

# Intumescent Foams—A Novel Flame Retardant System for Flexible Polyurethane Foams

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**ABSTRACT:** A combination of intumescent components was evaluated as a novel flame retardant system in a flexible polyurethane foam, and the incorporation of these components gave rise to a significant enhancement of the flame retardant properties of the foam. The heat release rate was lowered at an early stage as well as throughout the fire, the total heat production was decreased and the time to ignition was prolonged. Me-

chanical measurements of the foam revealed enhanced properties in terms of stiffness accompanied by a large decrease in elongation at break as compared with a reference foam. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2269–2274, 2008

**Key words:** intumescence; flame retardance; polyurethanes; foams

## INTRODUCTION

Flexible polyurethane foams are intensively employed in automotive seating, but due to the porous, open-cell structure and low density of such foams, they are highly flammable. Oxygen can easily diffuse through the pores of the combustible material and the large surface area provides a multitude of combustion sites. As a result of the flammability of polyurethane foams, a car accident, a smoldering cigarette, or an electrical failure in the seat heating system can easily cause fires. This fire risk, in combination with the fact that the most commonly used flame retardant for polyurethane foam contains halogenated species, which are planned to be phased out, is the driving force behind the development of a novel fire retardant system for flexible polyurethane foams.

The complex chemistry of flexible polyurethane foam synthesis involves several reactions that take place simultaneously. The reactions that form the basis of polyurethane chemistry are those between isocyanate and alcohols, amines, carboxylic acids, and water. In these primary reactions, urethane linkages, urea groups, and carbamic acid are formed. Carbamic acid subsequently converts into urea and carbon dioxide, which is responsible for the blowing

process. Urethane and urea can undergo secondary reactions in which they react with isocyanate to form allophanate and biuret groups, respectively. Woods gives a thorough description of the chemistry of polyurethanes.<sup>1</sup>

Flexible polyurethane foams can undergo degradation by pyrolysis, flame combustion, or smoldering. These processes are important since they all take part in a fire. Moreover, they have been the subjects of much research to gain a deeper understanding of the degradation and combustion behavior of flexible polyurethane foam materials. The degradation of polyurethanes in the absence of air, corresponding to pyrolysis in the condensed phase during fire, has been thoroughly studied,<sup>2,3</sup> and it has been shown that the biuret and allophanate groups are the least thermally stable components of the foam. These groups are decomposed between 110°C and 170°C thus generating their precursors isocyanate, urea, and urethane. Other groups, in order of increasing thermal stability, are urethanes, ureas, and isocyanurate. They too dissociate to form their precursors isocyanate, amine, and alcohol. The combustion behavior of polyurethane foams has been investigated with cone calorimetry<sup>4,5</sup> to obtain information concerning the heat release rate (HRR), which is an important factor determining fire properties.

Historically there have been three ways of fire protecting polyurethane foams: first, by the use of inorganic salts containing calcium and magnesium ammonium-phosphates; second, by modifying the structure of the polyurethane foam so as to minimize

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**TABLE I**  
**Formulations of the Reference Foam, the Intumescent Foam and the Foam Containing a Commercially Available Flame Retardant**

Component	Supplier	Reference Foam	Intumescent Foam	Commercial Flame Retardant
Polyol E837	Perstorp AB	500	500	500
DEOA-LF	Aldrich	5	5	5
Water	–	14.8	14.8	14.8
DABCO 33-LV	Air Products	2.34	2.34	2.34
DABCO BL-11	Air Products	0.4	0.4	0.4
Tegostab B 4113	EVONIK	3.5	3.5	3.5
DABCO DC5169	Air Products	1.5	1.5	1.5
Lupranat T80	BASF	187.34	209.63	187.34
Exolit AP 422	Clariant	–	15.55	–
Charmor DP40	Perstorp AB	–	5.75	–
Melamine	DSM	–	5.05	–
TCPP	LANXESS	–	–	60
Isocyanate index	–	100	100	100

the production of flammable gases during the fire; finally, by the use of organic flame retardants, usually containing phosphorus, chlorine or bromine.<sup>6</sup> Recently, the focus has been put on phasing out the use of halogenated species in flame retardants for polyurethane foams. Some of the more successful additives in terms of nonsmoldering, nonfogging alternatives are ethyl phosphate oligomers and monofunctional phosphates.<sup>7</sup>

In the area of fire protective coatings, a passive fire protection known as intumescent coatings has been developed.<sup>8</sup> The first formulations of intumescent coatings were clear coats for wood surfaces.<sup>9</sup> Intumescent systems are now developed for a variety of materials such as additives in polypropylene<sup>10</sup> and coatings for steel constructions.<sup>11</sup> In intumescent coatings a system of intumescent components are added in order for a foamed char layer to be formed during fire. The intumescent system comprises an acid (the char-forming agent), a carbon source that supplies carbon for the polymeric network formed in the intumescent process, and a blowing agent. The acid donor is known to react with the carbon donor in an alcoholysis. This important reaction determines the rate and efficiency of intumescence. The formed phosphor ester subsequently undergoes a ring closing esterification in which water and ammonia is released. A succession of these and similar reactions results in a char consisting of mainly carbon, but also small amounts of oxygen, phosphorus and nitrogen atoms. The blowing agent will sublime and decompose to gaseous compounds, causing the polymeric network to rise to a foam.<sup>8</sup> The components taking part in the reactions mentioned above are protecting the underlying material from fire in three ways. First, they undergo endothermic reactions, thereby cooling the surrounding and slowing down the fire. Second, they form a charred layer that prevents oxygen from reaching the combustible

material. Third, the thick foam is an effective insulator for the material underneath, preventing e.g., steel from rapidly reaching high temperatures. The formation of a char is believed to be beneficial for polyurethane foams, not only because it prevents oxygen from reaching the material, but also because the char is formed at the expense of volatile emissions from the material. Melamine has been evaluated as a char-forming agent in flexible polyurethane foams,<sup>12</sup> however it was not concluded whether melamine had a contributing effect to the increase in char formation.

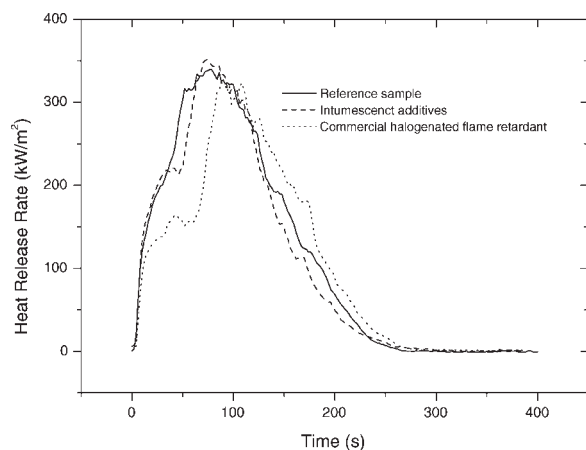
Intumescent systems in polyurethane foams have been evaluated by Modesti et al.<sup>13</sup> In this case, expandable graphite was used as the intumescent additive and the substrate was a rigid polyisocyanurate-polyurethane foam. It was found that this intumescent system could be successfully incorporated in the foam, thus lowering the HRR during fire. Furthermore, two patents concerning intumescent systems for polyurethane foams have been written.<sup>14,15</sup>

The aim of the present study was to explore the possibility of incorporating an intumescent system, similar to those used in coatings,<sup>11</sup> in flexible polyurethane foams, thereby creating an intrinsic fire protection. Moreover, the fire-retardant performance and mechanical properties of these foams were evaluated.

## EXPERIMENTAL

### Materials

The flexible polyurethane foam samples were prepared in a batch-wise free rise process. The used materials included polyetherpolyol E837, tap water, and isocyanate Lupranat T80 consisting of a 80/20 mixture of 2,4- and 2,6-toluene diisocyanate, surfactants and catalysts according to Table I. The commercially available, halogenated flame retardant was Levagard PP, a tris(2-chloroisopropyl) phosphate,



**Figure 1** The heat release rate as a function of time for a reference foam, a foam containing intumescent additives and a foam containing a commercial flame retardant. The data was collected from cone calorimetry measurements.

TCPP, from LANXESS Engineering Chemistry. This material is a commonly used flame retardant for polyurethane foams.<sup>16</sup> Three samples were compared: a reference sample containing no fire retardant species, a sample containing intumescent additives and a sample containing a commercial halogenated flame retardant. Five pphp of the intumescent components was added to the second formulation and 12 pphp of the commercial flame retardant was added in the third formulation. The foams were removed from the plastic containers and crushed by hand to prevent shrinkage due to closed cells.

### Cone calorimetry

Cone calorimetry uses the principle of oxygen demand, i.e., it assumes that heat release during the combustion of organic samples is directly proportional to the oxygen consumption of the process. The measurements were performed at the independent research institute, SP, with a Dual Cone Calorimeter from Fire Testing Technology, UK. The gas analyzer was a CO/CO<sub>2</sub>/O<sub>2</sub> Servomex 4100 Purity Analyzer. The instrument recorded the composition of the gases entering and exiting the combustion area of the calorimeter, and the HRR could then be calculated from the gas analysis results. The mass loss rate and smoke production were also measured by means of a laser system according to ISO 5660-2. The sample dimensions were 100 × 100 × 50 mm<sup>3</sup>.

### TGA

A TGA Q500 from TA Instruments was employed for the thermogravimetric analysis. The samples were heated with a rate of 10°C/min to 600°C under

a nitrogen flow of 60 mL/min. The sample amounts varied between 2 and 4 mg.

### Compression force deflection

Compression force deflection (CFD) measurements were performed with a Zwick Z010 testing machine. The upper plate diameter was 20.3 cm and the lower perforated compression plate was 40 × 40 cm<sup>2</sup>. The load cell used was 10 kN. The measurements were conducted according to ASTM D 3574 CFD and the sample dimensions were 100 × 100 × 100 mm<sup>3</sup>.

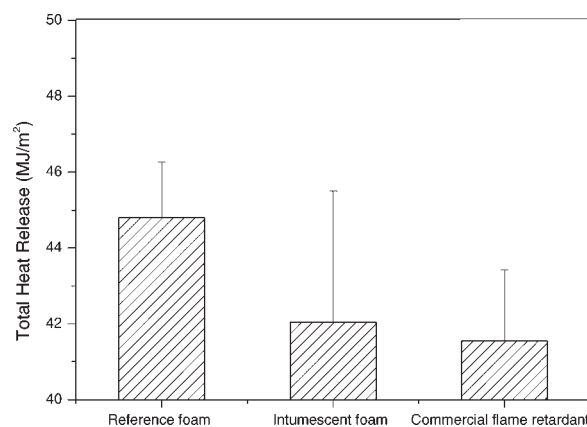
### Tensile measurement

Tensile measurements were performed with a Zwick testing machine according to ASTM D 3574 Tension.

## RESULTS AND DISCUSSION

### Cone calorimetry

The HRR, is considered the single most important parameter indicating fire retardant properties of materials. It was measured on a cone calorimeter, and the HRR graphs are shown in Figure 1. The combustion of polyurethane foam has been described as a two step process<sup>5</sup> in which the first step consists in the melting of the foam, creating a tar, and the second step is the burning of the tar. These two steps were difficult to identify for the reference foam sample in Figure 1, but became more evident for the foams loaded with flame retardant additives. The obvious suppression of the HRR at the early stage of the measurement, after about 20–60 s, observed for the foam sample containing a commercial halogenated flame retardant can also be



**Figure 2** The total heat released during the cone calorimetry measurement, for the reference foam, the foam containing intumescent additives and the foam containing a commercial flame retardant.

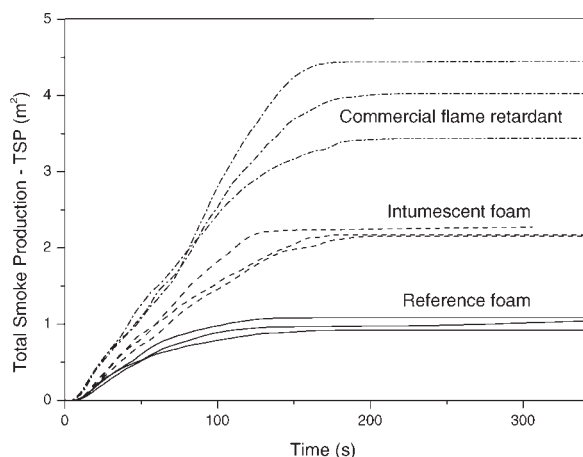
**TABLE II**  
**The Peak Heat Release Rates for the Reference Foam, the Intumescent Foam and the Foam Containing a Commercially Available Flame Retardant**

	Peak Heat Release rate (kW/m <sup>2</sup> )
Conventional foam	355 ± 45
Intumescent foam	371 ± 64
Commercial flame retardant foam	370 ± 59

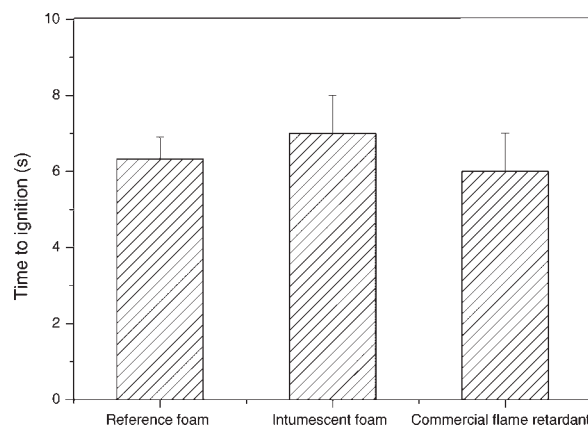
seen, although less pronounced, in the foam with intumescent additives.

This depression of the HRR that occurred at the first step of the combustion in the modified foams was the major process keeping the total heat release at a low level (Figure 2). This step has been proposed to represent the formation of tar and the low levels of the HRR for the two flame retarded foams indicate a suppression of the endothermic reactions responsible for tar formation. The fact that the intumescent foam and the commercial flame retardant foam displayed similar total heat release values can be explained by the latter part of the curve in Figure 1. In the time period between 120 and 220 s of the experiment it is evident that the foam containing intumescent additives had a lower HRR than the other two foams. A possible reason for this was the formation of char, known to form during the intumescent process.<sup>11</sup> The char could also be visually detected after the experiment. The peak HRRs are reported in Table II. As can be seen in the Table there is no significant difference in this quantity between the three foams.

A different way of evaluating the fire retardant capabilities of a material is to study the smoke production during burning. The amount of smoke produced is coupled to the characteristics of the com-

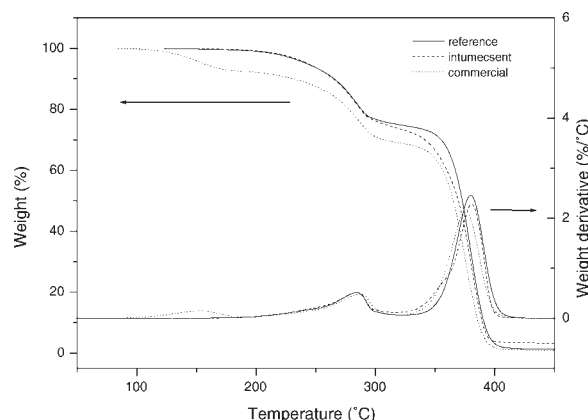


**Figure 3** The total smoke production as a function of time during the cone calorimetry measurement. All three measurements on each material are shown.



**Figure 4** The time to ignition for the reference foam, the intumescent foam and the foam containing a commercial flame retardant.

bustion reactions. The more smoke that is produced, the less complete is the combustion. The total smoke production during the cone calorimeter measurement was monitored as a function of time and the resulting curves can be seen in Figure 3. The figure comprises three measurements for each material. The sample with the highest degree of smoke production was the foam sample containing the commercial flame retardant, which was in accordance with the HRR data. The reference sample evidently demonstrated the lowest smoke production while the intumescent foam ended up in between. There has been an ongoing debate concerning a reduction of the smoke production during combustion of fire retardant polyurethane foams, especially since many conventional flame retardants emit highly toxic combustion products. The increase in smoke production seen for the intumescent foam compared to the reference foam was possibly an effect of a less complete combustion. Thus, the material forming the char did not contribute to the formation of toxic gases.



**Figure 5** TGA curves showing the weight loss and the weight derivative as functions of temperature for the three foams.



**TABLE III**  
**Results from Tensile Measurements, Compression Force Deflection Measurements and Density Measurements of the Foams**

	Stress at 50 % (tensile) (kPa)	Max Stress (tensile) (kPa)	Elongation at Break (tensile) (%)	Stress at 50 % (CFD) (kPa)	Density (kg/m <sup>3</sup> )
Conventional foam	12.6 ± 0.9	54 ± 7	204 ± 19	1.39 ± 0.01	28.0 ± 0.4
Intumescent foam	24.5 ± 0.4	51 ± 6	106 ± 12	2.39 ± 0.12	30.7 ± 1.0

Whether the combustion products from intumescent polyurethane foams are as toxic as the products from halogenated flame retardants still needs to be investigated.

Another important factor in fire properties of materials is the time to ignition—the longer a material can withstand ignition, the better. The results of time to ignition are presented in Figure 4. It can be seen from the figure that the differences were small, but it is clear that the intumescent foam displayed the longest time to ignition. Further investigation is required to conclude whether this is an effect caused by the intumescent additives.

### Thermogravimetric analysis

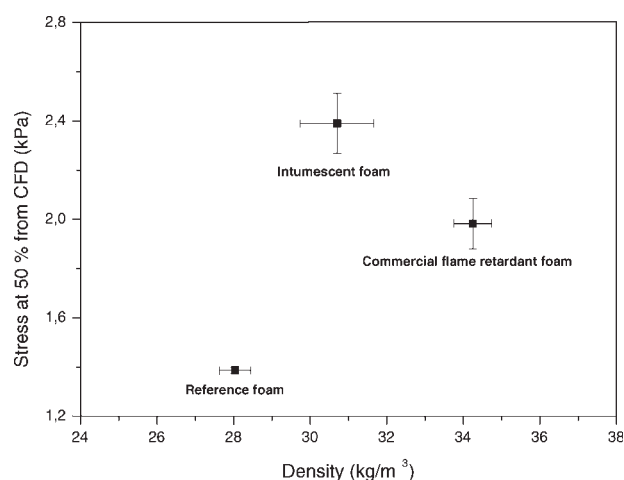
The thermograms of the three analyzed samples are shown in Figure 5. The foam containing the commercial flame retardant displayed a deviating characteristic as compared to the two other samples, i.e., a weight loss step of 8% at about 150°C, most likely related to the presence of TCPP in that sample. In principle, the intumescent foam followed the same curve as the reference sample up to the major weight loss between 350 and 400°C. In the beginning of this process, the rate of weight loss was significantly higher for the intumescent sample as opposed to the reference sample, as can also be seen in the derivative of the weight loss. This temperature range corresponded both to the temperature of thermal degradation of dipentaerythritol observed at around 370°C<sup>17</sup> and to the second step in the intumescent process. The first step of the intumescent process, which is known to begin at around 200°C<sup>8</sup> was not observed as a weight loss step in the TGA. Then again, this was an expected result since the intumescent process involved the formation of a nonvolatile char that remained after thermal degradation of the rest of the sample.

### Mechanical characterization

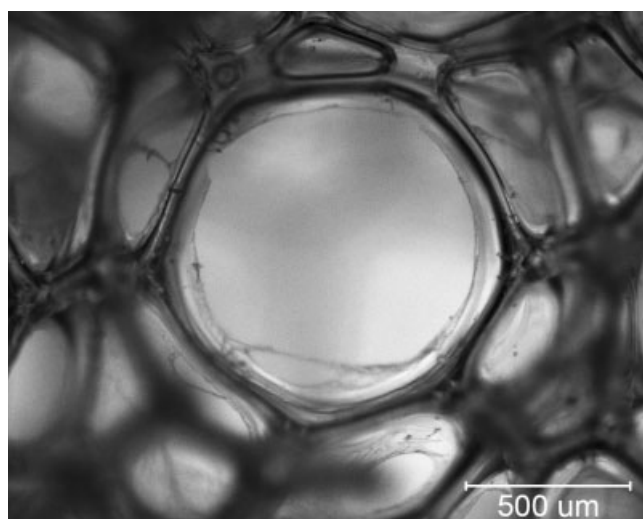
Mechanical analyses were performed to compare the behavior of conventional polyurethane foams with foams containing intumescent additives. Table III presents the results from tensile measurements, compression force deflection measurements as well as the densities of the foams. From the tensile measure-

ment it is evident that the polyurethane foam comprising the intumescent additives displayed a higher stiffness, i.e., value of stress at 50% deformation. Comparable results were obtained during the compression force deflection measurement. The maximum stress during tensile deformation was similar for the two investigated foams whereas the elongation at break was nearly doubled for the conventional foam without intumescent additives. This effect can be explained by the presence of hard particles in the foam containing intumescent additives. These particles likely contributed to crack formation and the subsequent breaking of the material when large tensile deformations were applied.

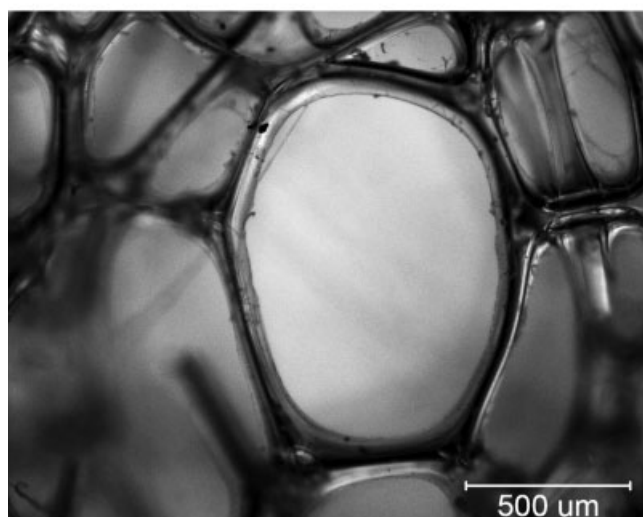
The higher values of stress at 50% deformation were first believed to be a consequence of the increased density of the intumescent foam. However when the stress obtained from the CFD measurement was plotted against density (Figure 6) the intumescent foam demonstrated a higher stress than the commercial flame retardant foam, but a lower density. This increase in stress was most likely due to the reinforcing properties of the intumescent additives. Such an effect is known for melamine in flexible polyurethane foams,<sup>16</sup> where it has been shown that a melamine particle size smaller than the thickness of the struts in the foam provided the best mechanical properties. These property enhancements also pointed at the fact that the intumescent compo-



**Figure 6** The stress at 50% deformation from the tensile measurements plotted against the density.



(a)



(b)

**Figure 7** Micrographs of (a) the intumescent foam and (b) the reference foam, taken with a stereo optical microscope.

nents remained dispersed in the polyurethane foam rather than becoming fully reacted in the polymer via the isocyanate, which would likely not result in such significant flame retardant effects. Images obtained with an optical stereo microscope revealed no clusters of particles in the cell struts (see Figure 7). The intumescent additives were thus most likely well dispersed in the polymer matrix. The mechanism of flame retardancy of this complex system needs still to be examined in detail. The present study reveals a clear flame retardant effect by incorporating an intumescent system in polyurethane foams but do not elucidate the exact mechanism of the process.

## CONCLUSIONS

The fire retardant properties of a polyurethane foam filled with intumescent components were evaluated by means of cone calorimetry, thermogravimetric analysis, and mechanical analyses. The fire retardant effect, in terms of the HRR, was significant for the foam containing 5 pphp intumescent additives. The same effect, but larger, was observed for the foam containing a commercial flame retardant. It should however be mentioned that the foam containing the commercial flame retardant was loaded with 12 pphp, i.e., more than twice as much as the intumescent foam. Furthermore the intumescent foam had not undergone any reformulation whatsoever. The mechanical properties of the intumescent foam were improved in terms of stiffness. This was partly due to an increase in density but was likely also an effect of the intumescent fillers acting as reinforcing agents in the foam. The elongation at break was significantly lower for the intumescent foam, which was believed to be caused by the presence of hard particles in the foam. The present study is important since it indicates that flexible polyurethane foams can be modified to improve fire retardant properties without the use of halogenated species.

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