. Due to the small size of the samples and resulting high surface-to-volume ratio, they have significant heat losses. Larger sizes of foam, as are more commonly used in practical applications, are able to better insulate the reactions occurring within, as a result of their lower surface area to volume ratio. Therefore, to simulate a larger, more practical foam sample, the sample was thermally insulated, and exposed to an external radiant heat flux. The heat losses from the sample sides were reduced by controlling the wall temperature with guard heaters on the exterior of the sample holder walls. The guard heaters maintain the walls at a temperature of 200 °C, which was chosen in order to avoid significant thermal decomposition by pyrolysis caused directly by the guard heaters. At 200 °C, the polyurethane foam degradation in isothermal thermogravimetric experiments is 5% by mass, but rapidly increases if temperature rises (i.e. at 220 °C the degradation is 20 %) [22].

The free sample surface was exposed to an external radiant flux of 4.5 or 5.5 kW/m<sup>2</sup>. The selection of these radiant heat flux values was based on preliminary testing which showed that a heat flux above 6 kW/m<sup>2</sup> would cause excessive pyrolysis on the free surface of the sample. The purpose of the radiant heater is not to promote pyrolysis but to supply additional heat to the sample (simulating a larger sample or an external heat source) and counter the convective heat losses on the free surface.

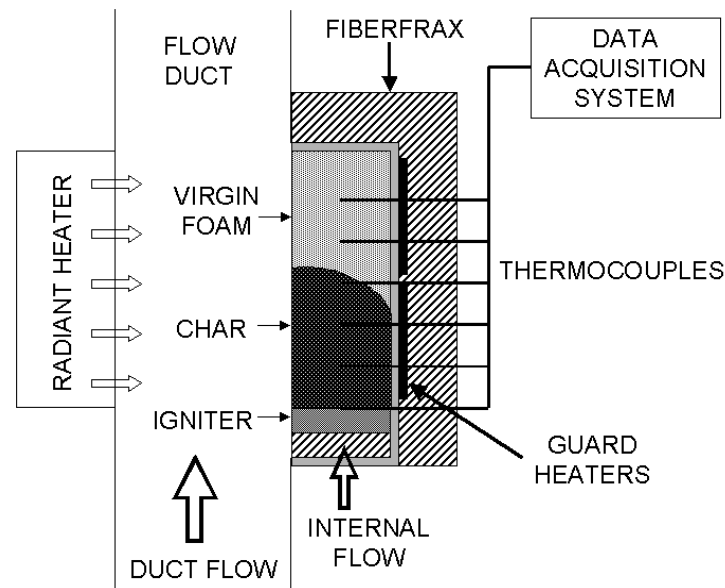


FIG. 1—Schematic of the Experimental Apparatus.

### *Experimental Apparatus*

The experiments are conducted in a small vertically oriented aluminum flow duct (Fig. 1), 380 mm long and with a cross-sectional area of 135 mm by 80 mm. Two walls of the flow duct are panes of borosilicate glass for optical access. The oxidizer flow entering the test section of the flow duct first passes through a settling chamber and a converging nozzle.

The sample holder is located 120 mm from the inlet to the flow duct and vertically oriented such that the front face of the fuel sample is flush with the interior wall of the flow duct. The sample holder is constructed of thin-walled (0.75 mm) brass sheets insulated with fiberglass blanket, with a central cavity to contain the fuel sample, and the igniter holder assembly. The

outer surfaces of the back and side walls of the sample holder each have a independently controlled guard heater.

An infrared radiant heater is mounted opposite the sample holder in the vertical wall of the flow duct to counter heat losses from the free surface of the fuel sample with a radiant flux perpendicular to the sample surface.

The bottom face of the sample lies upon an electrically heated ceramic honeycomb igniter of area 50 mm x 50 mm. It was found in early experiments that a gummy black residue formed from the samples during the tests would stick to the ceramic igniter. Therefore, to prevent the residue from damaging the igniter, a very thin layer of fiberglass blanket, of area 50 mm x 50 mm and 0.7 grams, was placed between the foam sample and igniter for all the experiments. The bottom face of the igniter is insulated with a layer of fiberglass blanket of thickness 15 mm. During the tests, there is a forced flow of oxidizer through the fiberglass blanket and the igniter, and into the fuel sample (hence “internal flow”) at a flow rate of 13.4 cc/s, which has been used as the standard internal flow rate for this experimental configuration in previous smoldering experiments with NFR polyurethane foam [9]. The internal oxidizer flow through the igniter is controlled using mass flow controllers.

For all experiments, the forced duct flow velocity was 0.15 m/s, which is in the range of typical airflow speeds aboard spacecraft due to ventilation systems aboard spacecraft. The duct flow is controlled using two identical sets of critical flow nozzles: one for air, and one for oxygen used to enrich the flow to elevated oxygen concentrations.

Six type-K thermocouples are located along the vertical centerline of the sample at distances from the igniter/foam interface of: 0 mm, 20 mm, 40 mm, 60 mm, 80 mm, and 100 mm. The six thermocouple probes (0.84 mm diameter, sheathed grounded-junction) are inserted through the back of the sample. A video camera views the sample at an angle of 45° through one borosilicate window. A high-speed camera (Kodak Ektapro<sup>®</sup> Model 2000), operating at 1000 frames per second, views the sample at angle of 45° through the other borosilicate window.

### *Pyrell Foam Samples*

As mentioned above, the Pyrell samples were of cross-section 50 mm x 50 mm, and 125 mm long. Tests were performed on the two commercially available densities of Pyrell: high-density (64.0 kg/m<sup>3</sup>) and low-density (35.3 kg/m<sup>3</sup>). Both foams achieved the top rating of HF-1 for the UL-94 flame resistance test. An Environmental Scanning Electron Microscope (ESEM) was used to take images of the cell structure of the virgin foams; examples are shown in (Fig. 2(a) and (b)). The images show the similarity in pore sizes between the two foams, and reveal that the high-density Pyrell has noticeably thicker solid strands, more surface area per unit volume, and smaller holes in the polyhedron faces than the low-density Pyrell. The average solid strand thicknesses of the high-density and low-density Pyrell, measured from the ESEM images, are approximately 102 μm and 61 μm, respectively. Since the total solid surface area per unit volume of foam is roughly proportional to the average solid strand thickness, it can be estimated that the high density Pyrell has approximately 67% more solid surface area than the low-density Pyrell.

The Foamex Technical Products catalog describes the flame-resistant behavior of Pyrell in air: “When flame is applied, Pyrell intumesces. The surface chars, tending to form a protective shield between the flame and the foam underneath. This carbon char has low thermal conductivity and high oxidation resistance” [23]. The intumescent behavior of Pyrell can be

seen in (Fig. 2 (c) and (d)): ESEM images of a surface of low-density and high-density Pyrell after being exposed to a direct flame. The images show that the most of the foam surface has intumesced and has lost its uniform cell-structure. Foamex does not provide data on the type or amount of fire retardants used in Pyrell because that information is proprietary. However, the Material Safety Data Sheet (MSDS) for Foamex's polyurethane foams states that their fire retarded foams may release hydrogen chloride, hydrogen bromide, hydrogen fluoride or phosphoric acid depending on the fire retardant additive [24]. In addition, halogen-phosphorus additives are known to promote the growth of a phosphorus-containing carbonaceous layer between the flame and the pyrolysis zone, which acts as a barrier for the transfer of heat and fuel [15]; this describes exactly the behavior of Pyrell. It therefore seems likely that Pyrell includes halogen-phosphorus-containing fire retardants.

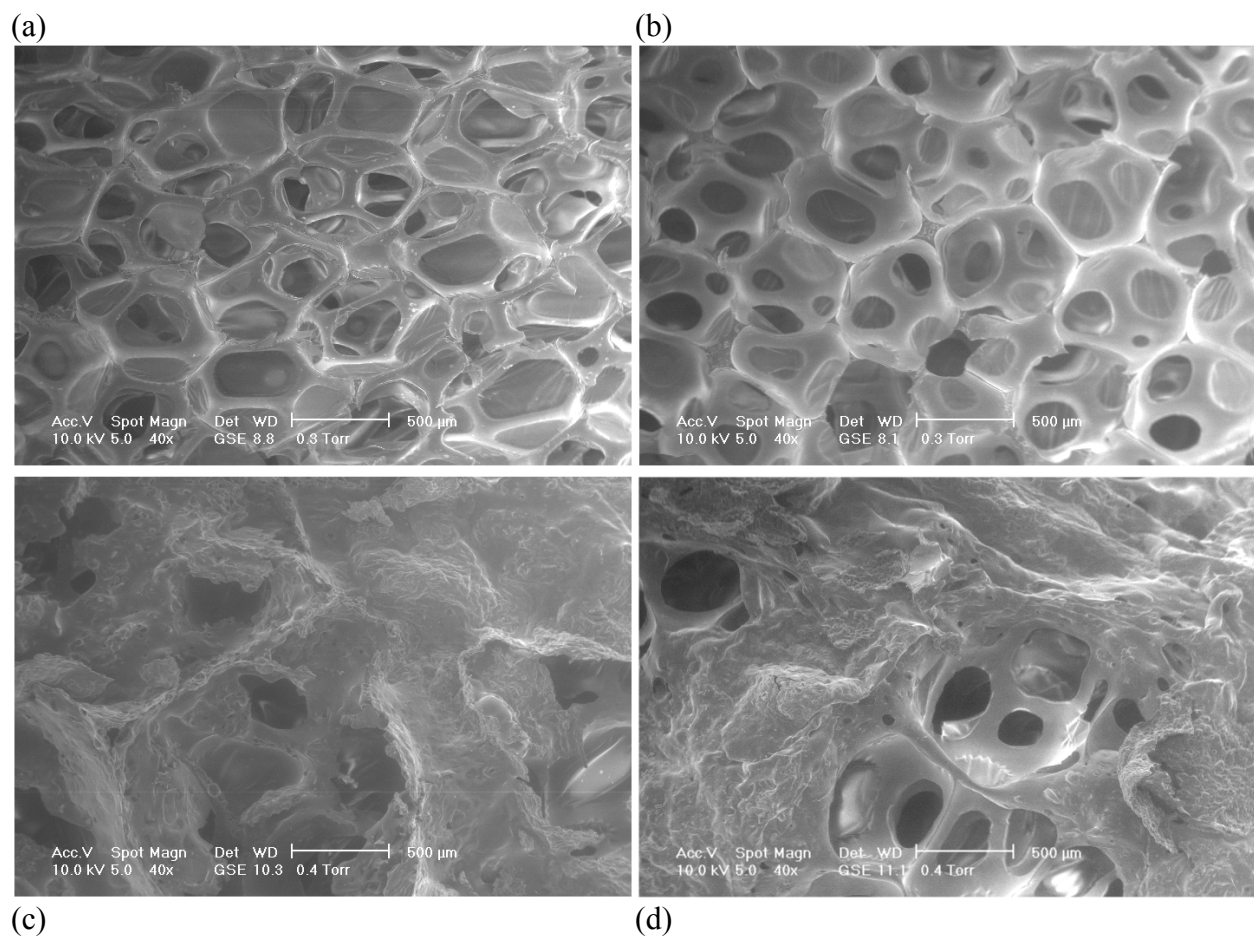


FIG. 2— Environmental Scanning Electron Microscope (ESEM) images of (a) virgin low-density Pyrell and (b) virgin high-density Pyrell; and after application of a flame, (c) intumesced low-density Pyrell and (d) intumesced high-density Pyrell.

#### *Experimental Procedure*

Tests are conducted on both high-density and low-density Pyrell varying the external radiant heat flux and oxygen concentration of the duct and internal flows. The radiant heat flux was

either 4.5 or 5.5 kW/m<sup>2</sup> and the oxygen mole fraction was varied from 0.30 to 0.60. It was found in early testing that if the oxidizer flows were set to their nominal elevated oxygen concentration at the beginning of the test, ignition was difficult to achieve because of the particular configuration of the sample; early in the test, elevated oxygen concentrations would enhance the smolder reaction and promote excessive mass loss in the high-temperature region near the igniter. A hole would be created at the bottom of the exposed sample face, thus allowing the internal oxidizer flow and hot pyrolysis gases to escape from the sample, and hindering the creation of a pocket of a high-temperature combustible gas mixture inside the sample. As a solution, the procedure was changed to allow the smolder reaction to travel away from the igniter before the enrichment of the oxidizer flows to the nominal oxygen concentration.

To begin the tests, the internal and duct flows were set to their nominal volume flow rates with air, the radiant heater was activated, and the guard heaters were set to a set-point of 200 °C. Once the guard heaters reached their steady state set-point temperature, the igniter was turned on to a power of 115 W. When the igniter reached a temperature of 500 °C, (as measured by the thermocouple at 0 mm, located between the igniter and foam sample) both the internal and duct flows were enriched to the nominal oxygen concentration.

## Results

### *Thermocouple and High Speed Video Camera Results*

In (Fig. 3 (a) and (b)), characteristic temperature histories are shown for a test with ignition, and a test without ignition, respectively. These tests were done with low-density Pyrell, however, the temperature histories for high-density Pyrell tests are similar in nature. The radiant heat flux was 5.5 kW/m<sup>2</sup> for both tests; the only difference is that test (a) was performed at 0.50 oxygen mole fraction, and test (b) at 0.35 oxygen mole fraction.

The temperature profiles for both tests show that the igniter is activated at approximately 200 seconds, shortly after the guard heaters reach their set-point temperature. The temperature of the igniter, shown by the thermocouple at 0 mm, rises sharply and approaches a steady state temperature of approximately 850 °C in both tests. The temperature in the foam sample at a height of 20 mm above the igniter also experiences a similar increase early in the tests at both 0.35 and 0.50 oxygen mole fractions. However, at 380 s, the temperature at 20 mm for test (a) increases sharply, due to a sudden intensification in the smoldering reaction. At approximately the same time of 380 seconds, at 40 mm, the temperature begins to rise significantly faster for the test at 0.50 than the test at 0.35 oxygen mole fraction, most likely because the higher oxygen concentration allows more vigorous smoldering to occur in the sample. Similar differences are observed between the two tests at both 60 mm and 80 mm, at subsequently later times. In test (a) at 551 seconds, the temperature jumps very sharply at both 20 mm and 40 mm, indicating an ignition event in the vicinity of, and most likely somewhere in between those two thermocouples, as corroborated by the high speed camera images shown and discussed below. At 552 seconds, the thermocouples at 0 mm and 60 mm jump sharply, indicating that the flame has spread in both vertical directions on the interior of the sample. The thermocouples at 80 and 100 mm experience a much slower temperature rise at approximately 570 and 575 seconds, respectively, indicating that the flame spread is significantly slower through the denser char in the upper region of the sample. The flame is then manually extinguished with a jet of carbon dioxide, causing the temperatures to decrease everywhere in the sample.



The temperature profiles in (Fig. 3(b)), at the lower oxygen mole fraction (0.35), show that the temperatures from 0 mm to 60 mm approach fairly steady values, and then slowly decrease, indicating that the smoldering reactions have weakened. During the same period, it is visually observed that the smoke production from the sample has noticeably decreased, and post-test inspection of the sample reveals the presence of large voids in the sample interior. Therefore, it is likely that the temperatures are decreasing because nearly all the solid fuel has been consumed by the smolder reaction. The temperatures at 80 mm and 100 mm are below 300 °C and approaching steady state, and by visual observation during the test, the smolder gas production is very low, so the test is declared “no ignition” and stopped.

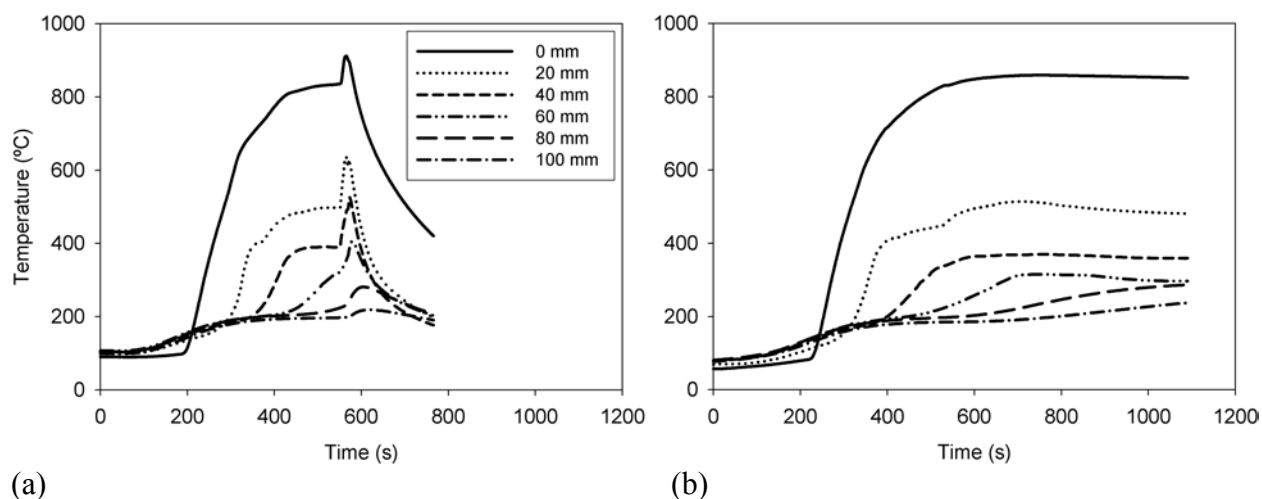


FIG. 3— Characteristic temperature histories for low-density Pyrell tests (a) with ignition, for 0.50 oxygen mole fraction and  $5.5 \text{ kW/m}^2$  radiant heat flux and (b) without ignition, for 0.35 oxygen mole fraction and  $5.5 \text{ kW/m}^2$  radiant heat flux. The height of each thermocouple above the igniter/sample interface is shown in the legend in plot (a).

A sequence of high speed camera images of the ignition in the test shown in (Fig. 3(a)) is presented in (Fig. 4). Though not shown here, high speed camera images of tests that ignited at other external conditions, and for both densities of Pyrell, showed similar behaviors of ignition and flame spread. The bright white object at the bottom of each photograph is the ceramic igniter. The first image in (Fig. 4(a)) shows that the smoldering reaction has progressed approximately 80 mm through the sample height. In the second image, a small, faint bluish flame emerges from the sample approximately 35 mm above the foam/igniter interface, which corroborates the finding from the temperature data that the ignition occurred somewhere in the char region between the thermocouples at 20 mm and 40 mm. The third image shows that the small bluish flame has grown into a larger, brighter flame at a height of 35 mm. The third through sixth images show that the flame has propagated upwards through the sample interior, and emerged into the duct.

The subsequent flame spread over the sample is shown in (Fig. 4(b)). The first image in (Fig. 4(b)) shows that the flame has attached itself to the sample, on the edges of the char region. The second through sixth images in (Fig. 4(b)) show the flame spread over the char and virgin foam. Interestingly, as the flame spreads over the virgin foam, the leading edge of the flame is preceded by a thin region of glowing green light. The green glow could be chemiluminescence due to the

oxidation of phosphorus, which is one of the most common components of fire retardant additives for polyurethane foam [14]. The radiative heat from the leading edge of the flame onto the virgin foam could be thermally decomposing the phosphorus-containing additives, allowing vaporized elemental phosphorus to react with oxygen and produce the chemiluminescent green glow.

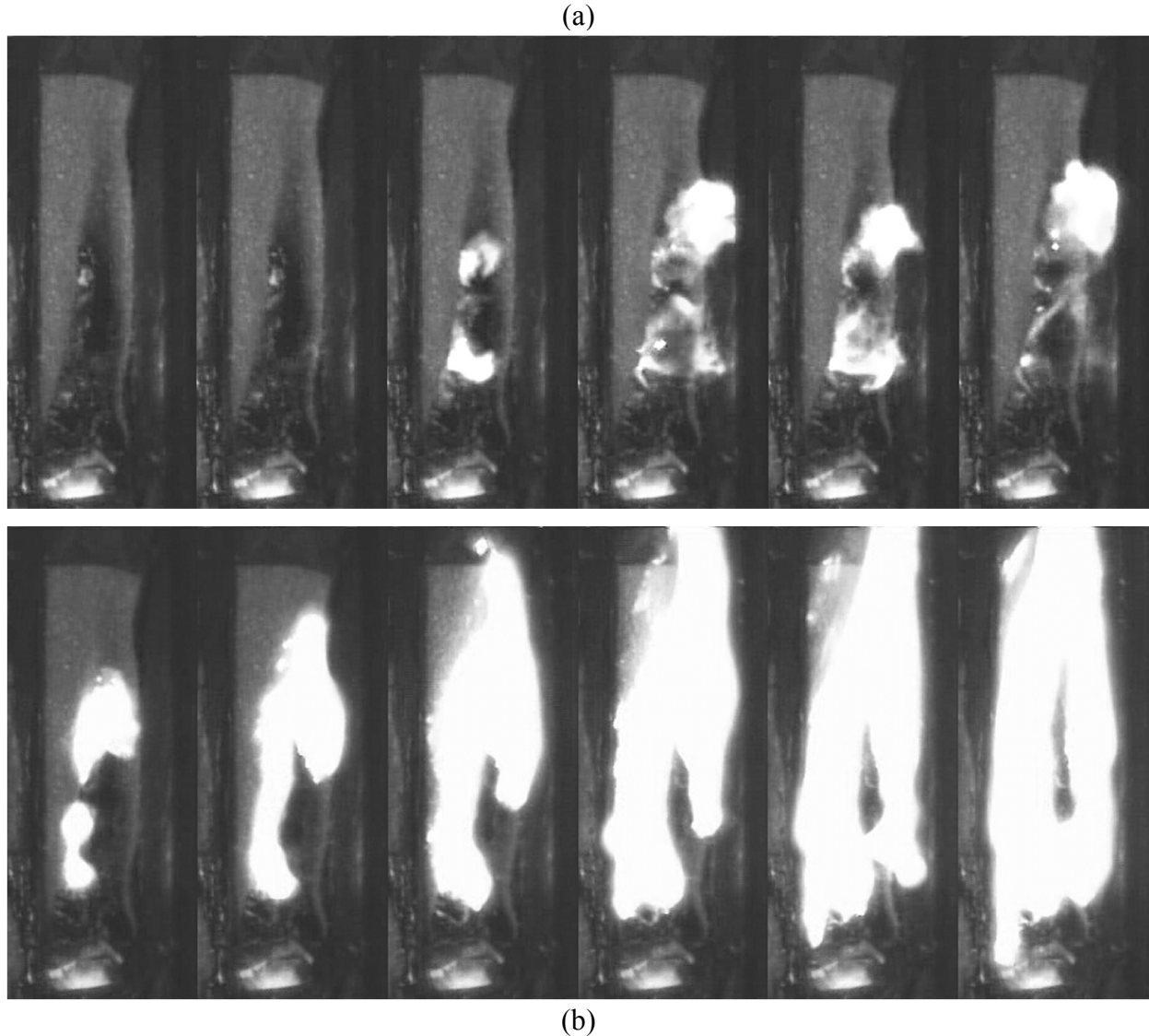


FIG. 4— High speed photographic sequence of (a) ignition to flaming in the test shown in (Fig. 3(a)) with a time lapse of 0.001 seconds between successive frames, and (b) the subsequent flame spread with a time lapse of 0.040 seconds between successive frames. The camera was positioned at an oblique angle of 45 degrees to the solid surface.

#### *Results of Varying Oxygen Mole Fraction and Radiant Heat Flux*

The results of this parametric study, in terms of ignition/no ignition for varying oxygen mole fraction and radiant heat flux, are presented in (Table 1). At the lower radiant heat flux, low-density Pyrell ignited at oxygen mole fractions above 0.50, while high-density Pyrell ignited at

oxygen mole fractions above 0.35. At the higher radiant heat flux, low-density Pyrell ignited at oxygen mole fractions above 0.35, while high-density Pyrell ignited at oxygen mole fractions above 0.30. These results indicate that high-density Pyrell is more flammable than low-density Pyrell. As expected, ignition in Pyrell is very sensitive to the oxygen mole fraction. In addition, increasing the radiant heat flux at a given oxygen concentration increases the likelihood of ignition.

TABLE 1—Test results for low-density and high-density Pyrell, with varying oxygen mole fraction and radiant heat flux. “Ign.” indicates ignition to flaming; “No Ign.” indicates no ignition.

Oxygen Mole Fraction	Low-density Pyrell		High-density Pyrell	
	4.5 kW/m <sup>2</sup>	5.5 kW/m <sup>2</sup>	4.5 kW/m <sup>2</sup>	5.5 kW/m <sup>2</sup>
0.60	Ign.	...	Ign.	...
0.55	Ign.	Ign.	Ign.	...
0.50	No Ign.	Ign.	Ign.	...
0.45	...	Ign.	Ign.	Ign.
0.40	...	Ign.	Ign.	Ign.
0.35	...	No Ign.	No Ign.	Ign.
0.30	...	...	...	No Ign.

## Discussion

Based on the temperature data and high speed camera images, the ignition mechanism for Pyrell is similar to that of non-fire-retarded polyurethane foam [8,9], in that the gas phase ignition occurs in pores located in the hot char region behind the smolder front. The smoldering char that contains the pores provides both the heat and fuel necessary for gas phase ignition; therefore, this process is called a transition from smoldering to flaming. For ignition to occur, the gas mixture inside the sample must be within the flammability limits, and at a sufficiently high temperature. The results of these experiments indicate that several factors influence the transition to flaming process.

### *Effects of Oxygen Mole Fraction and Radiant Heat Flux*

As seen in (Table 1), the oxygen mole fraction plays a critical role in the ignition of Pyrell. One effect is that the higher oxygen concentration allows the gaseous mixture inside the pores to be within the flammability limits. The second effect of increased oxygen is to intensify the smoldering reaction, increasing the heat release from the pore surfaces, which can trigger a gas phase thermal runaway. Therefore, if enough oxygen is available, thermal runaway will occur and lead to a gas phase ignition, such as that shown in (Fig. 3(a)) for 0.50 oxygen mole fraction. For 0.35 oxygen mole fraction, shown in (Fig. 3(b)), the exothermic smoldering reactions were not vigorous enough to trigger a gas phase ignition, or the gaseous mixture was not within the flammability limits, due to insufficient oxygen supply.

Similarly, the external radiant heat flux can be the decisive factor in the ignition process. The effect of the radiant heat flux on the ignition of Pyrell can be seen in (Table 1). The increased radiant heat flux to the free surface increases the heat transfer to the interior of the sample, where it raises the temperature and increases the smolder reaction rate, which produces

additional heat. Therefore, greater radiant heat flux can raise the temperature sufficiently to cause a gas phase thermal runaway and ignition in the pores.

Alternatively, if the gaseous mixture inside the pores is too fuel-lean, lacking sufficient volatile fuel for ignition, the additional radiant heat flux can increase the production of smoldering gases until the mixture is within the flammability limits. Although the gaseous mixtures within smoldering porous materials are usually rich, and the heterogeneous reactions are usually oxygen-limited, it is possible that the fire retardants in Pyrell could create a different scenario. The fire retardants probably include halogen-phosphorus-containing additives that vaporize and inhibit gas phase reactions in two ways: dilution of the volatile fuel mixture, and scavenging OH\* and H\* radicals in the gas phase. The vaporized fire retardants could change the gas phase kinetics such that more volatile fuel is needed to overcome these ignition-inhibiting effects.

#### *High-density Pyrell vs. Low-density Pyrell*

The observation that high-density Pyrell undergoes ignition at lower oxygen mole fraction and lower radiant heat flux than low-density Pyrell is interesting. It is possible that the two foams have slightly different chemical compositions, which could affect their kinetic behavior in both the solid and gas phases. In addition, the differences in the microstructure of the two foams must account for some differences in flammability. As mentioned previously, the high-density Pyrell has approximately 67% more solid surface area per unit volume of foam than the low-density Pyrell, which provides more locations for smoldering reactions to take place. As a result, high-density Pyrell can produce extra heat and gaseous fuel, which can lead to gas phase ignition. In addition, the high-density Pyrell has more total fuel than low-density Pyrell, so that the pyrolysis and oxidative reactions can occur for a longer duration of time, allowing a greater accumulation of volatile fuel and heat, which could lead to ignition.

#### *Comparison with Non-Fire Retarded Polyurethane Foam*

It is well known that NFR polyurethane foam is extremely susceptible to smoldering and transition to flaming [1,8,9]. In particular, Bar-Ilan et al. conducted a study on smoldering and transition to flaming, using the same experimental apparatus as the present study, with NFR flexible polyurethane foam of density 26.5 kg/m<sup>3</sup> [9]. It was found that the smoldering reaction, including secondary char oxidation, was responsible for producing the transition to flaming, by supplying heat and vaporized fuel to the gaseous mixtures within the char region.

Although the ignition mechanism for Pyrell is similar to that of NFR foam, in that the gas phase ignition occurs in pores located in the hot char region, there is still a major difference between the behaviors of the two foams: the smoldering reaction in Pyrell is much weaker (less endothermic) and requires significantly more external heat input in order to propagate. Similarly, Hshieh et al. described cone calorimeter experiments at high radiant heat fluxes (25 – 45 kW/m<sup>2</sup>), in which a smolder reaction in Pyrell quickly extinguished upon removal of the external heat source, showing that the heat generation of smoldering in Pyrell was insufficient to sustain itself [5].

The temperature histories of the smoldering reaction in Pyrell, shown in (Fig. 3 (a) and (b)), are quite different from those of stronger smoldering in NFR foam, which show the propagation of an exothermic reaction wave, with each thermocouple temperature rising and then falling as the smolder front approaches and then passes that location [8,9]. The movement of the smolder wave in NFR foam is exhibited by the changing location of the peak temperature in the sample.

Because the weak smoldering reaction in Pyrell has relatively low exothermicity, it requires considerably more external heat input in order to propagate and cause a gas phase ignition. In the present study, the power of the igniter needed to be set significantly higher for Pyrell (115 W) than for the NFR foam (23 W) studied by Bar-Ilan et al. [9]. The higher heat input from the igniter causes the peak temperatures to always be near the bottom of the Pyrell sample, rather than moving vertically up sample with the smolder front, as occurs in stronger smoldering reactions in NFR foam.

Smoldering inherently involves a combination of endothermic pyrolysis reactions and exothermic oxidation reactions [25]. The fire retardants in Pyrell can alter these reactions such that total reaction that is net endothermic, or very weakly exothermic. Pyrell could include melamine, for example, which is believed to act as a heat sink [21] and forms into thermally stable network structures [19]. Other retardants such as phosphorus-containing additives could also modify the kinetic behavior of polyurethane in the solid phase, and hinder the smolder tendencies of the foam. However, the results show that Pyrell can smolder if it is provided with sufficient oxygen and external heat. Symptoms of smoldering in Pyrell can be seen in the temperature histories; there are occasionally small zones of high exothermicity in Pyrell, especially at higher oxygen concentrations. For example, in (Fig. 3(a)) there is a steep rise in the temperature at 20 mm at 380 seconds, which indicates the presence of a small zone dominated by exothermic reactions, perhaps due to a sudden influx of oxygen caused by the changing char structure. It is likely that the gas phase ignition in a pore is triggered by a localized hot zone where the oxidative exothermic reactions receive enough oxygen to overcome effects of the fire retardants. For the test in (Fig. 3(a)), this localized hot zone would be between 20 and 40 mm.

## Conclusions

The experiments show that Pyrell foam can smolder and transition to flaming at enriched oxygen concentrations, and that the ignition process is also highly dependent on the radiant heat flux. Thermocouple data and high speed camera images show that, similar to the transition from smoldering to flaming in NFR polyurethane foam [8,9], the ignition occurs in pores located in the char region, and the smoldering reaction provides the volatile fuel and heat necessary for gas phase ignition.

The experiments also show that Pyrell undergoes relatively weak smoldering with low overall exothermicity. This behavior differs from the smoldering tendency of non-fire retarded polyurethane foam, which is more easily able to support propagating smoldering reactions [1,8,9]. The fire retardants in Pyrell can act in the solid phase to hinder the smolder tendency. Pyrell could include melamine, for example, which is believed to act as a heat sink [21] and forms into thermally stable network structures [19]. The exothermicity of the smolder reaction in Pyrell can further be reduced by other fire retardants such as phosphorus-containing additives that can also act in the solid phase and modify the smolder kinetics. In order to compensate for the low exothermicity of smoldering in Pyrell, the igniter power needed to be more than four times the power used in similar experiments on NFR foam in order to support smoldering and produce a gas phase ignition.

The fire retardants in Pyrell hinder not only smoldering, but also gas phase reactions, which further impedes the transition to flaming process. The fire retardants probably include halogen-phosphorus-containing additives that vaporize and inhibit gas phase reactions in two ways: dilution of the volatile fuel mixture, and scavenging  $\text{OH}^*$  and  $\text{H}^*$  radicals in the gas phase. The

green glow observed during the flame spread over the Pyrell sample surface could be the chemiluminescence of phosphorus oxidation, indicating the presence of phosphorus-containing fire retardants in Pyrell.

The experiments indicate that high-density Pyrell is more susceptible to the transition from smoldering to flaming than low-density Pyrell. The high-density Pyrell has more solid surface area for smoldering reactions to take place, thus producing more heat and gaseous fuel, which can lead to gas phase ignition. In addition, the high-density Pyrell has more total fuel, so that the pyrolysis and oxidative reactions can occur for a longer duration of time, allowing a greater accumulation of volatile fuel and heat, which could lead to ignition. Further testing is needed in other sample sizes and configurations in order to determine whether the high-density Pyrell is always more flammable than the low-density Pyrell.

Pyrell is one of the allowed materials for equipment stowage protection in the NASA space shuttles and the International Space Station because it performs very well in terms of fire resistance in environments with 21% oxygen. However, for future extended space flights, NASA is considering using higher spacecraft oxygen concentrations in order to lower the total cabin pressure. Based on the results of this study and others, such as Hshieh et al. [5], there should be concern about the flammability of Pyrell in these enriched oxygen environments.

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