

Pour in Place Polyurethane Foam Performance as an Impact Mitigation and Flame Retardant Material Used in Nuclear Material Transportation Containers – The Mechanism of Intumescence

Alan G. Pagni

General Plastics Manufacturing Company, 4910 Burlington Way, Tacoma, WA, 98409

Abstract

The purpose of this study is to explore the key mechanisms responsible for the effectiveness of General Plastic's radioactive material packaging systems, and to apply the most current findings towards their improvement. Predictable failure mechanisms have been shown to be important for optimal effectiveness as an impact mitigation material. A characteristic crush response serving to dampen energy transfer across interfaces is well established in our systems. However, previous findings have shown that the most significant distinguishing characteristic, when comparing General Plastics' systems to alternatives, is the unique intumescent properties. In simulated accident testing, where a sample container is damaged, then burned, the material exhibits the ability to self-heal as a result of the expansion associated with intumescence. This provides gas-phase flame inhibition, condensed-phase flame/heat blockage, and oxygen starvation through the closing off of fractures resulting from the simulated damage. In this study we have explored the mechanism of intumescence in greater depth, and utilized these principles in the development of new systems. Herein, two novel systems targeted at improving flame retardancy through optimized intumescence are described.

Introduction

General Plastics has provided packaging material for radioactive material transport systems since 1971. These systems have a proven record of effectiveness in crash and fire scenarios in both simulated and documented accidents in the field.^[1] Critical to this application are the thermal, mechanical (physical), and fire retardant properties of these specialized polyurethane formulations. While the physical and thermal properties are well understood, the precise mechanism of fire retardancy has, until recently, remained elusive.

The mechanism of intumescence, through which these materials yield their fire retardant characteristics, has been shown to be distinguishing among competitive systems. In addition to the commonly specified fire retardant quantifiers - extinguish times, burn area, burn propagation etc., the dynamic, expanding, and fluid character of intumescence has also exhibited the unique ability to self-heal, which in the case of a simulated crash followed by flame testing, serves to close off air vents and assist in extinguishing the flame.^[3] Intumescence in this particular case is understood to mean an expanding char phase induced by heat/flame. So instead of attempting to design lightweight, impact absorbing, materials with extremely high decomposition temperatures, General Plastic's materials are designed to undergo a controlled decomposition. Figure 1 is a model of intumescence offering a rough description of the chemical processes. Note the significant expansion in comparison to the "virgin material" section.

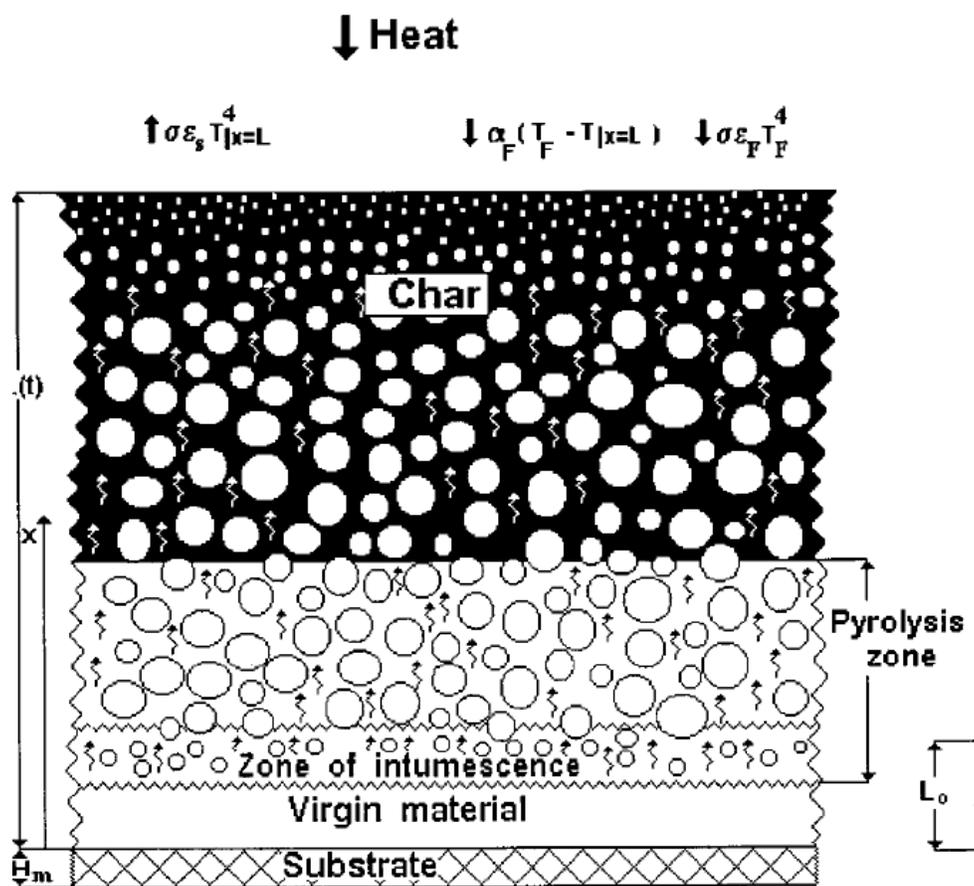


Figure 1: A schematic model of intumescence. Pyrolysis is a term for thermochemical decomposition in oxygen deficient conditions where larger molecules are broken down into smaller, carbon rich species resulting in a char/tar-like formation^[4].

The effectiveness of intumescent systems lies in their ability to do several things at once. The changes occurring at the chemical level are complex, but relatively recent findings have

PATRAM Symposium 2013

allowed us to paint an adequate picture of the main chemical transformations. [6,8] Intumescent systems contain any one of a multitude of proprietary additives and reactants, but an inorganic acid source is essential to both catalyze and take part in the key chemical steps in the synthesis of the expanding char phase. Figure 2 shows a proposed synthetic pathway to the char layer and inert gases.

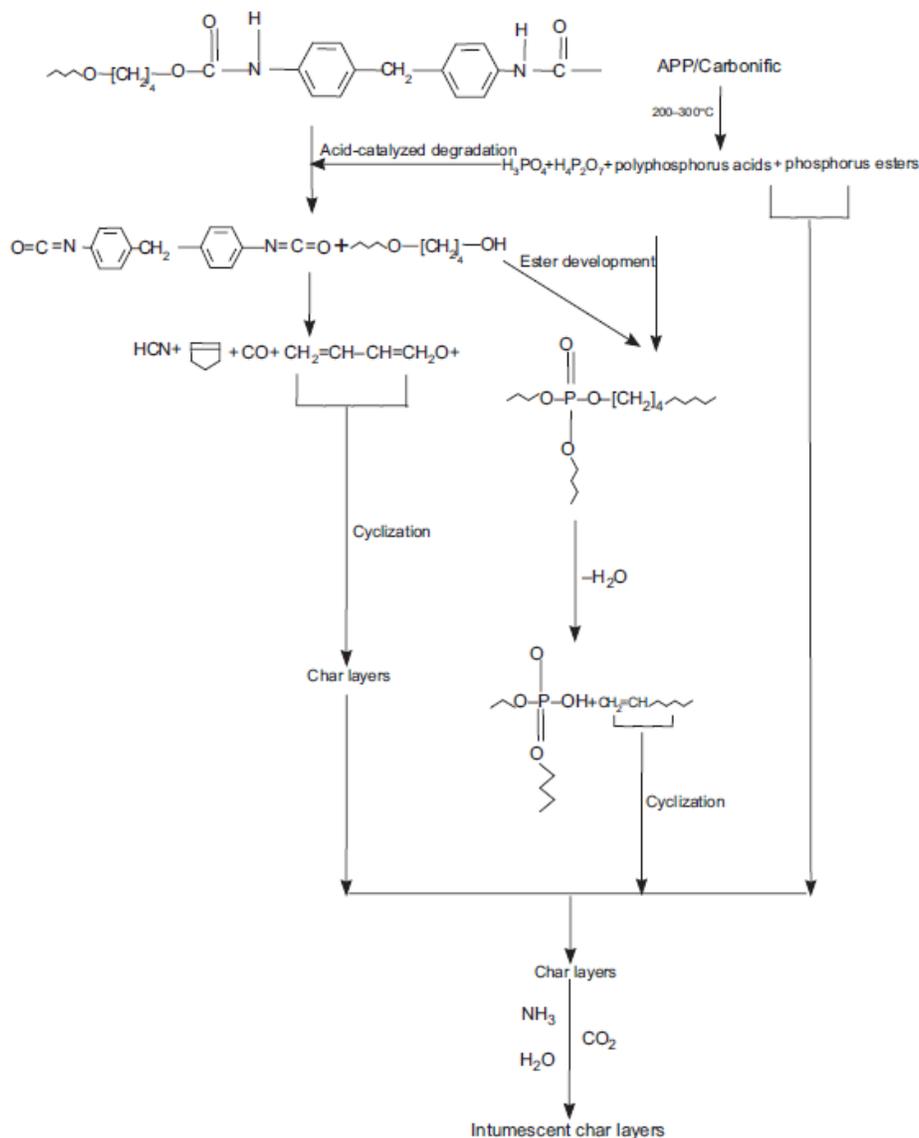


Figure 2: A proposed route to intumescence products. Decomposition and polymerization are occurring in rapid succession if not simultaneously. [8]

As the material rises in temperature upon heating from flame contact, intumescence begins at a system specific temperature normally above 300 °C. Within this temperature range

PATRAM Symposium 2013

the acid begins catalyzing the dehydration and subsequent pyrolytic breakdown of the polymer backbone leading to aromatization and graphitization.^[8] While catalyzing the breakdown of the polymer, the inorganic acid (in this case a phosphate) also begins to take part in cross linking reactions where graphenic pyrolysis products are connected through flexible P-O-C linkages. The gaseous by products of these transformations serve as both non-flammable diluents to other flammable gases, and as blowing agents for the expansion of the cellular char phase.

This is primarily a condensed phase mechanism (not gas), but there is evidence of a gas phase mechanism. PO• species evolving out of the char layer act as terminators in free radical mechanisms of gas phase pyrolysis and combustion. This is illustrated in figure 3. A similar mechanism is also seen in the condensed phase during the degradation of the polymer where the free radical mechanisms leading to complete pyrolysis of the polymer backbone are also inhibited. The end result is inhibition of combustion/pyrolysis while also catalyzing the synthesis and expansion of the char phase which fixes flammable decomposition products into the char matrix.^[7, 8]

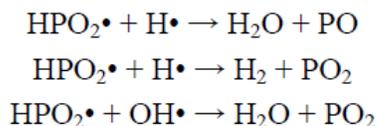
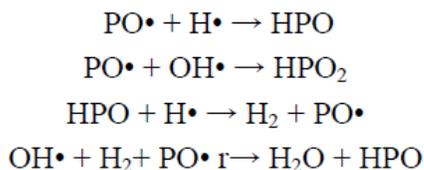


Figure 3: Above is the proposed gas phase mechanism. The key points are that the PO• and HPO• are quenching the H•, HO•, and H₂ species in the gas phase.^[7]

PATRAM Symposium 2013

The char phase is composed of crystalline macromolecular polyaromatic stacks bridged by flexible spans of the original polymer backbone, all of which are further linked together through phosphate ester groups. The amorphous phase (flexible linkages) has to be voluminous enough to encapsulate the crystalline phase so that the char will be fluid enough to expand and flow. It must exhibit optimal viscoelasticity so that the char layer will not drip, but will accommodate encapsulation of evolving gasses leading to an expanding, cellular char phase. A plot of viscosity vs. temp vs. time of an intumescent system is shown in figure 6. Note the significant increase in viscosity across a narrow temperature range. The rheological and mechanical characteristics of the char phase is often the most significant property when formulating an intumescent system e.g. increasing the thermal stability of the char, maximizing the expansion rate, modifying or stabilizing the backbone of the amorphous phase, or decreasing the temperature of the onset of expansion.^[2,8]

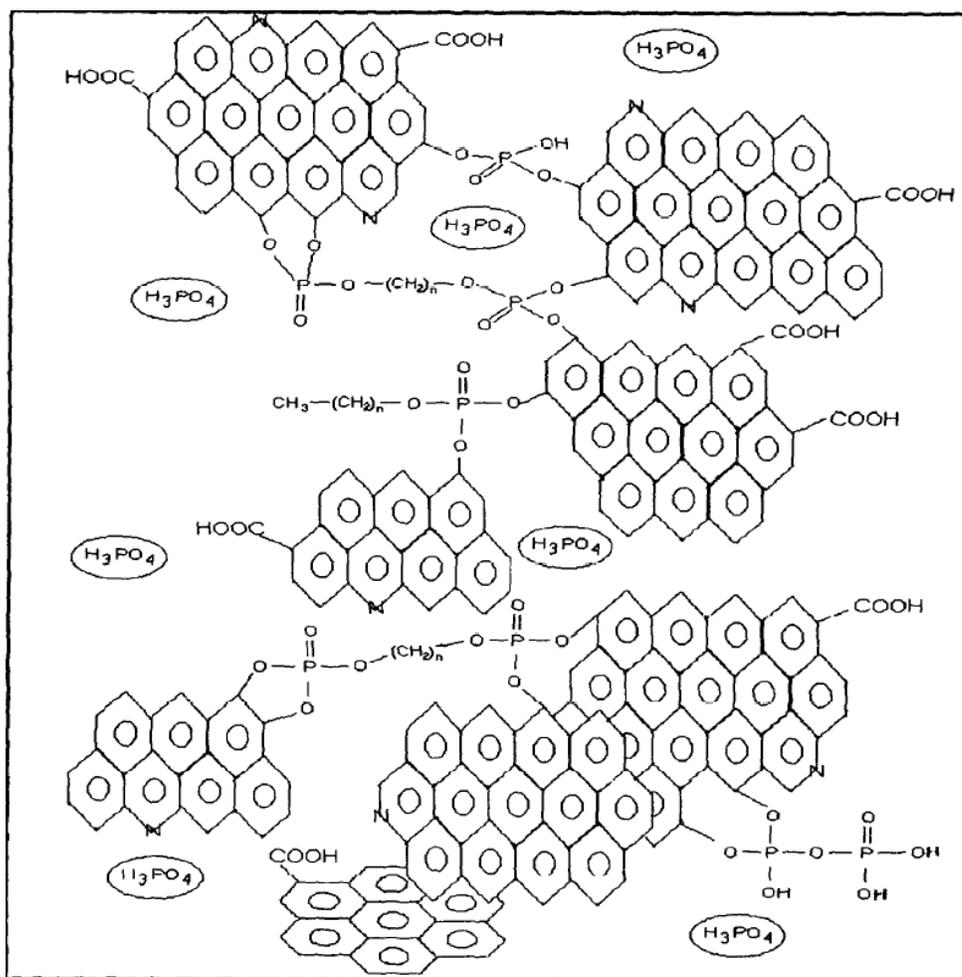


Figure 4: Above is a proposed structure of the char phase. The hexagonal clusters are the polyaromatic crystalline domains and the groups connecting them are the flexible linkages.^[1]

PATRAM Symposium 2013

Intumescent systems interrupt the self-sustained combustion of the polymer at its earliest stage i.e. the thermal degradation leading to evolution of gas phase fuels. The synthesis of the char phase incorporates these nascent fuels into the char matrix. Expansion and flow of the char phase slows down mass and heat transfer by acting as both a physical barrier, and through the use of pyrolysis products in its synthesis. The majority of these pyrolysis products would be further broken down in to flammable gases if not incorporated into the char phase.^[2,8]

The two-step or multistep decomposition of an intumescent material is an important feature. This can be quantified through both thermogravimetric analysis (figure 5), and rheometric analysis (figure 6). The two step process illustrated in figures 5 and 6 are described in the numbered points below.

1. The first step consists of pyrolytic decomposition where we see an initial mass loss. This proceeds until a certain system specific temperature, at which point decomposition slows drastically while the char phase is synthesized and expanded. The mass loss rate decreases and the viscosity of the char increases.
2. The second step is the decomposition of the char at higher temperatures exhibited by increased mass loss rates and viscosity decreases. In a properly formulated intumescent system this last decomposition step will not yield enough fuel to sustain a flame.^[7, 8]

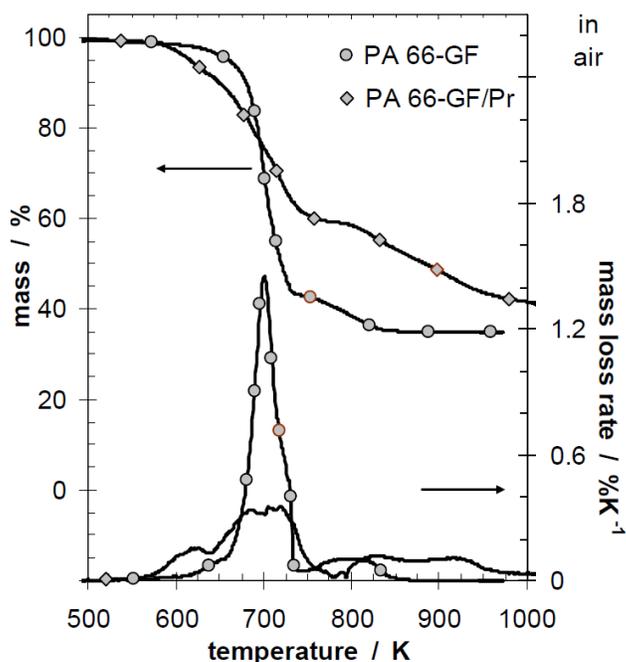


Figure 5: Above is a model TGA test showing mass versus temp. The intumescent system is the PA 66-GF/Pr. The staggered, two step profile is clear in the PA 66-GF/Pr vs. the single step decomposition of the PA 66-GF.^[7]

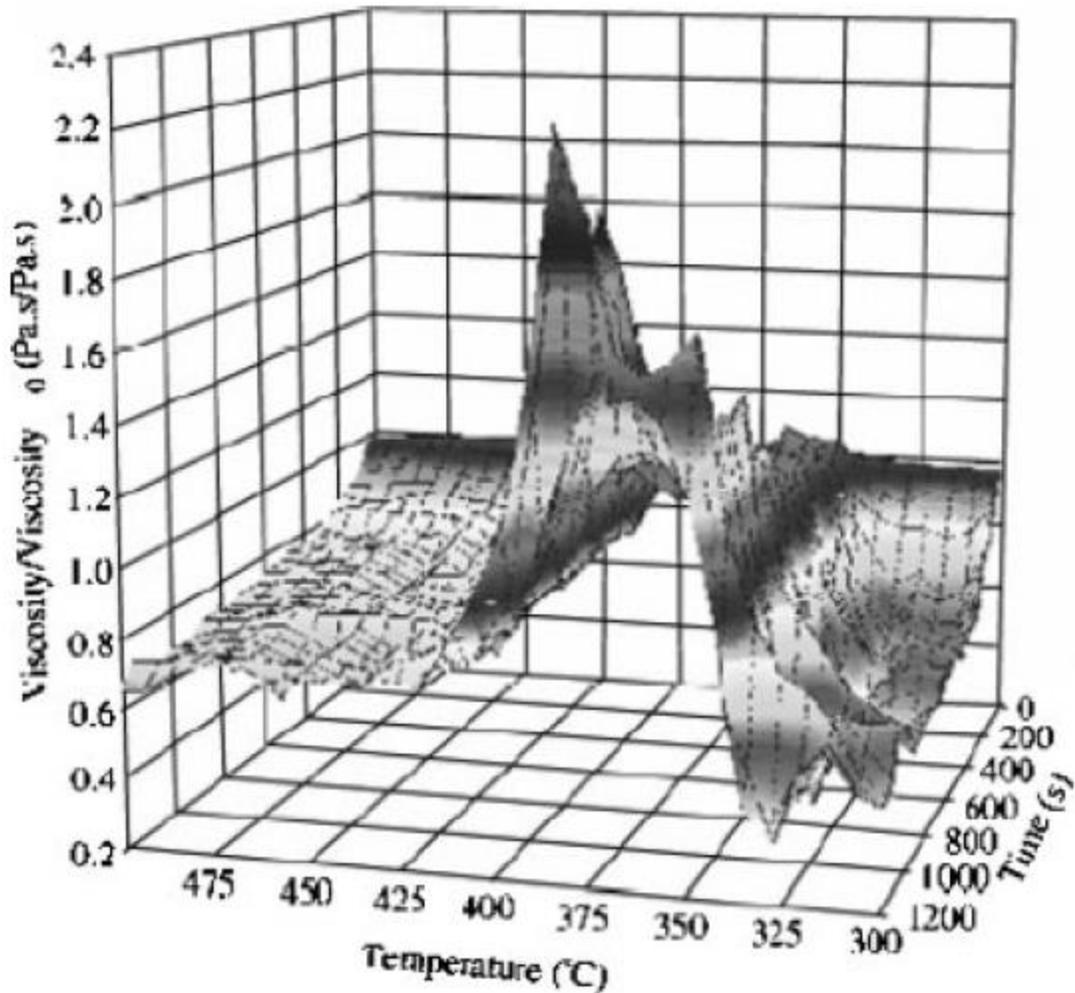


Figure 6: Above shows a 3D graph of viscosity vs. temp. vs. time. The key point in this figure is that the char phase increases in viscosity following the 1st decomposition step, then drastically decreases as it enters the 2nd decomposition step, which in this case is at approximately 400 °C.^[2]

A self sustained flame requires that a minimum flux of reactants be maintained. This is to provide a sufficient exotherm to continuously breakdown and supply reactants in a positive feedback loop. This flux can be indirectly measured through HRR (heat release rate), and is the reason why HRR is a more useful measure than THR (total heat release). Whether or not a material will self-extinguish is largely, if not entirely dependent upon the HRR. Experiments measuring heat flux vs. HRR and THR with special attention to the apparent char barrier have strongly indicated that the HRR is almost entirely a function of the physical barrier effect of the char phase. This suggests that formulation techniques should be directed at improving the physical/rheological properties of the char itself, rather than direct flame inhibition or increased decomposition temperatures. In fact, intumescent systems that begin to char at lower temperatures are typically more effective in lowering self extinguish times and HRR profiles,

PATRAM Symposium 2013

which is further proof of the effectiveness of designed decomposition over decomposition resistance.^[8]

In the following sections we describe two systems that were formulated to improve flame resistance by modifying different components of the intumescence mechanism. Material A is General Plastics' standard system, and materials B and C are experimental systems. We employed cone calorimetry to measure heat release and thermogravimetric analysis (TGA) to measure mass loss vs. time (decomposition rate).

Materials and Methods

A TA Q500 TGA analysis module equipped with auto-sampler and Thermal Advantage release 5.4.0 software for Windows was used for these analyses. The TGA conditions used for these analyses included an equilibration step at 40 °C and a subsequent ramp at 10 °C/min to 950°C. The analyses were performed in an air atmosphere.

Heat release experiments were performed using a custom cone calorimeter set at a radiant heat flux of 3.5 watts/cm².

Results and Discussion

Material B was formulated to increase the concentration of inorganic material through the use of a proprietary mineral silicate and a low density glass material. The standard inorganic acid complex currently being used was also increased in concentration. The targeted effects were to increase the stability of the char through elevated dehydration catalysis, increase the number of flexible branch points within the char phase, and to strengthen the flexible branch points through the creation of organic mineral-silicophosphate complexes. The stronger branch points would result in a decrease in the scission of flexible bonds which are vital to the stability of the flexible phase of the char. This system was also a nonexpanding syntactic system, which by nature contains a significantly higher concentration of inorganic, noncombustible material, which should improve flame retardancy due to the decrease in available combustible material.

Material C was formulated to incorporate a different inorganic acid complex, a multipurpose additive, and a different type of mineral silicate than that used in Material B. The targeted effects in this formulation were to (1) Increase the number of flexible branch points through the use of a different, more efficacious, inorganic acid complex (2) employ an additional catalyst/reactant in the creation of flexible branch points (3) add more blowing agent to increase

PATRAM Symposium 2013

the rate of char phase expansion, and (4) to strengthen the flexible branch points through organic mineral-silicophosphate complexes that would reduce scission of the bonds in the flexible phase of the char. This formulation targeted every known means to create a more voluminous, tougher, and more thermally stable char phase.

In the TGA below (figure 7) all three systems exhibit a two-step decomposition, as described in the introduction. System C exhibits significantly less decomposition in the 1st step with an early decrease in the rate of mass loss, and a slower rate of decomposition during the 2nd step. This indicates both a more rapid on-set of char expansion and a more stable, voluminous char phase. Only in the higher temperatures above 700°C does it decompose to masses below that of Material B, and this would be due to the higher noncombustible, inorganic content of Material B.

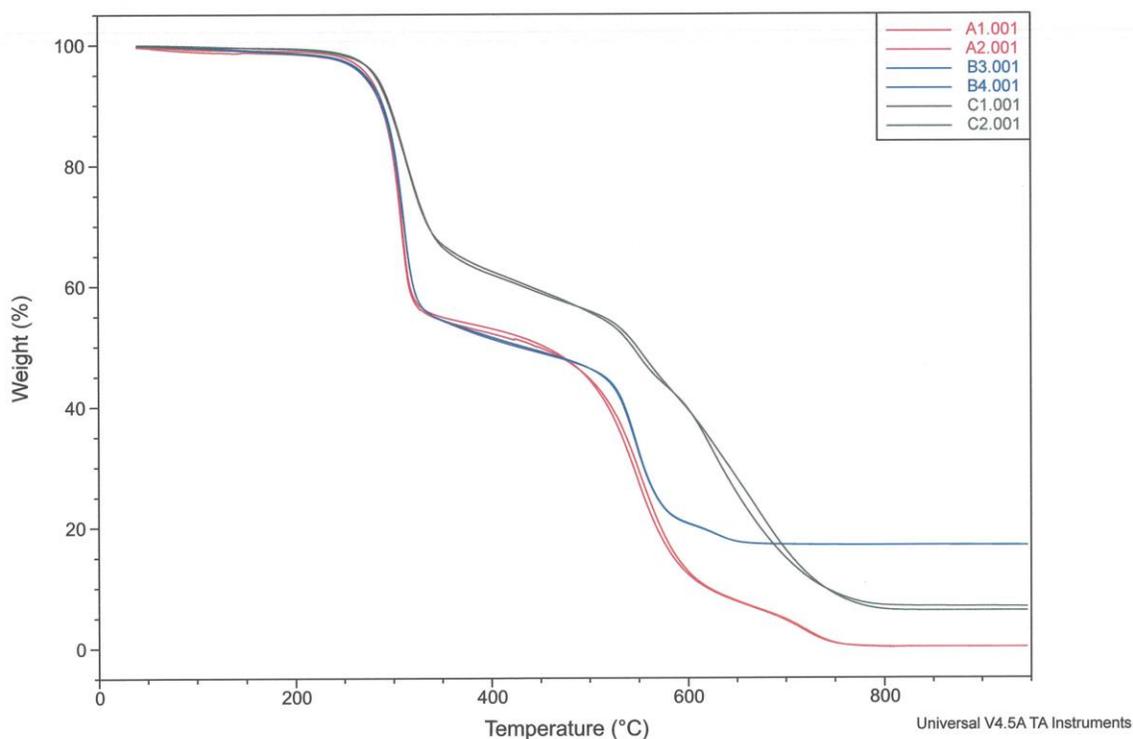


Figure 7: Above is a TGA plot of each system overlain.

The heat release experiments are consistent with the results of the TGA, but much more pronounced. Material A and B exhibit similar profiles with slight differences in the HRR (rate of heat release), and negligible differences in the THR (total heat release). Material C shows a significant reduction in both the HRR and the THR throughout the entire duration of the test.

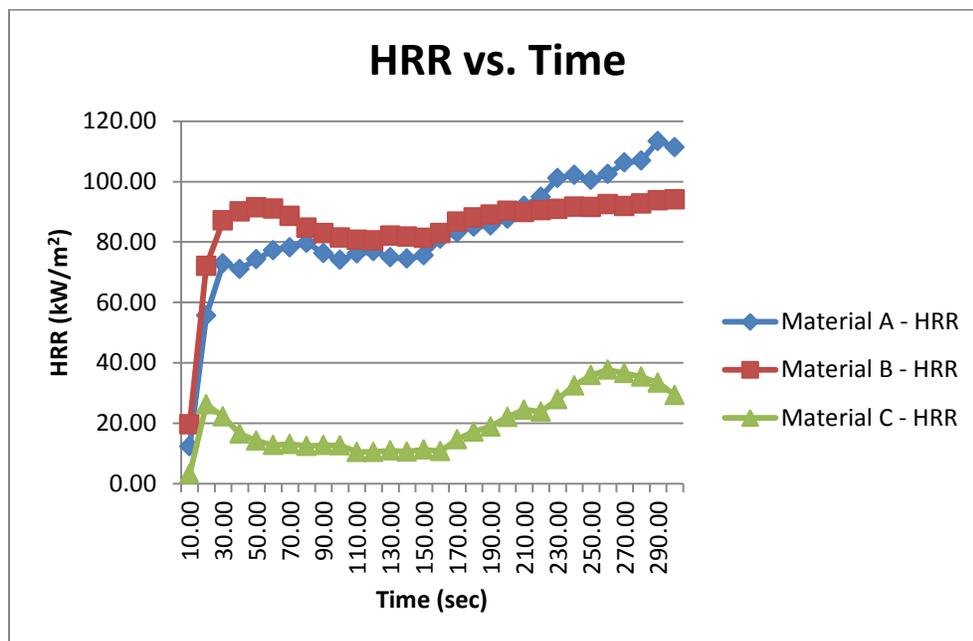


Figure 8: Rate of heat release vs. time.

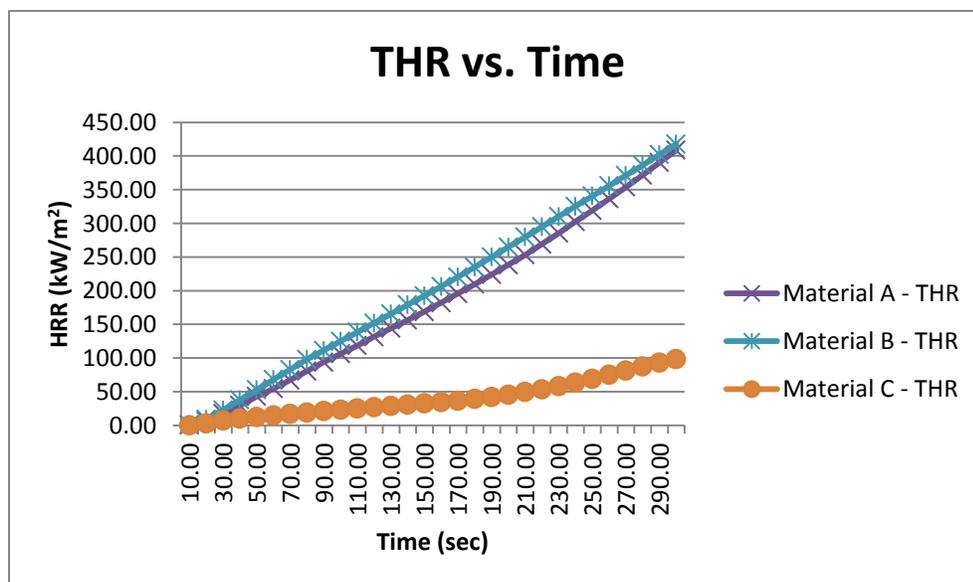


Figure 9: Total heat release vs. time.

PATRAM Symposium 2013

The difference between the two formulations was twofold. Not only did we use different ingredients aimed at augmenting the char phase through different respective mechanisms, but Material C targeted several more key characteristics of the char phase resulting in a larger, more rapidly expanding, and more stable char phase. The formulation changes in Material B yielded no significant improvements to its fire retardancy as shown in both analytical methods. This is in stark contrast to Material C, which yielded very significant improvements.

Conclusion

The utilization of Intumescence has proven an effective method of incorporating flame retardancy into rigid polyurethane foam systems. This is accomplished through a designed degradation where when heated the polymer is broken down, then subsequently synthesized into an expanding cellular char phase. During the synthesis of the char phase, flammable decomposition products are fixed into the polymer matrix, and inert gas products are evolved, both serving to expand the char phase and dilute any flammable gases acting as fuel. The expanded char phase then serves as a physical barrier preventing mass and heat transfer, all of which combine to yield a self-extinguishing material. The mechanism is complex and offers many challenges to those attempting to design improvements. In this case we were successful with a formulation approach aimed at augmenting several aspects of the char phase: the new inorganic acid complex lowered the onset temperature of char formation, the mineral silicate stabilized the structure of the char, and the blowing agent accelerated the expansion of the char. The resulting material presents a new technology platform to build upon.

References

1. Bourbigot, S., Le Bras, M., Delobel, R. **1995**. Carbonization Mechanisms Resulting From Intumescence – Part II. Association with an Ethylene Terpolymer and The Ammonium Polyphosphate-Pentaerythritol Fire Retardant System. *Carbon*, 33, 283-294
2. Bourbigot, S., Le Bras, M., Duquesne, S., Rochery, M. **2004**. Recent Advances for Intumescent Polymers. *Macromolecular Materials and Engineering*, 289, 499-511
3. C.L., Williamson, Z.L, Iams. **2005**. Thermal Assault and Polyurethane Foam – Evaluating Protective Mechanisms for Transport Containers. *Waste Management '05 Symposium*. #5426
4. Gibov, K. M., Mamleev V. SH. **1997**. The Kinetics of Crosslinking in Process of Intumescence of Fireproof Polymer Compositions. *Journal of Applied Polymer Science*, 66, 329-338
5. Griffin, G. J. **2010**. The Modeling of Heat Transfer Across Intumescent Polymer Coatings. *Journal of Fire Sciences*, 28, 249-277

PATRAM Symposium 2013

6. Levchik, S.V., Weil, E.D. **2004**. Thermal Decomposition, combustion and fire-Retardancy of Polyurethanes – a Review of Recent Literature. *Polymer International*, 53, 1585-1610
7. Scharrel, B. **2010**. Phosphorous-based Flame Retardancy Mechanism---Old Hat or a Starting Point for Furture Development. *Materials*, 3, 4710-4745
8. Wang, J., Chen, Y. **2005**. Flame-retardant Mechanism Resulting from an Intumescent System. *Journal of Fire Sciences*, 23, 55-74