ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

RIGID POLYURETHANE FOAMS WITH IMPROVED REACTION TO FIRE AND LOW EMISSION PROPERTIES

Ph.D. THESIS

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Department of Polymer Science and Technology

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

GELİŞTİRİLMİŞ YANGIN DAYANIM PERFORMANSLI VE DÜŞÜK EMİSYONLU RİJİT POLİÜRETAN KÖPÜKLER

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ŞUBAT 2023

Berrin Degirmenci, a Ph.D. student of ITU Graduate School student ID 515112009, successfully defended the thesis/dissertation entitled “RIGID POLYURETHANE FOAMS WITH IMPROVED REACTION TO FIRE AND LOW EMISSION PROPERTIES”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my family,

FOREWORD

I would like to deeply thank to my advisors Assoc, Prof. Nesrin KÖKEN and Prof. Dr. Ahmet AKAR for their endless support throughout my PhD journey.

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Last but not least, I cannot thank enough my family, as none of this would have been possible without their constant support.

February 2023

Berrin DEĞİRMENCİ
(Polymer Scientist)

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ABBREVIATIONS

APB	: Ammonium pentaborate
APP	: Ammonium polyphosphate
ATH	: Aluminium trihydroxide
CM	: Combustion Modifier
CT	: Cream time
DEEP	: Diethyl ethylphosphonate
DEHP	: Diethyl hydroxymethylphosphonate
DO11 (DOPO)	: 9,10-Dihydro-9-Oxy-10-Phosphaphenanthrene-10-Oxide
DSC	: Differential Scanning Calorimetry
EN	: European Norm
Fc	: Ferrocene
FR	: Flame Retardant
FRD	: Free rise density
GT	: Gel time
LOI	: Limiting Oxygen Index
MDI	: 4,4'-Methylene Diphenyl Diisocyanate
OTEP	: Oligomeric TEP
PIR	: Polyisocyanurate
PMDI	: Polymeric MDI
PU (PUR)	: Polyurethane
RDP	: Resorcinol bis(diphenyl phosphate)
RPUF	: Rigid Polyurethane Foam
SS	: Smoke Suppressant
STD	: Sodıum tetraborate decahydrate
TCPP	: Tris (1-Chloro-2 Propyl) Phosphate
TEP	: Triethyl Phosphate
TGA	: Thermo Gravimetric Analyzer
ZB	: Zinc Borate

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RIGID POLYURETHANE FOAMS WITH IMPROVED REACTION TO FIRE AND LOW EMISSION PROPERTIES

SUMMARY

During the course of one of business meetings, once when I was asked why I have been pursuading a PhD in Polymer Science and Technology, it seemed challenging to provide the motivation as the study covers broad aspects. However, having concluded this work, the answer now is simple. I wanted to deliver efficient solutions on one of the well known and versatile performance material -rigid polyurethane foam- which at the same time allows a better profile in environment, health and safety aspects. I am glad that these objectives are fully met as a valuable outcome of this study.

In this work, different combustion modifiers were evaluated in rigid polyurethane/polyisocyanurate foam with regards to their reaction to fire and emission performance. Terminology of combustion modifiers cover both flame retardants and smoke suppressants. The difference between flame retardants and smoke suppressants derive from the action they exhibit during the combustion. Flame retardants delay the combustion action whereas smoke suppressants aid lowering the smoke and harmful compounds generated during the burning of the substance. Having said that it in the research or in the application area, it is possible to see that combustion modifiers and flame retardants definitions can be used interchangeably.

Initially, a literature screening was completed to choose the right flame retardants that are commercially available for rigid polyurethane foams. While most of the found candidates are phosphorous based, few examples such as Hexion TL 91-805D polyol that is nitrogen based, was also in scope. In the flow of the study, flame retardants were then classified according to being reactive or not towards isocyanates. This classification is particularly important when evaluating emission performance of the said substances. On the smoke suppressants side, Zinc borate and ferrocene represent non-phosphorous substances that are suitable to incorporate in this particular application.

Performance examination of each combustion modifier was completed using 2 methodology. First methodology was determined as the incorporation of one combustion modifier each time at the same weight in the selected formulation. It was then followed by the incorporation of a combination of one flame retardant and one smoke suppressant in rigid Polyurethane foams. DIN 4102 small scale flame device and NBS smoke chamber instruments were chosen to perform the analysis. This method was useful to reveal synergy between different candidates in the foams. Results showed that among the candidates, interaction of Triethyl phosphate and Zinc Borate as well as Triethyl phosphate and Ferrocene created a synergic impact and greatly improved combustion properties in Polyisocyanurate foams.

For the investigation of the found results, thermogravimetric and scanning electron microscope characterizations were carried out. It was revealed that Zinc borate creates a thermal barrier and prevents the cell from a complete destruction once the foam is exposed to ignition. While reaction to fire performance was improved, it was detected that addition of Zinc borate has an impact on the reactivity and free rise density of the foams. Gel time occurred to be longer and density of the foams were measured to be

higher with respect to reference. This might be explained by Zinc borate acting as an inert filler.

Triethyl phosphate-Ferrocene study also put forward interesting results. While addition of a little amount of Ferrocene provided the best fire performance in rigid Polyisocyanurate foams, more than certain amount of Ferrocene incorporation has led the complete burning of the foam. Therefore, for an enhanced smoke and fire performance, Ferrocene amount should be optimized in the formulations.

In the latter step, three compound combustion modifier combinations were examined. Loading of oligomeric Triethyl phosphate into the Triethyl phosphate and Zinc borate combination aided to provide a superior performance in fire properties with respect to Triethyl phosphate and Zinc borate containing foam. In order to confirm the results with the same amount of combustion modifiers loading, second methodoloy was used: Analyses were successively repeated by adjusting the foams to the same molded density and P% content in the final material. Cone calorimeter was selected to perform the ultimate combustion test and displayed additional parameters such as Total Heat Release, Peak Heat Release Rate and Total Smoke Production in 11 formulations.

Outcome of cone calorimeter study was evaluated using Triethyl phosphate (mod 1) containing formulation as the reference. In this way, it was possible to confirm the synergism in other formulas. Formulations that surpassed the performance of reference foam were found to be the same as of those completed in laboratory: Triethyl phosphate-Zinc borate (mod 3), Triethyl phosphate-Ferrocene (mod 12) and Triethyl phosphate-Oligomeric Triethyl phosphate-Zinc borate (mod 9) combinations. These 3 combinations displayed either a lowered Total Heat Release or Total Smoke Production Rate or both than the reference.

In the final stage, further analysis was completed to check the emission properties of these 3 foams and reference using Head space gas chromotograpy mass spectrometry characterization method. While Triethyl phosphate showed an elevated pique especially in the reference foam due to the high addition amount, Ferrocene also confirmed to migrate because of the sublimation at high temperatures.

Cone calorimeter and head space analysis confirmed that Triethyl phosphate-Oligomeric Triethyl phosphate-Zinc borate combination proved to be the most efficient combination with regards to both reaction to fire and emission properties in rigid Polyisocyanurate foams. This result is also a proof of how oligomeric substances can enhance the emission properties of end material.

As a final word, this study showed that fire and emission properties of rigid Polyurethane-Polyisocyanurate foams can be enhanced through the addition of right combustion modifiers at a right amount. Said properties are not only governed by the P% content but also synergism and molecular structure might play an important role to improve the properties in polyurethane formulations.

GELİŞTİRİLMİŞ YANGIN DAYANIM PERFORMANSLI VE DÜŞÜK EMİSYONLU RİJİT POLİÜRETAN KOPÜKLER

ÖZET

Bu doktora çalışmasıyla ilgili son periyotta yaptığım görüşmelerde karşılaştığım önemli sorulardan biri, bu çalışmayı neden yürüttüğüme dair idi. İşin özünde malzemenin performansının güçlendirilmesi oldukça önem arz etmekle birlikte amaçlarımdan en önemlisi, yaygın olarak kullanılan performans malzemesi rijit poliüretan köpüğün; çevre, sağlık ve güvenli kullanımı açısından da özelliklerini iyileştirmekti. Çalışmaların sonunda belirtmek isterim ki, iki hedef de uzun ve tempolu bir doktora periyodu sonucu gerçekleştirilmiş oldu.

Bu çalışmada farklı yanma alev geciktiricilerinin rijit poliüretan ve poliizosiyanürat köpüklerdeki yangın dayanım performansı ve emisyon özellikleri test edilmiştir. Terminoloji olarak yanma düzenleyicileri iki sınıfı da kapsamaktadır: alev geciktiriciler ve duman bastırıcılar. Bununla birlikte literatürde yanma düzenleyicileri ve alev geciktiriciler sıklıkla birbirlerinin yerine de kullanılmaktadır. Alev geciktiriciler ve duman bastırıcı malzemeler arasındaki temel fark, yanma sırasında göstermiş oldukları mekanizmadan kaynaklanmaktadır. Alev geciktiriciler yanmayı geciktirirken duman bastırıcılar yangın sırasında oluşan duman ve zararlı maddelerin oluşumunu azaltmaktadırlar.

Bu çalışmada izlenen yol şu şekildedir: İlk olarak, doğru alev geciktiricileri tercih edebilmek icin halihazırda ticari olarak rijit poliüretan köpüklerde kullanıma uygun olarak üretilen alev geciktiriciler için bir literatür taraması yapılmıştır. Saptanan adaylardan birçoğu fosfor içeren bileşiklerdir; bununla birlikte çok az sayıda da olsa Hexion TL 91-805D polyolu gibi tamamen azot bazlı kimyasal da çalışmaya dahil edilmiştir. Çalışmanin akışına uygun olarak, alev geciktiriciler izosiyanatlar ile reaksiyon verip vermemesi açısından, reaktif yahut non-reaktif olarak sınıflandırılmıştır. Bu sınıflandırma özellikle emisyon performansı açısından önemlidir. Reaktif komponentlerin nihai malzemenin kendi kimyasal yapısı içeriğine bağlanması, onların emisyon yayılım değerlerinin düşürülmesine katkısı vardır. Duman bastırıcılar sınıfından ise, çinko borat ve ferrosen, fosfor bazlı olmayan ve uygulamada kullanılabilecek kimyasallar olarak belirlenmiştir.

Yanma düzenleyicilerinin performansı bu çalışmada 2 farklı metot ile değerlendirilmiştir. Birinci metot, her yanma düzenleyici maddeden ağırlıkça aynı miktarda ve her defasında yalnızca bir maddenin seçilmiş formülün içine katılması olarak belirlenmiştir. İkinci metot ise aynı yüzdede fosfor olacak şekilde seçili alev geciktiricilerin formüle katılması ile gerçekleştirilmiştir.

Ilk metot uygulamasi, ikinci aşamada, bir alev geciktirici ve bir duman bastırıcı kombinasyonu oluşturularak rijit poliüretan köpük içine katılması ile tamamlanmıştır. Bu aşama komponentler arası olası sinerjik etkinin ortaya çıkarılması açısından çok etkili olmuştur. Performans değerlendirmesi, DIN 4102 kücük alev testi ve NBS duman cihazı aracılığı ile yapılmıştır. Elde edilen sonuçlar Trietil fosfat-çinko borat ve trietil fosfat ve ferrosen kombinasyonlarının sinerjik etki yarattığını ve Poliizosiyanürat köpügün yanma özelliklerini önemli derecede iyileştirdiğini göstermiştir.

Bulunan sonuçları daha iyi anlanmlandırabilmek için, termogravimetrik ve elektron mikroskobu ile analizler yapılmıştır. Sonuçlar ve görüntüler, çinko boratın termal bir bariyer oluşturduğunu ve yanma esnasında hücre yapısının tamamen bozulmasını önlemesiyle bu iyileşmenin mümkün olduğunu göstermiştir. Bununla birlikte, yapılan deneyler esnasında, çinko boratın reaktivite değerlerine ve serbest köpük yoğunluğuna da etkisi olduğu tespit edilmiştir. Çinko boratlı formülün, çinko borat içermeyen referansa göre iplik zamanının uzadığı, köpük yoğunluğunun arttığı gözlemlenmiştir. Bunun sebebi çinko boratın inert bir dolgu malzemesi yapısında olması ile açıklanabilir.

En etkin kombinasyonlardan biri olan Trietil fosfat-Ferrosen çalışması ise ilginç sonuçlar ortaya koymuştur. Küçük miktarlarda (%4´ten daha az) katılan Ferrosenin rijit poliizoyanürat çalışmalarındakı en iyi yangın dayanımı performansı verdiği tespit edilirken, bunun üstündeki oranların ise köpüklerin tamamen yanmasına sebep oldugu gözlemlenmiştir. Bu yüzden, geliştirilmiş duman ve yangın dayanım performansı için, Ferrosenin formüllerdeki miktarı optimize edilmelidir.

Çalışmalarda sonraki adımda, içeriğinde 3 farklı yanma düzenleyici kombinasyonunun katıldığı köpükler test edilmiştir. Oligomerik trietil fosfatın, trietil fosfat ve çinko borat kombinasyonuna katılmasıyla, trietil fosfat ve çinko borat içeren köpüğe gore daha da geliştirilmiş yangın performansı elde edilmiştir. Bulunan bu neticeyi teyit etmek için, ikinci metodoloji kullanılmıştır: Analizler, aynı kalıp yoğunluğu ve aynı fosfat yüzdesine sahip alev geciktirici kombinasyonlarını içeren rijit köpüklerin hazırlanması ile devam ettirilmiştir. Kon kalorimetri tamamlayıcı yanma parametrelerini sağlayan bir cihazdır ve son analizler bu cihaz ile tamamlanmıştır. Saptanan bulgular toplam ısı salınımı, ısı salınım pik noktası ve toplam duman yoğunluğu değerleri olarak sıralanabilir. Bu bulgular 11 formül için de çalışma içerisinde paylaşılmıştır.

Kon kalorimetre sonuçlarını değerlendirirken, alev geciktirici olarak yalnızca Trietil fosfat (mod1) içeren köpük referans olarak alınmıştır. Bu sayede, diğer formüllerde sinerjik etki gosteren bileşenlerin saptanması kolaylaşmıştır. Referanstan (mod1) daha iyi sonuçlar veren formüller laboratuvardaki analizlerde de performansı teyit edilen formüller ile aynıdır: Trietil fosfat-çinko borat (mod3), Trietil fosfat-Ferrosen (mod12) ve Trietil fosfat-Oligomerik Trietil fosfat-çinko borat (mod9) kombinasyonlarıdır. Bu üç kombinasyondan her biri ya toplam ısı salınımı değerlerinde, ya toplam üretilen duman yoğunluğu değerlerinde, yahut her iki parametrede de referans köpükten daha iyi sonuçlar vermiştir.

Son analiz olarak Head space gaz kromotografi kütle spektrometresi metoduyla bu bahsedilen 3 formül (mod3, mod9, mod12) ve referans formülden (mod1) alınarak hazırlanan köpük numunelerinin emisyon özelliği test edilmiştir. Referans köpük, içerdiği yüksek trietil fosfat sebebiyle yüksek bir pik gösterirken, ferrosen içeren köpükten de ferrosenin migrasyonu gözlemlenmiştir. Bu durum ferrosenin süblimleşme özelliğinden kaynaklanmaktadır.

Kon kalorimetre ve emisyon analizleri Trietil fosfat-Oligomerik Trietil fosfat-çinko borat kombinasyonunun hem yangın, hem emisyon açısından poliizosiyanürat köpüklerde kullanılabilecek en etkin kombinasyon olduğunu göstermiştir. Bu sonuçlar, oligomerik maddelerin emisyon performansının nasil iyileştirilebileceğine dair son derece güzel bir örnektir. Ferrosen ise, çok iyi yangın dayanımı performansı göstermesine rağmen, yüksek emisyon degeri ve toksikoloji açısından sağlığa zararlı bir yapıda olması sebebi ile bu uygulama alanında kullanımı sınırlı olabilir. Gelecek çalışmalar açısından Ferrosenin oligomerik versiyonlarının veyahut izosiyanat ile reaksiyona girebilecek modifikasyonlarının bu uygulamada kullanımı açısından daha avantajlı olabileceği söylenebilir.

Son sözler olarak, bu çalışma, poliüretan-poliizosiyanürat köpüğün yangın dayanım performansının ve emisyon özelliklerinin doğru yanma düzenleyicilerin doğru kombinasyon ve miktarlarda katılımı ile iyileştirilebileceğini göstermiştir. Bahsedilen bu özellikler maddelerin yalnızca fosfor içeriğine bağlı olmamakta, sinerjik etkileşimler ve molekül yapıları da yangın dayanım ve emisyon performansı açısından belirleyici etkenleri oluşturmaktadır.

1. INTRODUCTION

Rigid polyurethane/polyisocyanurate foam is one of the most consumed cellular polymeric materials in the insulation industry, including wide-range applications such as the transportation of goods, the automobile industry, building and construction including sandwich panels for industrial buildings and other building elements, and spray foams because of its low thermal conductivity and good shock absorption properties. However, rigid polyurethane foam (RPU) is flammable, easily ignited, burns vigorously, and releases dense smoke and toxic gases [1].

Combustion of polyurethane (PU/PUR) foam can lead to the generation of intense smoke and toxic gases which can be lethal in case of continuous inhalation. A fire incident that happened at The Station Nightclub in Rhode Island, USA, in 2003 was concluded tragically as 95 people died because of the PUR foam that was placed f of acoustic insulation on the walls. Intense smoke production and accelerated fire progress resulted people being stucked in the building and kept away from escaping [2]. To reduce the combustibility of these foams, various combustion modifiers are added during the production stages. The fire-retardant (FR) compounds typically used in the RPU foams contain halogen atoms, nitrogen, phosphorous and boron, and may be inorganic or organic, reactive or non-reactive toward isocyanate, and monomeric or polymeric in nature.

Flame retardants do not fully prevent the combustion but once the material is exposed to ignition, they can help delay flame spread before the complete burning of the substance occurs; they also reduce the smoke formation. To obtain a combined effect of these two properties (flame spread reduction / smoke reduction or suppression), the study of synergistic effects of different agents is a good strategy to obtain both at the same time.

Synergism between two or more substances (e.g. combustion modifiers acting on the reaction to fire properties of a PU foam) in achieving and possibly outperforming a certain desired performance is one of the most effective ways to improve the properties of a material. A synergistic effect may result in unmatched material performances or, alternatively, in a match of incumbent performances while using a relatively low amount of loading of the substances in the targeted system.

Halogen-containing compounds are highly effective flame retardants but produce toxic gases and hazardous fumes during the fire and may leach out of the polymer during its normal use. The most common fire retardant used in RPU foams is liquid tris(2-chloropropyl)phosphate (TCPP); its use and related effects on human beings, at the moment of writing, is being questioned, it’s a harmful compound that may be classified as toxic in the near future. Recently, and consequently, the use of non-halogenated and non-toxic fire retardants for RPU foam is becoming an important research area.

There are several factors that limit scientists, companies, and associations from using effective flame retardants. Focusing on the aspects of non-toxicity, non-hazardousness, effectivity, availability, and cost as well as environmentally friendly solutions is putting some constraints on the studies.

The environmental impact of flame retardant is one of the utmost important aspects. Over time, some flame retardants can migrate out of polyurethane foam and become a problem. This also presents a fire safety problem in the sense that the foam over time loses its protection if enough of the flame retardant leaves the product. So now it is important to consider developing new flame retardants that either react into with the polyurethane macromolecule itself (so that the FR molecules cannot leave the polymer throughout its life cycle) or are polymeric in structure so as to have low volatility.

Volatile Organic Compounds (VOC) Emissions, which is the measure of the volatility of the substance incorporated in the polymer matrix, started to draw more attention also for rigid PUR and polyisocyanurate (PIR) foam applications to mitigate indoor air pollution. Recent advancements in rigid foams research are based on the fact that some chemicals of concern - e.g. tris-(2-chloroisopropyl)phosphate TCPP, or triethyl phosphate (TEP) - may migrate on the surface of the foam into which they are embedded as flame retardants, and then in the air. To reduce resulting emissions during the life cycle of the product, the incorporation of various oligomeric/polymeric/reactive flame retardants in rigid foams can be a way to improve the aspect. This study targets to deliver rigid polyurethane/polyisocyanurate foam solutions that provide an improved reaction to fire and low emission properties.

2. THEORETICAL PART

2.1 Purpose of Thesis

The principal target of this thesis study is to provide an improved reaction to fire and low emission properties for rigid polyurethane/polyisocyanurate foam applications through the addition of halogen-free combustion modifiers (CM).

The difference between rigid polyurethane and polyisocyanurate foam is the presence of isocyanuric rings in polyisocyanurate foams that are generated by the excess of -NCO groups and trimerization catalyst structure [3]. In this project, the fire performance of both types was attempted to be enhanced via the incorporation of various combustion modifiers.

Combustion modifiers are primarily classified according to their ability of physical or chemical bonding in the final polymer matrix, which is expressed as ‘non-reactive’ and ‘reactive’ types.

In the first part of the study, the performance of various non-reactive CMs and their interactions in rigid polyurethane foam are investigated.

In the second part, a detailed study for the evaluation of the non-reactive type of phosphorus-based flame retardants (FRs) and Zinc Borate (ZB) combinations in the selected PIR system is presented.

In the third part, the performance of Ferrocene, which is an alternative to ZB, is screened with phosphorous-based non-reactive FRs in PIR foams.

The fourth part covers the investigation of the reactive type of CMs and their interactions with ZB and Ferrocene in the selected PIR foam system.

The fifth and sixth part instead, reveals the cone calorimeter and emission results of best-performing approaches.

Identified research objectives in these 6 parts:

- Replacement of TCPP and TEP in rigid polyurethane and PIR foam applications
- To reveal the interactions: synergism – antagonism mechanism between different CMs in PUR and PIR foams and resulting in the reduction of total P% content in PIR foams

- Evaluation of the impact of CMs addition on reactivity and free rise density of the PIR foams
- Evaluation of emission performance of best-performing formulations thus improving Volatile Organic Compounds (VOC) aspect of PIR foams

2.2 Polyurethanes

Today, Polyurethanes (PUs) take place in many areas of our lives including domestic and industrial applications. Insulation boards, mattresses and seatings, artificial leather, shoe soles, adhesives and binders are only some of the examples of its versatile use. Figure 2.1 represents example of a matress made of flexible polyurethane foam.

Figure 2.1 : Mattress made of flexible polyurethane foam.

Polyurethanes are organic polymers that is consisting of the urethane group in the structure which is formed from the reaction between a polyol and a diisocyanate. Besides said components, the reaction may involve other additives such as surfactants, chain extenders, catalysts and blowing agents. The incorporation and amount of these additives determine the properties of final material and its use area. The entire process can be carried out in one step by arrangement of the chemistry. Figure 2.2 illustrates the urethane structure.

$$R\text{-}NCO + R\text{-}OH \longrightarrow R\text{-} NH \text{-} \overset{\overset{O}{\parallel}}{C} \text{-}O\text{-}R'$$

Figure 2.2 : Formation of urethane structure.

Rigid polyurethane foam is one of the main application area of PUs due to its excellent thermal insulation and mechanical properties. Especially, in construction, cold storage, refrigeration and sandwich panels, rigid PU foam is the preferred performance material thanks to its enhanced performance. The polymerization of rigid PU foam mainly requires either a polyether or a polyester polyol, a polymeric methylene diphenyl isocyanate (MDI), a surfactant, catalysts, a blowing agent and combustion modifiers. Surfactants might be based on silicon chemistry for the purpose of improvement in emulsion and insulation properties. Catalysts might be incorporated to adjust the reactivity profile of the PUR foam. Blowing agents, instead, can be added to lower the free rise density as well as to enhance the insulation. Figure 2.3, Figure 2.4 and Figure 2.5 are representing main building blocks of rigid polyurethane foam structure.

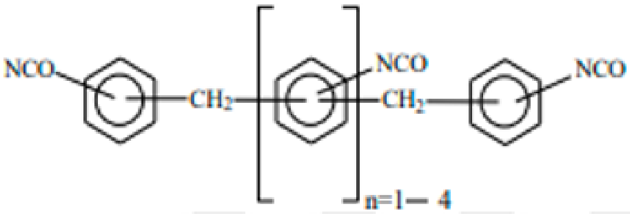


Figure 2.3 : Polymeric MDI (PMDI).

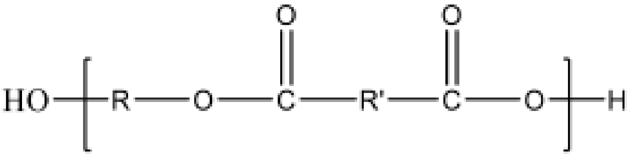


Figure 2.4 : Polyester polyol.

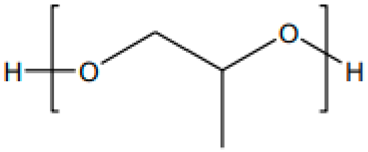


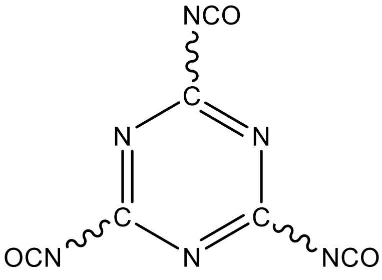
Figure 2.5 : Polypropylene glycol (polyether polyol).

While each polyurethane compound can be a research subject separately, nowadays recent trends and researches emphasized in rigid polyurethane foam area are: Renewable compounds, halogen free, non-toxic and smoke suppressant fire retardant structure. The main aim of this work, which was decribed previously, is to produce polyurethane foam with improved smoke, fire and emission properties using different combustion modifiers. A sandwich panel made of RPUF is illustrated in Figure 2.6:

Figure 2.6 : Sandwich panels made of rigid polyurethane foam.

Depending on the amount of isocyanate and type of catalyst, rigid polyurethane foam might contain polyisocyanurate ring in the structure. Isocyanurate is an aromatic ring that increases cross-linking during the production of polyurethane foams. In order to have isocyanurate structures in Polyurethane foams, an excess amount of isocyanate and a trimerization catalyst is required. PIR foams composed of a stable three-dimensional network structure enhance char formation and reduce smoke during burning. More isocyanurate structure makes PIR more resistant to fire and thermal treatment.

It would be convenient to express that isocyanurate structure is an embedded structure in rigid polyurethane foam as long as the conditions are met, therefore in this study polyisocyanurate foam refers to the foam that contains polyisocyanurate-polyurethane structure together. Isocyanurate ring structure is shown in Figure 2.7:



isocyanate component

isocyanurate ring

Figure 2.7 : Formation of isocyanurate ring.

To process rigid PUR or PIR foams, different processing technique exist such as double belt continuous lamination, discontinuous open or close mold processess. In each of thic process, there is a commonly used terminology to determine the reactivity of the material and adjust the process conditions. Some of the terminology that is used to describe the characteristics of the foam: cream time, gel time and free rise density.

Cream time (CT) is the moment when the polymerization of polyurethane foam starts, the viscosity builds up and accompanied by the foam rise.

Gel time (GT) indicates the instant when polymerization reaction is close to the termination. For instance, when reactive mixture is drawn by a stick, it has a fibrous structure and not liquid.

Free rise density (FRD) is the density of the foam when the reactive mixture is poured into a box, cup or a bag and grows without an exterior impact/control.

These parameters are important both at bench scale product development as well as industrial manufacturing of polyurethane foams.

In this work, while main target is to attempt to enhance reaction to fire performance and emission properties of rigid PU and PIR foams, their reactivity profile and parameters are also in scope.

2.3 Combustion Modifiers

In the literature, Combustion Modifiers that are used for Polyurethanes find a broad space. While the terminology of flame retardants is used as interchangeably with combustion modifiers; in reality, CMs cover both ‘Flame Retardants’ and ‘Smoke Suppressants’. Specifically, flame retardants aid in delaying the combustion action, and smoke suppressants help reduction of the generated smoke of RPUF. Screening literature on the flame retardants technology can provide many alternative ways to the researchers on the development of new substances however, considering upcoming concerns on halogenated compounds, environmental impacts, VOC and economical aspects and so on, it becomes challenging to find efficient and commercially available FRs to be used in rigid polyurethane foam applications [3].

One of the most efficient ways to improve the reaction to fire properties of PU foams is the incorporation of combustion modifiers. Selection of appropriate flame retardants is a key to improving fire and smoke properties as well as keeping the properties of rigid polyurethane foam such as high thermal insulation, low density, high specific strength, good dimensional stability, adhesion strength, and aging resistance.

Flame retardancy of RPU foam is a well-studied topic in the industry. Most of the companies that are active in this field are executing their research activities to develop new offerings which are high performing and in compliance with possible changes in environmental health & safety (EH&S) regulations.

To realize targeted research objectives, a roadmap was identified for the selection of the right candidates as shown in Figure 2.8:

Figure 2.8 : Flame retardants evolution strategy.

The most efficient way to mitigate the impact of volatile organic compounds (VOC), is the incorporation of reactive FRs in the polymer matrix which provides a permanent solution as the substance is chemically bonded in the structure. However, due to the limited choice of reactive FRs for rigid PU applications, the next best alternatives such as polymeric/oligomeric additive types are also in the evaluation list.

Another important point when selecting the right FR is whether it is a phosphorous-based substance or not. Since it is easy to find commercially available CM offerings based on phosphorous where it is rare to retrieve technologies that are purely derived from Nitrogen, Boron, or another effective type of fire retardant substance, most of the CMs used in this study are phosphorus derivatives.

For the CMs used in the study, to facilitate the selection, they are primarily classified according to being reactive or non-reactive towards isocyanates. A second distinction was made whether they are derived from phosphorus substances or not. Further classification is made according to a number of repetitive chemical units of the substances: Monomeric, oligomeric, and polymeric. This third segmentation is important when evaluating the VOC performance of the final articles.

Figure 2.9 displays the classification that is used for the study flow and selected candidates for PIR applications:

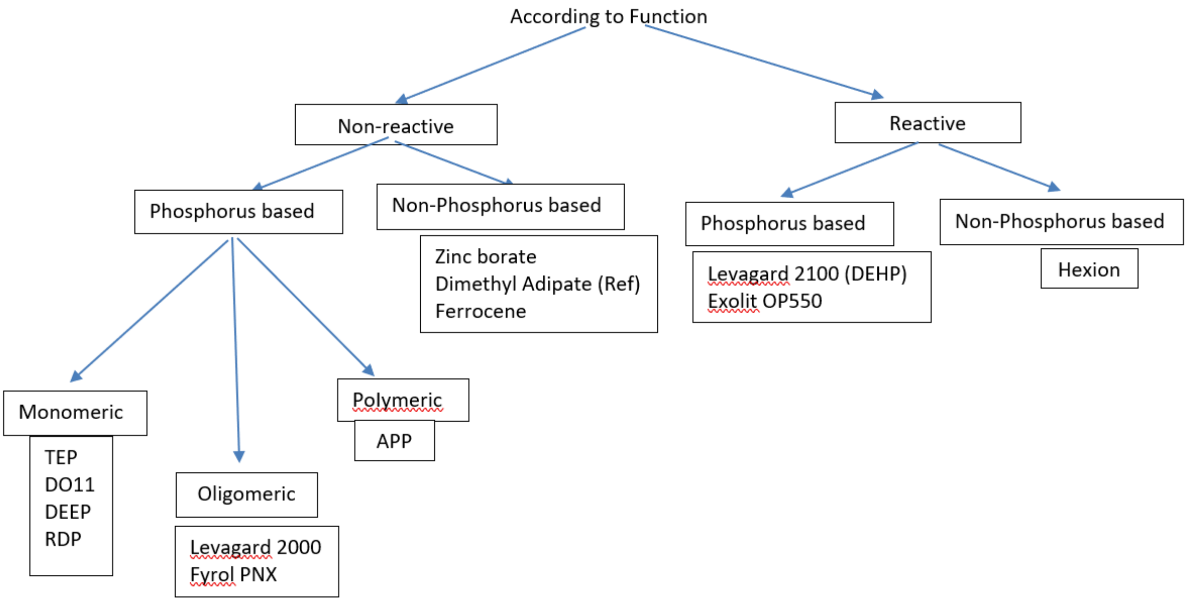


Figure 2.9 : Classification of combustion modifiers.

This classification was prepared and aligned with the VOC target of the study. Another general classification that might be helpful to understand Combustion Modifiers, would be to divide them into Flame Retardants and Smoke Suppressants (SS).

2.3.1 Flame retardants

Flame retardants are compounds that are physically or chemically bounded in the selected polymer matrix. They enhance the combustion properties by delaying the fire and/or reducing the flame spread. Flame retardants do not necesarily suppress or improve the smoke aspect during burning; even though in some cases they also assisst in inclination of smoke formation.

Depending on their structures, flame retardants can be classified organic, inorganic; polymeric, oligomeric or monomeric; reactive or non-reactive. In this study, instead, FRs are rimarily classified as

- Phosphorus compounds
- Non-phosphorous compounds

Organophosphorus flame retardants can be subdivided as phosphinates, phosphonates and phosphate esters. In Figure 2.10, structure of organophosphorus compounds are presented.

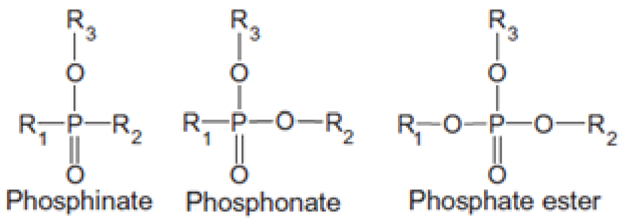


Figure 2.10 : Phosphorous family.

During the literature review, it was detected that commercially available flame retardants are mainly pertaining to the phosphate ester family. In order to evaluate different phosphorus structures and determine whether it has a significant impact on fire properties, at least one substance was selected from each family. Table 2.1 represents the selected flame retardants with their phosphorus structures.

Table 2.1: Phosphorous flame retardants used in the study.

Phosphate ester	Phosphonate	Phosphinate
TEP	DEEP	DO11
RDP		
Levagard 2000		
Fyrol PNX		
APP		
Levagard 2100		
Exolit OP550		

Impact of these structures on combustion properties will be discussed in the results and discussion section.

2.3.2 Smoke suppressants

Smoke suppressants represent a distinct group of substance than flame retardants. Their primary function is to reduce the generation of smoke and toxic gases; nevertheless some flame retardants, such as melamine, can both act as flame retardant and smoke suppressant. As in the case of FRs, they can be incorporated into the polymers physically or chemically, depending on their chemistry.

While flame retardants are mainly phosphorus compounds, smoke suppressants can be classified into 5 different types:

- Metal-organic compounds
- Metal compounds (including metal oxides, organic metal compounds, metal salts, and metal hydroxides)

- Carbon materials
- Melamine and its derivatives
- Others [4]

In this study, selected smoke suppressants are Zinc borate and Ferrocene. Dimethyl adipate was also examined in one case.

In rigid PU foam industry, flame and smoke performance are evaluated together. One of the ways to measure the flammability of the PU materials is the Limiting Oxygen Index (LOI). In the literature, it was revealed that Polyurethane foam has an LOI in the range of 16–19%, meaning a vigorously burning polymer. This means, once the combustion starts, it accompanies with the generation of dense smoke and toxic gases. In case no flame retardant or smoke suppressant is incorporated, the use of PU might be greatly restrictied in many fields [5-8]. Because it is used in building and construction applications, there are special requirements and codes governed by national building regulations, states and local authorities.

There are 3 types of hazards which harm people during the combustion of PU:

- Toxic gases (e.g. such as low molecular weight hydrocarbons, CO, HCN, MeOH) are released once the PU foam initiates to ignite that lead poisoning and suffocation.
- PU combustion produces significant amount of heat that causes thermal damage as well as progression of the fire rate.
- High density of the smoke has a negative impact on sight and visibility, thus escaping and/or rescuing becomes highly difficult [9, 10].

In order to highlight the impact of hazards during the absence of FR and SS, thermal dissociation behaviour of polyurethanes should be investigated.

2.4 Thermal Dissociation of Polyurethanes

Thermal behaviour of Polyurethanes is a well-studied topic in the literature. Several pyrolysis and TGA works revealed the decomposition mechanism of PU materials as a 2 or 3 steps degradation process, where first mass loss occurs between 200–350 °C and the second and third loss takes place approximately at 350–600 °C [11-16].

Decomposition stages of polyurethanes is determined by several factors such as:

- Type of polyol and isocyanate components present in PU,
- Testing conditions (nitrogen, air)
- Initial temperature
- Heating rate

Polyurethane degradation is dependent on the hard and soft segments content in the structure. While longer polymer chains and aliphatic structures will decompose first and reduce the degradation temperature, shorter polymer chains and aromatic structures will alterate the dissociation.

Table 2.2 summarizes the decomposition stages of various specific bonds present in Polyurethane structure:

Table 2.2: Decomposition temperature of specific bonds in PU [17, 18].

Bond type	Onset of degradation (°C)
Carbodiimide	250-280
Isocyanurate	270-300
Aliphatic allophanate	85-105
Aromatic allophanate	100-120
Aliphatic biuret	100-110
Aromatic biuret	115-125
Aliphatic urea	140-180
Aromatic urea	160-200
Aliphatic urethane	160-180
Aromatic urethane	180-200
Disubstituted urea	235-250

One of the most important outcome of Table 2.2 is, the great difference between the thermal stability of isocyanurate and aromatic or aliphatic urethane bonds. This is an indication of an improvement in reaction to fire properties in isocyanurate foams rather than solely PUR foams. This will be confirmed/not confirmed during the discussion of experimental studies in part IV.

2.4.1 Mechanism and evaluation of smoke generation and toxicity for polyurethane products

Once ignited, polyurethane foams generate at a high rate of smoke. There are 3 stages of smoke production:

- Thermal degradation in the condensed stage,

- Release across carbon layer,
- Formation of smoke fragments in the gas stage T

During the combustion of PU, several toxic gases are produced. Reported some of decomposition products by mass spectrometry include carbon monoxide, hydrogen cyanide, pyrrole, pyridine, benzonitrile, naphtalene and so on [19, 20].

Time concentration profiles of decomposition products and their toxicity levels are 2 major parameters to take into account while asssessing the toxicity fire hazard aspect of PU products. 2 methods are commonly used to calculate the toxicity: Volatile organic compounds (VOC) emissions as well as toxicity testing on animals [21]. For the detection of toxic gases, there are several analytical methods implemented such as FTIR linked to cone calorimeter, TG-MS, TG-FTIR and pyrolysis GC-MS [22, 23].

Purser's Fractional Effective Dose model was implemented to estimate toxic products level according to the equation 1 displayed below [24]. This model provides the data by dividing the concentration of single fire effluents to their fatality level and aims to deliver a sum of FED using hyperventilation factor [25]. Greater FED data results in higher toxicity level. According to the study, it was reported that, in a ventilated environment, 11 g Polyurethane foam or 8 g Polyisocyanureate foam produces 1 m^3 toxic air.

$$FED_{CO} = 3.317 \times 10^{-5}[CO]^{1.036}(V)(t)/D$$

Figure 2.11 : Equation of Purser´s Fractional Effective Dose model for carbon monoxide.

V: volume of air breathed each minute (L)

$LC_{50,X}$: exposure dose (percent COHb) for incapacitation

2.4.2 Smoke production contributing aspects in Polyurethane foams

Physical conditions and chemical structure of PU might impact the smoke formation during combustion. Overall, 4 categories can be associated to the smoke production of Polyurethane foams.

2.4.2.1 Chemical composition of polyurethane foam

As mentioned in previous sections, PU decomposition steps are highly dependent on the aromatic/aliphatic structures as well as longer/shorter chains in the polymer [26]. Polymeric structures such as poly (ether ketone)s, polyesters, as well as aromatic poly (ether imide)s and can greatly enhance thermal stability once they are deployed in rigid polyurethane foams [27-30]. Additionally, polyol backbones that are mofidied by phosphorus and/or nitrogen compounds can further contribute to a higher reaction to fire performance [31, 32].

Thermal dissociation of PU is governed not only by the type of polyol/isocyanate but also their functionality thanks to the resulting crosslinking density of Polyurethane foam. Higher functionality of said components lead more stable and strong networks and that resulting in less smoke generation once ignited [33, 34].

Another route to improve thermal stability of PU/PIR foams is to work with higher isocyanate index. Especially for PIR formulations, it is possible to work an index value between 180-400. One of the recent study showcases how smoke release of PIR foams improve when working with an index of 150 versus 250 results are confirmerd via TGA studies by indicating the increase of the char residues significantly (e.g. 17.4% to 25.1%) [33].

2.4.2.2 Conditions during combustion

Type of the material, the onset temperature of the ambient, and oxygen concentration are determinative parameters that influnce the concentration and composition of the gases and smoke during combustion. In the literature it can be found, how the change of cone calorimeter parameters impact dissociation rate of polymer chains such as heat flux. Output of cone calorimeter like total heat release (THR), total smoke production (TSP) as well as fire effluents concentrations display an increase with an increment in heat flux rate [35].

2.4.2.3 Size and density of specimen

Heat release rate (HRR) is greatly influenced by the thickness, surface area and density of the samples [36]. It was reported in several studies that an increment in the density and thickness is accompanied with the increment of the generated smoke, mainly occurred due to the less available oxygen in a limited area [37, 38].

2.4.2.4 Presence of combustion modifiers

In order to understand how combustion modifiers mechanism works, terminology of physical and chemical action should be introduced:

Physical action of combustion modifiers

There are 3 modes of physical action:

- Cooling: FRs that contain water of hydration in their structure, release their water during combustion which aids the temperature of substance to be dropped and creates a cooling effect. Some examples include Aluminium hydroxide, zinc borate etc [39].
- Formation of a protective layer: a solid or gaseous protective layer is generated by the FR, thus preventing the needed amount of oxygen to be included in the combustion (e.g. Phosphorus compounds) [39, 40].
- Dilution: Inert gases (e.g. water) introduced in the polymer by FRs, dilutes the fuel in the solid and gaseous phase (e.g. Aluminium hydroxide) [41].

Some hydrated compounds release water, which can dilute the concentration of toxic gases. Other additives hinder by interfering in the solid phase. Some additives enable a delay in the release of volatiles from the substrate and facilitate the formation of a compact char layer.

Chemical action of combustion modifiers

- Vapor/gas phase reaction: Interruption of radical mechanism of combustion is accompanied with the termination of exothermic reactions (e.g. halogenated flame retardants, phosphorus compounds) [42].
- Solid/condensed phase reaction: on the polymer surface a carbonaceous layer is generated (e.g. phosphorus compounds) [40].

Combustion modifiers may involve in different phases during burning of the polymers; during heating or decomposition, and so on. Smoke suppressants are usually those ones that are performing in solid phase [43, 44]. Ammonnium Polyphosphate is a good example of a condensed phase flame retardant [45].

Tris (1-chloro-2-propyl)phosphate (TCPP), Dimethyl methyl phosphonate (DMMP) are amongst the ones that are active in vapor phase. On the contrary of condensed phase reactions, these substances release active compounds that inhibit progression of the fire by coupling with OH* and H* which further results an increment of toxic fire effluents as well as smoke concentration [46-49].

Boron compounds have both a physical as well as a chemical action, depending on their type and synergim with other combustion modifiers [50]. Figure 2.12 expresses boron compounds fire reaction mechanism.

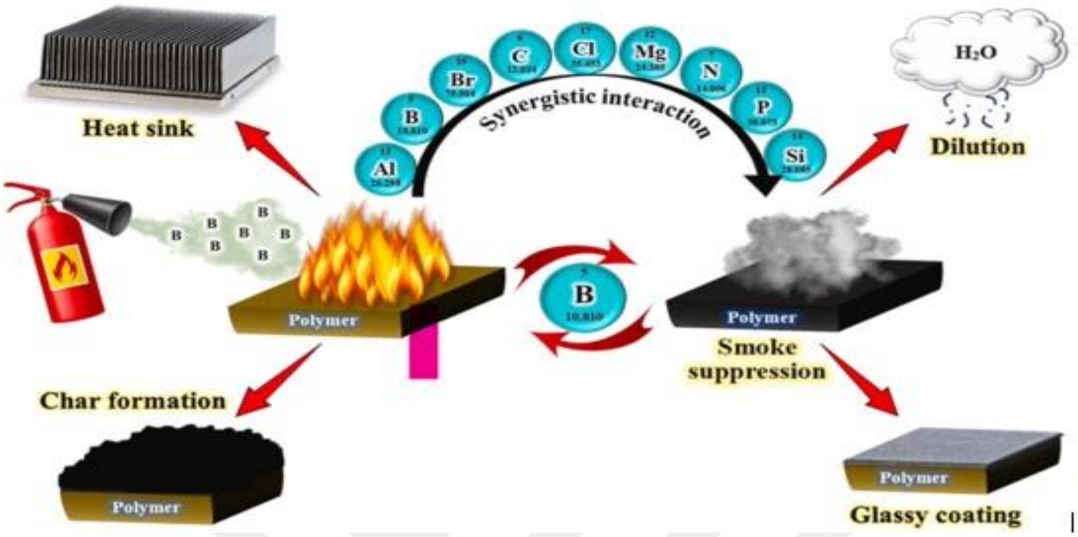


Figure 2.12 : Boron compounds fire reaction mechanism [50].

On the smoke suppressants side, chemical actions are derived from

- Friedel–Crafts reactions.
- Reductive coupling reactions
- Lewis acid effects,
- Lewis acid sites in metal compounds

These mechanisms help to formation of char on the substance as well as the reduction of toxic gases generation [4].

Smoke suppressants may include elements such as Cu, Fe and Zn as well as their derivatives. Some works done on incorporation of iron derivated substances (e.g. ferrite) was reported as a char forming compound and elevating activation energy of dissociation of the polymers [51, 52]. Furthermore, thermal decomposition can be altered by the addition of transition metals into the structure [53, 54].

Ferrocene and its derivatives have become popular due to their significant impact on the reduction of smoke density in various polymers by forming char on the surface [55-57]. Different studies on ferrocene derived substances confirmed the improvement of thermal stabilitisation (through increment in LOI and/or char formation) of polymers once incorporated [58-60]. Besides, it was proven that phosphoric acid and Ferrocene can establish networks that are able to contribute to char formation [61].

One of the interesting studies by Chen et. al report the comparison of smoke density performance between APP and FeOOH -another ferrous derived compound- in TPU composites. Addition of FeOOH at a rate of 3.75 wt% delivers a better luminous flux than 20% wt APP loading in the same formulation. Additionally, same folks also completed some works to showcase the synergistic impact between ferrous and phosphrous compounds. According to a study completed by Jiao et al. combining APP and ferrous powder created a synergic impact in a TPU formulation and provided a higher luminous flux [62].

It is possible to improve the reaction to fire properties of thermoplastic polyurethanes by the loading of metal salts – e.g. Fe_2O_3, ZnO, MgO - together with phosphorus compounds in the polymer matrix. The synergistic impact brought by these compounds are further assumed to generate char during combustion [63].

Some studies showed that, zinc containing compounds such as Zinc borate (ZB), $ZnFe_2O_4$ $ZnAl_2O_4$, and Zn_2SiO_4 in different polyurethane applications can suppress smoke through promoting char formation. Additionally, it was detected that the formation of toxic gases such as CO, and hydrogen cyanide was also reduced thanks to its condensed phase action [64].

From metal hydroxides family, Aluminium trihydrate (ATH) and magnesium hydroxide (MH) are well-recognized combustion modifiers [65]. Their mode of action is both physical and chemical, through cooling and diluting as well as a condensed phase reaction which aids reduction of smoke formation and heat release during combustion [66, 67].

Some of the examples from literature, proves the efficiency of ATH in polyurethane applications. Either alone (20 or 40 wt% of the polymer) or when used with DMMP, as well as with APP; ATH confirmed a significant decrease in smoke release and toxic gases emissions such as CO and CO_2 [68-70]. Nevertheless, in order to obtain such effective reaction to fire properties, high loadings are required which might greatly deteriorate final polymer’s mechanical properties [71].

In halogen-free CMs family, melamine derivaties take an important place including melamine phosphate, melamine oxalate, melamine cyanurate (MC) and so on [72].

Melamine can be used as an FR in various PU applications, mainly in flexible PU foams. Loading rate can be as high as 60% of the polymer. According to a study with such a quantity in flexible PUF, reported Total Smoke Rate (TSR) is 8 $m^2\ m^{-2}$, which is 10 times lower than the foam prepared without melamine [73].

Melamine cyanurate has physical and chemical mode of action during combustion process. During degradation, while generation of ammonia is providing the dilution in the fuel and decelerates fire propagation, the char constructed by melam, melem and melom formation, aids smoke suppression [74, 75].

Carbon based additives represent other important combustion modifiers family. Carbon nanotubes (CNTs) and Expandable graphite (EG) are the popular ones used as FR in PU applications [76]. EG is a typical intumescent FR that expands during combustion and forms a swollen char that prevents heat transfer between the material and combustion environment which also acts as a diluter of the fuel and reducer of smoke and toxic gases such as HCN and CO [45, 77]. Formation of cross-linked char results in depression of smoke [78] thanks to solid phase action mechanism [79, 80].

2.4.3 Reaction to fire performance methods in rigid Polyurethane foams

There are different methods to measure reaction to fire performance of rigid polyurethane foams. This may include LOI, cone calorimeter, NBS smoke chamber as well as UL-94 tests and so on.

In a study conducted by Linteris, impact of irradiance level, flame, specimen thickness and density are examined on the cone calorimeter test results. The density of the samples has a large influence on the intensity of combustion; it is also a factor that negatively affects smoke production [81].

In Europe, EN 13823 Standard sets 3 criteria according to Single Burning Item (SBI) test to measure the reaction to fire performance:

- Fire propagation, that is, contribution of the building element to the development of a fire
- Smoke opacity
- Dripping of parts of the building element during the test (flaming or non-flaming parts)

While dripping does not usually happen during testing of building elements made with rigid PU/PIR foams, smoke generation during combustion is the most important determinative parameter for the classification.

In the specific case of building elements classified according to the Euroclass standard, fire propagation is evaluated by means of combustion parameters during the SBI test (total heat released in a 10 min combustion experiment, rate of heat release, peak of heat release etc.). Based on these parameters, sandwich panels made of PIR foams can reach Euroclass “B”, while Euroclass “A” is impossible to obtain for organic materials as other tests have to be carried out (in particular, a calorimetric bomb test in which an average PIR material displays combustion values many times higher than maximum thresholds) in addition to the SBI test. Nonetheless, obtaining Euroclass B is a must for PIR panels (that is, a parameter to be maintained at all costs) and it is a non-obvious target for PU panels; consequently, evaluation of fire propagation is an important parameter to be evaluated throughout all developments.

2.5 Volatile Organic Compounds Emission Evaluation in Rigid Polyurethane Foam

Volatile organic compounds (VOC) are a group of chemical substances that are emitted from solids as well as liquids at room temperature. Generally, they are low molecular compounds. Depending on their chemistry, they might be hamful with regards to health, safety and environmental aspects.

In polyurethane applications, VOC is a well studied topic especially in flexible foams where products like mattresses or seatings are part of everyday lives so more stringent requirements and tests are already in place.

In rigid polyurethane foam applications instead, evaluation of VOC aspect is a recent development and started with the the introduction of AgBB scheme by The Committee for Health-related evaluation of Building Products. AgBB scheme is illustrated in Figure 2.13:

Figure 2.13 : AgBB scheme.

AgBB scheme sets test criteria for VOC emissions which is annually reviewed and edited. In June 2021, the last version was published.

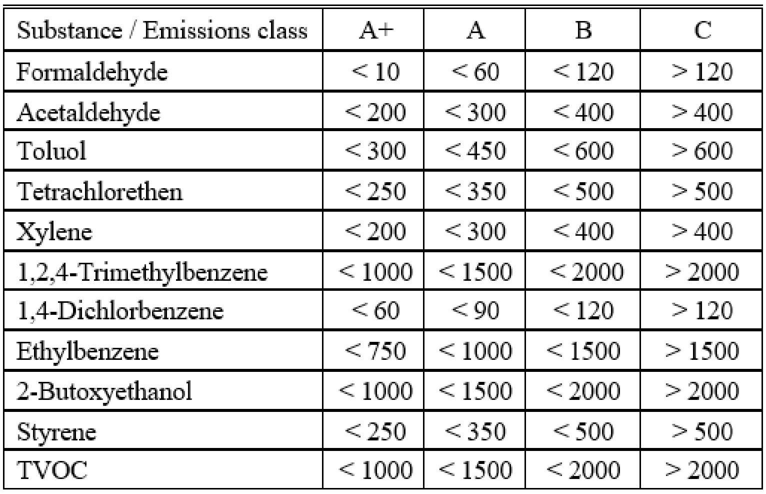
AgBB scheme introduces parameters such as TVOC, TSVOC and so on to establish the prerequisitions for building products compliance for indoor uses. Based on this scheme, German Institute for Structural Engineering developed the “Approval principles for health-evaluation of indoor construction products” in 2004. These are crucial for obtaining the U mark for certain products as part of the national technical approval.

For hazard prevention and health protection, Germany has implemented AgBB scheme context into the Model Administrative Regulation on Technical Building Regulations (MVV TB). Since 2017, indoor construction elements should be evaluated based on AgBB test criteria and validate its compliance.

AgBB scheme takes into account DIN EN 16516 in conjunction with the ISO 16000 series of standards, which are globally pioneering for construction products, and is thus based on national and international requirements. Therefore, products that meet the AgBB requirements are also recognized for use in international LEED building projects. AgBB tests can additionally be evaluated according to legal requirements (e.g. in France and/or Belgium) or for applying for voluntary test marks [84].

Reported in Table 2.3, the limit values of the emissions classes refer to the total of the VOC emissions and also to the evaluation of 10 single substances (in µg/m^3):

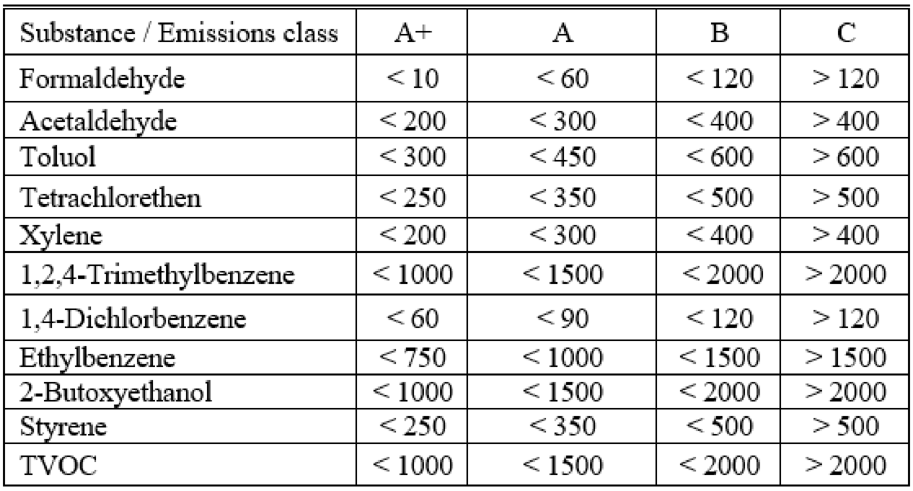
Table 2.3 : Limit values French A+ VOC Label [85].



Substance / Emissions class	A+	A	B	C
Formaldehyde	< 10	< 60	< 120	> 120
Acetaldehyde	< 200	< 300	< 400	> 400
Toluol	< 300	< 450	< 600	> 600
Tetrachlorethen	< 250	< 350	< 500	> 500
Xylene	< 200	< 300	< 400	> 400
1,2,4-Trimethylbenzene	< 1000	< 1500	< 2000	> 2000
1,4-Dichlorbenzene	< 60	< 90	< 120	> 120
Ethylbenzene	< 750	< 1000	< 1500	> 1500
2-Butoxyethanol	< 1000	< 1500	< 2000	> 2000
Styrene	< 250	< 350	< 500	> 500
TVOC	< 1000	< 1500	< 2000	> 2000

Table 2.4 displays overview European VOC emission limits for certain chemical substances after 28 days:

Table 2.4 : Overview European VOC emission limit values after 28 days [85].



Substance / Emissions class	A+	A	B	C
Formaldehyde	< 10	< 60	< 120	> 120
Acetaldehyde	< 200	< 300	< 400	> 400
Toluol	< 300	< 450	< 600	> 600
Tetrachlorethen	< 250	< 350	< 500	> 500
Xylene	< 200	< 300	< 400	> 400
1,2,4-Trimethylbenzene	< 1000	< 1500	< 2000	> 2000
1,4-Dichlorbenzene	< 60	< 90	< 120	> 120
Ethylbenzene	< 750	< 1000	< 1500	> 1500
2-Butoxyethanol	< 1000	< 1500	< 2000	> 2000
Styrene	< 250	< 350	< 500	> 500
TVOC	< 1000	< 1500	< 2000	> 2000

In this study, in order to reveal the emission performance of selected combustion modifiers in the system, Headspace Gas Chromotography Mass Spectrometry Analysis was used. In this way it was possible to measure the amount of VOCs generated by the rigid polyurethane foam under pre-determined conditions. It was confirmed that not only low molecular liquid compounds such as triethyl phosphate can migrate from the end product; but also substances such as Ferrocene as well as n-pentane can diffuse out from the products during its life cycle.

2.6 Hypothesis

In this study, commercially available and halogen free combustion modifiers were examined in a reference rigid PUR and PIR formulation. Hypothesis is that combining halogen free fire retardants with inorganic smoke suppressants in both systems would provide a same or better performance than the original systems in terms of reaction to fire and emission performance.

Analysis showed that, in order to meet a certain performance for PUR foams (DIN 4102 B2 small flame height), very high loading of halogen free combustion modifiers is necessary; which leads to dimensionally instable foams with poor mechanical properties.

For PIR foams, 2 routes were chosen to confirm the research hypothesis:

- The combination of Zinc borate (ZB) and phosphorous/non-phosphorous flame retardants in PIR formulations

- The combination of Ferrocene (Fc) and phosphorous/non-phosphorous flame retardants

Analysis showed that an improvement in fire and smoke aspects is possible through the synergism between ZB and Triethyl phosphate (TEP) as well as with TEP/Oligomeric TEP/ZB combination. While the use of oligomeric TEP in junction with ZB allowed the reduction of VOCs, it was proven that the presence of monomeric TEP makes the difference in terms of fire performance; consequently, its elimination from the PIR formulations was not possible, yet a reduction (of about ~55%) was demonstrated.

Differently from ZB, when used at elevated amounts, foams incorporating ferrocene can become highly flammable. On the other side, with the condition of a use of limited amount, ferrocene can be an alternative to ZB in terms of smoke suppression: it catalyzes soot decomposition, as reported in literature [82]. Ferrocene was also reported to show, potentially, synergistics effects [83].

As an outcome of cone calorimeter analysis, the foam containing Fc and TEP combination, peak heat release rate (PHRR) value is reduced significantly with respect to foam containing TEP as a sole FR; however, the sublimation of Fc resulted in poor VOC performance in PIR foam.

The preferred route for the reduction of VOC´s is was the incorporation of reactive FRs in the system. This is due to the ability of chemically bonding of the Combustion Modifiers and thus elimination of the diffusion from the end material. However, the reactive type of FRs examined in the study such as diethyl hydroxymethylphosphonate (DEHP - Levagard® 2100) did not perform as good as Triethyl Phosphate or oligomeric triethyl phosphate with regards to reaction to fire performance when added at the same P% amount. It was found that reactive FRs like DEHP, caused to increase free rise density of the foam, so either the quantity incorporated in the formulated polyol or formulation type should be reviewed.

Aligned with the research objectives, one formulation confirmed the research hypothesis in both reaction to fire and emission aspects, that is the combination of Triethyl phosphate-oligomeric triethyl phosphate-Zinc borate. Using this combination, it was possible to reduce the VOC emission caused by triehyl phosphate and at the same time, provide a more thermally stable-advanced fire performance ir rigid polyisocyanurate foams.

3. EXPERIMENTAL

In the experimental part; raw materials, characterization methods and preparation of PUR/PIR foams will be introduced briefly.

3.1 Raw Materials

Raw materials are displayed in Table 3.1 and Table 3.2 accordingly with either being a rigid polyurethane foam main component or a combustion modifier that is used to enhance reaction to fire properties of the PUR/PIR foam.

Table 3.1 : Main components in rigid polyurethane formulations.

Polyol	Polyether polyol (OH nr: 300) (Dow Chemical)
VORANATE™ M600 ISOCYANATE	Polymeric MDI, f:2.7 (Dow Chemical)
n-pentane	Blowing agent (Univar)

Table 3.2 : Combustion modifiers.

TCPP	Trischloro isopropyl phosphate (Lanxess)
TEP	Triethyl phosphate (Lanxess)
ATH	Aluminium trihydroxide (Sigma Aldrich)
Sodium Tetraborate Decahydrate	Sodium Tetraborate Decahydrate (Sigma Aldrich)
Ammonium Pentaborate Tetrahydrate	Ammonium Pentaborate Tetrahydrate (Borax)
Boric Acid	Boric Acid (Borax)
Dimethyl Adipate	Dimethyl Adipate (Millipore Sigma)
DEEP	Diethyl ethyl phosphonate (Sigma Aldrich)
Levagard® 2000	Oligomeric TEP (Lanxess)
DO11	9,10-Dihydro-9-Oxy-10-Phosphaphenanthrene-10-Oxide (Metadynea)
Levagard® 2100	Diethylhydroxymethyl phosphonate (Lanxess)
Exolit OP550	Polyol with OH nr 370 (Clariant)
Hexion TL 91-805D	Polyol with OH nr 460 (Hexion Inc)
Fyrol PNX	Alkylphosphate Oligomer (ICL)
Ferrocene	Ferrocene (Sigma-Aldrich)
RDP	Resorcinol bis(diphenyl phosphate) (ICL)
FirFirebrake ZB $2ZnO.3B_2O_3.3.5H_2O$	Zinc borate (Borax)
APP	Ammonium Polyphosphate (Lanxess)

3.1.1 Combustion modifiers

Combustion modifiers will be presented in 2 class; flame retardants and smoke suppressants. Flame retardants decelerate or delay the combustion action, whereas smoke suppressants aid in suppressing or lowering the generation of smoke and harmful substances. In this work, while a broad variety of flame retardants were studied, only 2 smoke suppressants were in scope: Zinc borate and Ferrocene, which will be presented in details in the coming part.

3.1.1.1 Flame retardants

Tris (1-Chloro-2 Propyl) phosphate

TCPP, being a chlorinated alkyl phosphate ester, provides excellent reaction to fire performance thus finds a wide use in different polyurethane applications. However, TCPP is toxic and can migrate from the matrix in which it is embedded hence can create EH&S issues. TCPP structure is displayed in Figure 3.1:

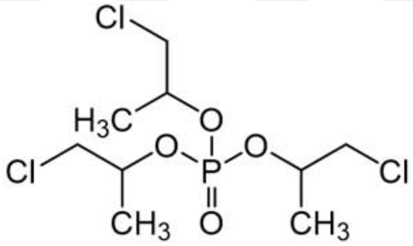


Figure 3.1 : Chemical structure of TCPP.

Triethyl phosphate

Likewise TCPP, TEP is a non-reactive type of flame retardant. TEP started to draw more attention as the next best alternative of TCPP. Besides being an efficent and non-halogenated FR, it is also used as a viscosity cutter in PU industry. It contains 17% of P in the sructure and has a viscosity of 1.4 mPa.s @25 °C. Biggest drawback about TEP is being monomeric, thus prone to create emission issues when tested its VOC performance. Figure 3.2 represents chemical structure of TEP:

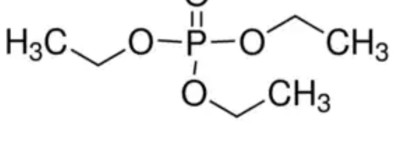


Figure 3.2 : Chemical structure of TEP.

Aluminium trihydroxide

ATH is a non-halogenated white powder flame retardant with a melting point around 220 °C. ATH structure is reported in Figure 3.3:

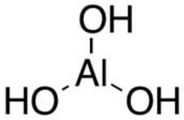


Figure 3.3 : Chemical structure of ATH.

Sodium tetraborate decahydrate

Sodium tetraborate decahydrate, also known as Borax, is a white solid which contains crystalliyation water. It contains Boron atoms as an active flame retardant component and has a melting point of 743 °C. Borax configuration is shown as in Figure 3.4:

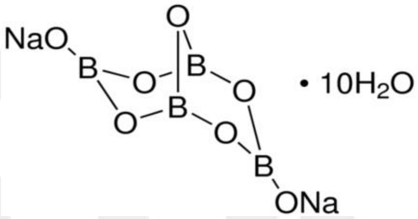


Figure 3.4 : Chemical structure of Borax.

Ammonium pentaborate tetrahydrate

APT is a white powder with a melting point of 110 °C. It has Boron and Nitrogen atoms in the structure that contribute to flame retardancy of the materials in which it is inserted. Figure 3.5 illustrates chemical structure of APT:

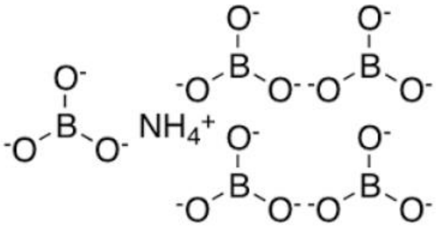


Figure 3.5 : Chemical structure of APT.

Boric acid

Boric acid, a white powder which is called as borate, is donated as H_3BO_3. One of the reasons for its popularity of use as a flame retardant can be associated to the content of the water of hydration in the structure. Its melting point is around 170 °C. Chemical structure of boric acid is shown in Figure 3.6:

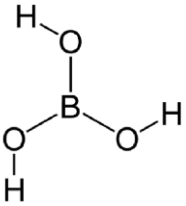


Figure 3.6 : Chemical structure of boric acid.

Dimethyl adipate

A low viscous (2.5 mPa.s), colourless liquid that is used to reduce smoke generation in polymers. Figure 3.7 displays the structure of dimethyl adipate:

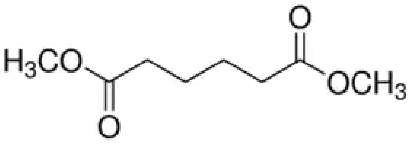


Figure 3.7 : Chemical structure of dimethyl adipate.

Diethyl ethylphosphonate

A yellowish liquid that is mainly used as a chemical weapon precursor. DEEP often finds use as a combustion modifier due to its high P% (18.6) content. Structure of DEEP is reported in Figure 3.8:

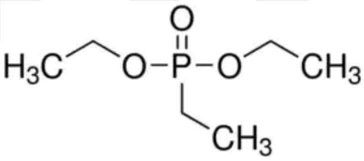


Figure 3.8 : Chemical structure of DEEP.

Levagard® 2000 (oligomeric triethyl phosphate)

Levagard® 2000 is a recently patented oligomeric TEP by Lanxess. It has a viscosity of 100 mPa.s and a P content of 16.4%. Monomeric TEP in the substance is reported to be between 1-10%.

Hypothesized oligomeric TEP structure is displayed as in Figure 3.9.

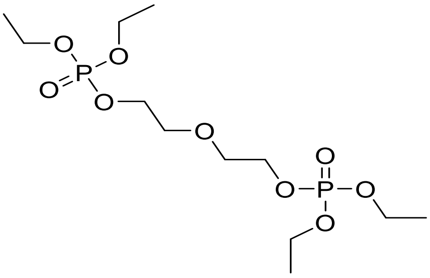


Figure 3.9 : Hypothesized chemical structure of oligomeric TEP.

DO11 (9,10–Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide), DOPO

DO11; a white solid, which often referred as DOPO; illustrated with a chemical formula of $C_{12}H_9O_2P$ and a P% content of 14.3%. Its melting point is approximately about 250 °C. Chemical structure of DOPO can be seen in Figure 3.10:

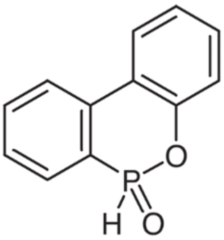


Figure 3.10 : Chemical structure of DO11.

Levagard® 2100, Veriquel™R₁₀₀ (Diethyl hydroxymethyl phosphonate)

DEHP is a reactive, high phosphorus (18.4%) content substance which finds use in rigid PU and PIR applications. Figure 3.11 indicates the structure of DEHP:

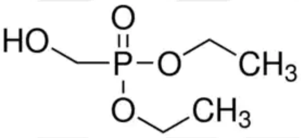


Figure 3.11 : Chemical structure of DEHP.

Exolit OP550 $CH_5O_3P·(C_2H_4O)n·(C_2H_4O)n$ polyol

Exolit OP550 is one of the reactive and non-halogenated polyol grades in Clariant´s portfolio which was developed specifically for polyurethane applications. It has P content of 17%. Chemical structure of Exolit OP550 polyol is shared in Figure 3.12:

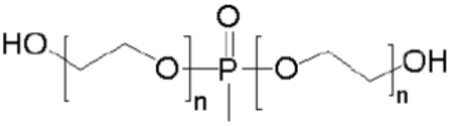


Figure 3.12 : Chemical structure of Exolit OP550 polyol.

Hexion TL 91-805D polyol

An alkoxylated triazine – arylhydroxy – aldehyde condensate compound that is recently introduced by Hexion Inc in 2019. An example of a patented non-phosphorous polyol structure can be seen in Figure 3.13:

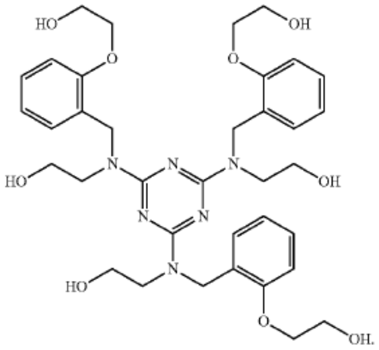


Figure 3.13 : Chemical structure of Hexion TL 91-805D polyol.

Fyrol PNX Oligomeric ethyl ethylene phosphate ($C_6H_{15}O_4P \cdot C_2H_4O \cdot O_5P_2$)n

Weight loss (decomposition) of PNX starts at 185 °C, which is at the limit of use for polyurethane applications as during the polymerization, the temperature of the foam core might exceed this value. It has a P content of 19%. A simple illustration of Fyrol PNX is reported in Figure 3.14:

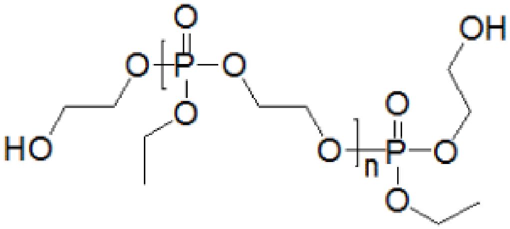


Figure 3.14 : Chemical structure of Fyrol PNX.

Resorcinol bis (diphenyl phosphate) ($C_{30}H_{24}O_8P_2$)

RDP is an aromatic phosphate flame retardant which is widely used in electric and electronic equipment. A 10.7% of P is present in its structure. RDP structure can be seen in Figure 3.15:

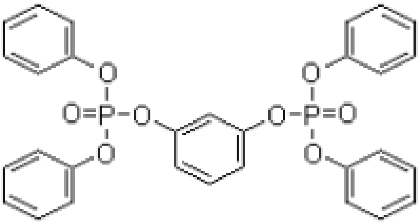


Figure 3.15 : Chemical structure of RDP.

Ammonium polyphosphate (NH_4PO_3)

APP is an inorganic salt of polyphosphoric acid and ammonia containing both chains and possibly branching.

The properties of APP depend on the polymerization degree; which is the rate of the repeatinf monomeric unit. In case, the number of repeating monomer -n < 100, despites the increment in solubility, a higher degree of unstability towards water and heat is expected. It is a P rich substance with a P conten of 30%. Figure 3.16 proposes APP structure:

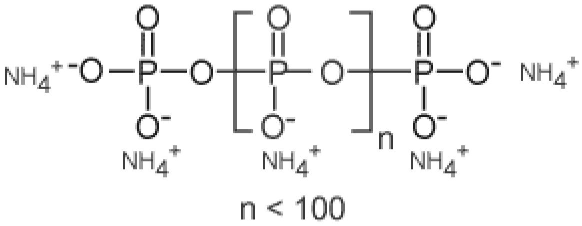


Figure 3.16 : Chemical structure of APP.

3.1.1.2 Smoke suppressants

Ferrocene

Ferrocene is an organometallic compound with the formula $Fe(C_5H_5)_2$. The molecule is a complex consisting of two cyclopentadienyl rings bound to a central iron atom in oxidation state (II). It is an orange solid that sublimes above room temperature, melts around 172 °C and is soluble in most organic solvents. It has an excellent stability towards bases, water, air and heat with a decomposition temperature as high as 400 °C. Basic illustration of Fc is shared in Figure 3.17:

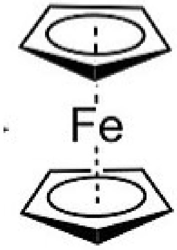


Figure 3.17 : Chemical structure of Ferrocene.

Firebrake Zinc Borate ($2ZnO.3B_2O_3.3.5H_2O$)

Zinc borate, an important member of borate family, is exceptionally versatile with regards to its use; that includes paint industry, flame retardant and anti-corrosion technologies etc. While its reaction to fire efficiency was confirmed for different polymers, in PU technology, its use is rather limited.

Conformotional array of Zinc borate depends on the coordination between oxygen and boron atoms e.g. BO_3 or BO_4; which results in different molecules as well as different degree of polymerization; from monomeric to polymeric. It has a melting point around 290 ℃.

While it is possible to synthesize different type of Zinc borate, 2 types of commercially available Zinc borate are in used for polymer applications. Zinc borate 500 is a non-hydrous FR that is commonly used where high processing temperature is required. Firebrake ZB instead contains crytallization of water and selected when this charateristics is desired. Figure 3.18 reports the configuration of Zinc borate:

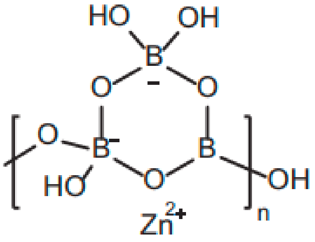


Figure 3.18 : Configuration of Zinc borate.

3.2 Characterisation Methods

Table 3.3 displays characterisation types and methods used in the study.

Table 3.3 : Characterisation methods used in the study.

Reaction to fire	DIN 4102 Small Scale Flame Test
Reaction to fire	UL-94 Horizontal burning test
Reaction to fire	NBS Smoke Chamber
Reaction to fire	Cone Calorimeter
Reactivity	Foamat
Reactivity	Reactivity check by handmix
Morphology	Scanning Electron Microscope (SEM)
Morphology	Open Cell Content (OC)
Thermal	Dynamic Mechanic Analyzer (DMA)
Thermal	Thermo Gravimetric Analyzer (TGA)
Emission	HS-GC-MS

3.2.1 Reaction to fire measurements

Reaction to fire methods cover different aspects of combustion on which is used to measure the affinity of a material once ignited. The most common aspects are flame spread and smoke opacity; however, there are also a number of other outputs such as Heat Release Rate, Total Combustion time, Total Smoke Production Rate, Peak Heat Release, Time to Ignition etc. As previously cited, the most importand reaction to fire standard regarding the evaluation of building elements is EN 13823 which sets criteria according to SBI test. This test asseses fire, smoke and dripping properties of th analyzed materials. Accordingly, in this chapter, these devices will be associated whether they assess smoke or flame spread properties.

3.2.1.1 Flame spread measurement

Measuring flame spread for rigid polyurethane/Polyisocyanurate foams is carried out either using a DIN 4102 small scale flame istrument or UL-94 testing. In this study, preferred method is DIN 4102 device.

DIN 4102 small scale flame test

This test is executed on the foam samples in vertical position. The sample has dimensions of (2.5x10x19) cm. Flame is applied to the front bottom of foam samples, inclined at 45℃ for 15 seconds and this operation is repeated 3 times for the same formulation/sample. There are 2 categories to determine the performance: B2 or B3. B2 performance criteria is met if during and after the combustion of the sample, the tip of the flame height does not exceed 150 mm. In all other situations, materials are classified as B3.

DIN 4102 testing is not a separate standard but it is a prerequisition of having a better fire retardancy classification in Single Burning Item (SBI) test which is explained in EN 13823 Standard. DIN 4102 is used to measure the flame spread properties of foam during combustion. Figure 3.19 illustrates the cross section of DIN 4102 equipment:

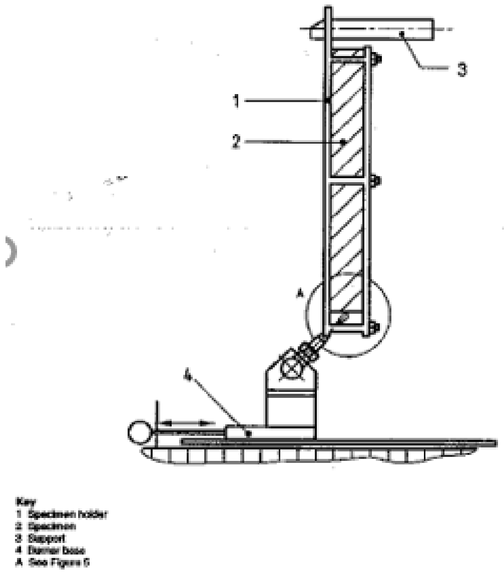


Figure 3.19 : Cross section of DIN 4102 equipment.

UL-94 Horizontal burning test

UL 94 is a horizontal burning (HB) fire hazard testing used for plastic materials. There is a burner and flame is applied on the tip of the polyurethane foams specimens until it reached the 25 mm mark. Prepared RPUF samples have a dimension of (125 X 13 X 3) mm. This test was selected for the first experimentals to obtain a ranking through HB evaluation to assess the fire propagation risk as well as the phenomena of glowing and flaming drip advantages over other fire tests. The burning time was measured and indicated as (Ts). Specimens were classified as HB if the flame propagation terminated within 10 seconds after the ignition. UL-94 horizontal burning test example can be seen in Figure 3.20:

Figure 3.20 : UL-94 horizontal burning test.

3.2.1.2 Smoke rate and opacity measurement

Smoke opacity is the masure of the rate of the smoke that is generated during the combustion. In Single Burning Item test, in cone calorimeter as well as smoke chamber devices, main target is to measure the smoke density in a certain time and determining the materials performance using the reference values.

In this study, preferred methods are NBS smoke chamber and cone calorimeter, respectively. Cone calorimeter assesses other important parameters such as Total Heat Release and Peak Heat Release Rate. These properties will be mentioned under cone calorimeter heading.

NBS Smoke Chamber

Smoke density or smoke opacity is the complementary parameter to determine the smoke performance of the rigid Polyurethane/Polyisocyanurate foams. It is measured via ASTM E 662 as an absorbance (Ds), that is, a quantity proportional through a geometric factor dependent on the combustion cabinet to the amount Log (100/T), where T is the transmittance of the generated smoke; the absorbance is defined as dimensionless.

The main principle of NBS is to screen the smoke density measurement in time intervals during a combustion experiment of the sample being ignited by a 25 kW vertical furnace and six small flames touching the sample.this combustion experiment lasts for 10 minutes. A reduced value of maximum absorbance during the test (DsMax) indicates that clear smokes are produced by the combustion or that amount of smoke is anyway generated. Sample dimension is reported to be as (75x75x25) mm. A model of NBS smoke chamber can be seen in Figure 3.21:

Figure 3.21 : NBS smoke chamber.

Cone calorimeter

Cone calorimeter is the most commonly used bench-scale device to measure the fire reaction of solid materials. The instrument can provide a rich database regarding fire behaviour of materials under controlled levels of radiant heat from a cone heater. The operation and testing procedure can be followed using ASTM E1354 and ISO DIS 5660 standards.

Testing is done on a specimen with dimensions of (100x100x50)mm that is mounted under cone heater. The radiant heat is applied to stimulate the fire conditions. Figure 3.22 represents a basic scheme of a cone calorimeter.

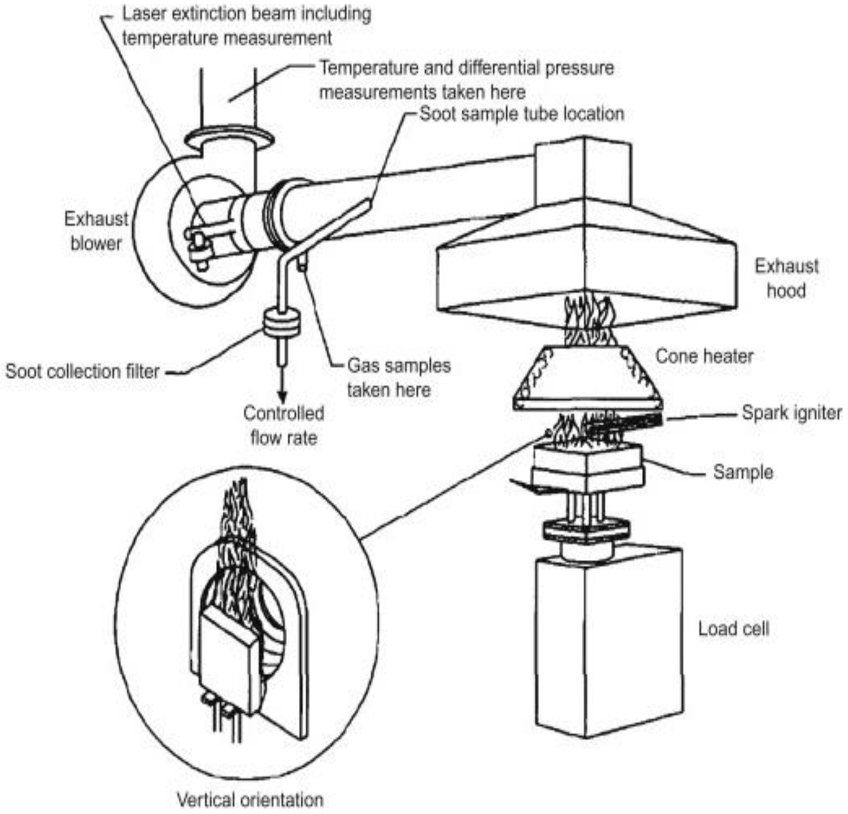


Figure 3.22 : Scheme of a cone calorimeter.

Different parameters as well as the composition of combustion gases can be determined through cone calorimeter. In order to detect thegases that are occured during the process, an IR is connected to cone calorimeter.

Most important outputs from this analysis are heat release rate (HRR) and smoke production rate (SPR). HRR is governed by various combustion processes. Release of a more amount of hydrocarbon volatiles indicate a higher HRR.

In order to describe heat release rate of a material, several parameters are used. Peak HRR describes the maximum release rate of heat during the combustion process and is an important measure of the maximum flammability and flashover potential of a material.

Heat Release Rate is the principal parameter that is impacting fire progress. It leads the link to mass loss rate and gas yields. As in Limiting Oxygen Index (LOI) analysis, oxygen consumption of the specimen during combustion is used to deliver heat release rate and total heat release parameters. For the generation of a 13.1x10^3 kJ of heat, 1 kg of oxygen is consumed.

Table 3.4 displays the cone calorimeter settings that were applied to the testing of 11 polyurethane/polyisocyanurate foams.

Table 3.4 : Cone calorimeter settings.

Parameters	**Unit**	**Value**
Thickness of the foams	mm	50
Specimen surface area	cm^2	88.4
Orifice flow rate calibration		0.042-0.0437
Heat flux	kW/m^2	50
Exhaust system flow rate	m^3/s	0.024
Test end time	s	600

3.2.2 Reactivity measurements

Reactivity (cream time, gel time), temperature of the foam core and other properties during the polymerization of PUR/PIR foams can be measured both by electronic devices as well as by hand-mix activities. In this study, both methods were used.

3.2.2.1 Reactivity measurement by Foamat

Foamat is an instrument which aids determination of reactivity profile, reaction temperature, and pressure, weight loss as well as the viscosity changes during polymerization reaction of a free rise foam in a cylindrical container in the desired time. An ultrasonic fan-sensor addresses the changes in the parameters. Thanks to a software, results are transmitted to databse and displayed on local computers. Foamat example is shared in Figure 3.23:

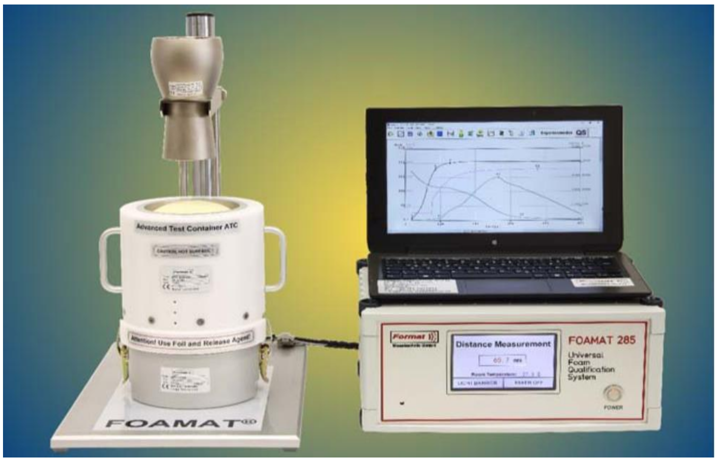


Figure 3.23 : Foamat.

3.2.2.2 Reactivity measurement by hand-mix activities

In PU industry, the most common method to measure the reactivity of the formulations is hand-mix activity. This is a conventional and practical method that is applied to rigid and flexible foams. Terminology covers two main parameters including cream time and gel time.

Cream time (CT) denotes the instant of the beginning of polymerization activity, that is accompanied by an increment in the viscosity of reactive mixture.

Gel time (GT) indicates the termination of polymerization of reactive mixture where the rise of the foam is almost completed. Both cream time and gel time is expressed in seconds.

Cream time and gel time are important performance parameters that determine process conditions. Another terminology that is often used with these parameters is the free rise density denoted as g/L or kg/m^3.

Free rise density is the main characteristics of the processing technologies in which the foam is produced as most of the properties are governed by the density of the material.

3.2.3 Morphology measurements

Morphology of the cells in PU foams play an important role to determining the final properties such as thermal insulation, dimensional stability as well as reaction to fire properties. While SEM and TEM are the chosen methods for displaying the shape of the cells, open cell content measurement is another technique for validation of the % of the open/closed cells present in the structure.

3.2.3.1 Morphology assessment by scanning electron microscope

SEM is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample. The electron beam is scanned in a certain pattern, and the position of the beam is combined with the intensity of the derected signal to produce an image. In the most common SEM mode, secondary electrons emitted by atoms excited by the electron beam are detected using a secondary electron detector.

A SEM instrument provides detailed images of the surfaces of cells, particle signal counting and size determination. In this study, foam particles were first coated with gold and then exposed to analysis. Figure 3.24 represents the set up of a scanning electron microscope:

Figure 3.24 : Scanning electron microscope.

3.2.3.2 Morphology assessment by open cell content

Cellular plastics, composed of membranes or wall of polymer separating small cavities or cells, can be classified as open cell or closed cell materials. Rigid PU/PIR foams can contain an open cell content of up to 20%. ASTM D6226-21 test method determines numerical values for open cells. It is a porosity determination, measuring the accesible cellular volume of a material. The remaining volume that is occupied by closed cells and cell walls.

3.2.4 Thermal analysis

Thermal analysis is useful to measure thermal stability of a material under different flows (e.g. nitrogen, air, oxygen) which provides information on the material composition and characteristics, glass transition and melting temperature, stress-strain properties and so on. Typically, a small piece of substance is placed into the loading cell and exposed to heating under chosen flow. Temperature range can be set from 0 to as high as 800 ℃. Sequence can be set accordingly. Most common methods are Thermo Gravimetric Analyzer (TGA), Differential Scanninc Calorimetry (DSC) and Dynamic Mechanical Analysis (DMA).

3.2.4.1 Thermal analysis by thermo gravimetric analyzer

Thermogravimetric analyzers measure changes in mass or weight in response to increases in temperature or time. This measurement provides data on the thermal stability of a material, response to oxidation, composition, decomposition kinetics, moisture content and more.

Analysis can be carried out by changing;

- Temperature resolution
- Temperature range
- Gas flow (oxygen, air or nitrogen)

In figure 3.25, a laboratory scla TGA is illustrated:

Figure 3.25 : Thermo Gravimetric Analyzer.

In this study, all TGA experiments were carried out under the air flow. Sequence was set as 10 ℃/min from room temperature up to 700 ℃.

3.2.4.2 Thermal analysis by dynamic mechanic analyzer

Dynamic mechanic analyzer measures the mechanical properties of materials as a function of time, temperature and frequency, In addition to basic material properties, DMA also quantigies finished part characteristics, reflecting the important contribution that processing has on end-use performance. DMA is commonly used to measure glass transition temperatures and secondary transitions, orientation caused by processing, cold crystallization, cure optimization, filler effects in composites and much more. DMA provides an accurate measure of material stiffness (modulus) but also other important mechanical properties such as damping, creep and stres relaxation. Figure 3.26 shows a basic type of DMA:

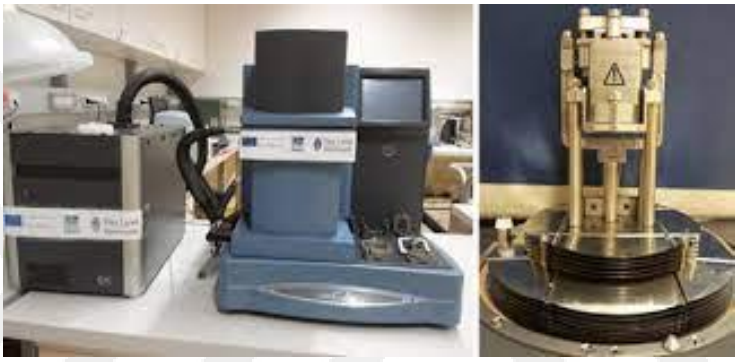


Figure 3.26 : Dynamic Machanical Analyzer.

In this study, all TGA experiments were carried out under the air flow. Sequence was set as 10 ℃/min from room temperature up to 700 ℃.

3.2.5 Emission analysis by Headspace gas chromotograpy mass spectrometry

Headspace gas chromotography mass spectrometry (HS-GC-MS) is a sample preparation method for determining volatile compounds in solid and liquid samples. The techniques is being used since 1950´s. With this technique, only the gas phase above the sample is introduced into the Gas Chromotography (GC) column. Head Space analysis is a simple and a clean method for introduction of volatile analytes into a gas chromatograph. Principle of the static headspace sampling technique is shown in Figure 3.27:

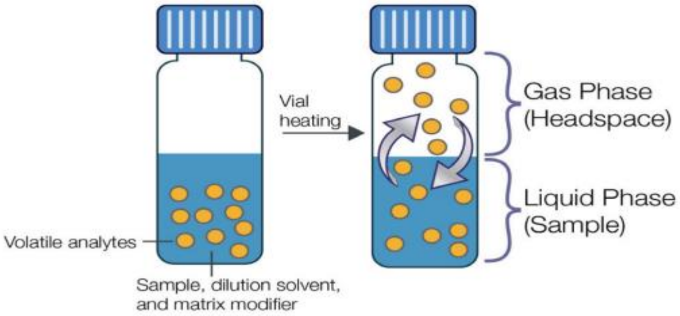


Figure 3.27 : Principle of the static headspace sampling technique.

For quantitative estimation of the TEP amounts, an external calibration was performed with a TEP standard. Calibration solutions were prepared in DMSO and 10 µl of this solution was added in a 20-ml headspace vial and analyzed by HS-GC-MS with the same conditions as used above.

4 foam samples were analyzed by means of HS-GC-MS after incubation at 150°C for 15 min, in duplicate.

A small piece of foams of approximately 0.02 g of sample was put into a 20 ml Perkin Elmer Headspace vial and closed with an aluminum crimp cap, containing a PTFE/silicone coated septa. To the closed vial, 100 µl of an internal standard solution of perdeuteriotoluene in air, containing 2 µg toluene-d8 was added.

3.3 Preparation of Rigid Polyurethane/Polyisocyanurate Foams

Different techniques exist to produce rigid PUR/PIR foams. In the industry, rigid foams can be made through different processes and lay outs including continuous and discontinous processes. In discontious process, the method is to fill the mold with certain dimensions under pre-determined conditions (flow of reactive PU mixture, mold temperature etc). Free rise foams, instead, are produced for informative pruposes; reactive mixture is poured into a plastic bag to determine the free rise density of the foams.

In this study, experimentals were concluded at a laboratory scale; free rise foams were produced into a wooden box of (20x20x25) cm and molded foams were produced in (20x20x20) cm molds.

3.3.1 Free rise foam preparation

During the studies foams were prepared using one shot process. Formulated polyol blend was prepared in an 1200 mL plastic cup, including catalysts, silicone surfactants and water but excluding combustion modifiers and blowing agent from reference system.

On top of polyol mix, each time, either one type or a combination of different CMs was incorporated physically and mixed immediately by means of a Heidolph stirrer operating at 3000 rpm. In total; always 34.64 gr of one Combustion modifier or a combination of different combustion modifiers wass added to the polyol blend. This CM package always include either Zinc borate or Ferrocene as a smoke suppressant and might contain up to 2 different flame retardants. Table 3.5 – Table 3.6 represent how the formulations are made.

Table 3.5 : Formulations made with Zinc borate by grams of weight.

Components	One CM addition	2 CM addition	3 CM addition
Polyol	96.00	96.00	96.00
n-pentane	12.85	12.85	12.85
CM-1	34.64	20.27	10.00
CM-2	-	-	10.27
Zinc borate	-	14.67	14.67
Sum	144	144	144

The same type of preparation was also applied to Ferrocene containing formulations as in Table 3.6:

Table 3.6 : Formulations made with Ferrocene by grams of weight.

Components	2 CM addition	3 CM addition
Polyol	96	96
n-pentane	12.85	12.85
CM-1	20.27	10
CM-2		10.27
Fc	4	4
Sum	134	134

In the experimental part, formulations are primarily characterized according to their chemistry; being a rigid polyurethane or polyisocyanurate foam.

In rigid PUR foam part, firstly synthesized chemicals were incorporated into the system. Name of the specimens were coded as F1-F26 for 26 formulations.

For the formulations reported in PUR part 4.1.2, either one or two type of commercially available conventional and novel combustion modifiers were inserted in the system. All the formulations were named with a number after the word ´PUR´. In total, 16 formulations were tested.

In rigid PIR foam part, a series of different combinations were tried. The prepared formulations using this method are denoted with a certain coding system. When one type of combustion modifier is used in the formulation, the donation is displayed with 1 after the word ´PIR´ such as PIR1.1. The second number instead, denotes the number of the experimental. If there is one reactive combustion modifer in the system, then ´R´ letter was inserted between the number of component and number of experimental such as PIR2R2. Table 3.7 summarizes the coding system and number of formulations.

Table 3.7 : Formulations nomenclature.

	PUR Formulations	PIR Formulations				
		One CM addition	1 non-reactive + 1 reactive CM combination	2 non reactive CM combination	3 non-reactive CM combination	2 non-reactive + 1 reactive CM combination
Nomenclature	F1-F26 PUR1.1 - PUR1.16	PIR1.1 - PIR1.4	PIR2R1 – PIR2R2	PIR2.1 - PIR2.18	PIR3.1 – PIR3.7	PIR3R1 – PIR3R8
Number of formulations	42	4	2	18	7	8

Two or three combustion modifiers combinations always contain Zinc borate or Ferrocene in the structure. The rest of the CMs are flame retardants; can be reactive or non-reactive, phosphorus based or not. If there is one reactive FR in the formulation, nomenclature always include a letter ´R´. In other cases, no letter was included after numbers. Chosen FRs are: TEP, APP, DO11, OTEP, Levagard 2100, Hexion TL 91-805D, Exolit OP 550, Fyrol PNX and Fyrol RDP. Detailed formulations can be found in the experimental part.

After the incorporation of CMs into polyol (component A), blowing agent n-pentane was added and mixed. On top of this mixture, 202 gram Polymeric MDI (component B) was added and stirred for 5 seconds.

Before the beginnning of the foam rise, reactive mixture was poured into a wooden box to obtain a cubic sample of (20x20x25) cm. Figure 3.28 draws the preparation of the free rise foams by handmix:

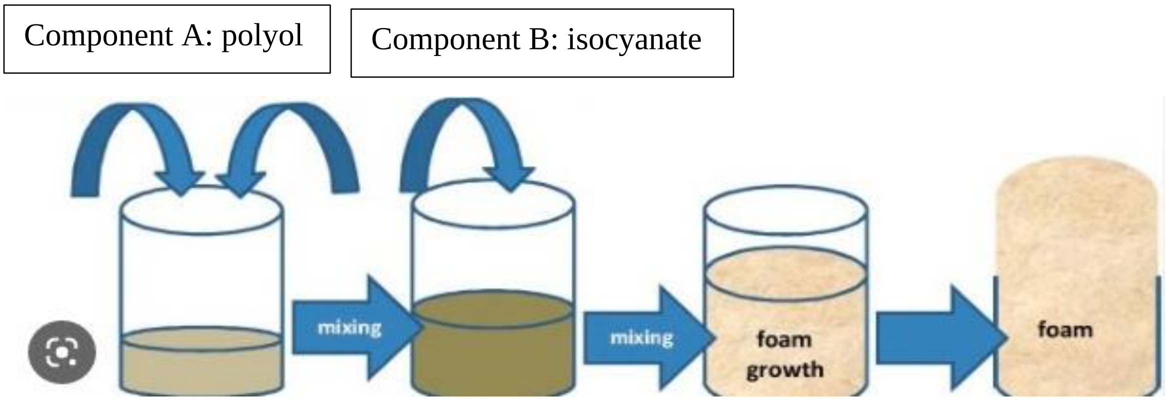


Figure 3.28 : Preparation of the free rise foams by handmix.

Foam reactivity was checked by hand-mix. Free rise density of each foam was measured, which is an indication of the results interaction of diverse CM in the selected system.

3.3.2 Molded foam preparation

Molded foam samples were preped exclusively for cone calorimeter analysis, in order to eliminate deviations occurring in P% and density of different formulations. While polyol blend preparation steps were identical, there were some differences with regards to the amount of ingredients unlikely in free rise foam preparation.

2 preliminary studies were conducted pior to starting preparation of the polyol blend for each formulation:

- Equalizing molded density of the selected formulations
- Equalizing total P% content in the foams

In order to determine the reduction in the free rise density through the addition of 1 g of extra blowing agent – (n-pentane), an exercise was carried out in the selected reference formulation that contains only TEP as a CM in Figure 3.29:

	Mod1
Polyol blend	96
n-Pentane	12.85
TEP	34.64
PMDI	202
FRD (kg/m³)	32.7

	Mod1 rev.
Polyol blend	96
n-Pentane	13.85
TEP	34.64
PMDI	202
FRD (kg/m³)	31.3

Figure 3.29 : -n-pentane modification on the reference Mod1 formula.

1g of n-pentane addition leads approximately 1.35 kg/m^3 reduction in the FRD of the reference foam.

This information is used for the preparation of similar density foams in the molding process. When density reduction was needed in the PIR foam, more blowing agent n-pentane was added to the system.

For what it concerns to the P% adjustment of the final foam, 3 variables were taken into consideration:

- ❖ Quantity of total blowing agent present in the final foam
- ❖ PMDI amount
- ❖ P% in the CMs, in order to set a similar P quantity, an equation delivered below is to be used for the CMs that successfully passed primary reaction to fire tests (Table 3.8):

Table 3.8 : Equation used for the equivalent P% in the foam.

CM	P% content	Equalized P%
TEP	17.0	x
APP	30.0	0.566x
Levagard 2100	18.4	0.924x
Levagard 2000	16.4	1.037x

Polyol blends were prepared for each formulation with some changes in the amount of blowing agent and combustion modifiers. After the addition of PMDI, reactive mixture was poured into the mold of 20x20x20 cm dimension. 30 minutes later, foams were demolded from the mold operating at 50 °C and molded density of each foam was measured which was previously set to a range of 38-40 kg/m^3.

Foams were let free-standing for 2 days in order to obtain a complete curing of the material.

For cone calorimeter exercise, all the prepared foams were coded with word ´Mod´ different than previous experimentals to distinguish. In total, 11 foams were coded with ´Mod´ and sent to cone calorimeter testing.

4. RESULTS AND DISCUSSION

In this part, Polyurethane (4.1) and Polyisocyanurate (4.2) formulations will be discussed separately as these two different chemistries have different thermal stability performance due to aromatic polyisocyanurate ring structure present in PIR foams.

In the parts 4.3, 4.4 and 4.5; reaction to fire performance of PIR formulations will be presented according to the formulation structure whether including Zinc borate or Ferrocene. Part 4.6 will cover emission aspect of the best performing formulations.

4.1 Polyurethane Formulations

In the rigid Polyurethane foam experimental part, results of the incorporation of synthesized chemicals, as well as commercially available combustion modifiers loadings in polyol blends will be discussed respectively.

4.1.1 Polyurethane foam containing synthesized and commercial substances

4.1.1.1 Synthesis of borates

Polyammonium diborate synthesis - 1

A total of 100 g of boric acid (orthoboric acid) was kept in an oven for one day at 125°C to dehydrate about 1 mol of water per molecule of the boric acid. Then it was slowly added to 100 g of 25 wt% aqueous ammonia solution, containing 25 wt% ammonia, at ambient temperature and pressure. The mixture was cooled down to keep the temperature below the boiling point wherein the ammonia.

Polyammonium diborate synthesis - 2

A total of 100 g of boric acid (orthoboric acid) were heated to 140°C until 5 mol of water per molecule evaporated. The product was added slowly to 100 g of aqueous ammonia containing 25 wt% ammonia while agitating. The mixture was allowed to react for 12 h. The tetraboron oxyacid changed to diboron oxyacid and boric acid that reacted with the ammonia to produce ammonia salt of boric acid and polyammonium salt of polyboron oxyacid. Afterward, the mixture was dried and a powdered PAB formed. Two mols of the ammonia salt of boric acid reacted to give PAB.

First, PAB formed from boric acid and ammonium hydroxide, and then, the element analysis was carried out by Thermo Scientific Phenom XL Desktop Scanning Electron Microscope. Boric acid lost a part of its water upon heating in air to above 75°C. At around 120°C–130°C, mainly cyclic trimer metaboric acid $(OH)_3B_3O_3)$ formed (Figure 4.1).

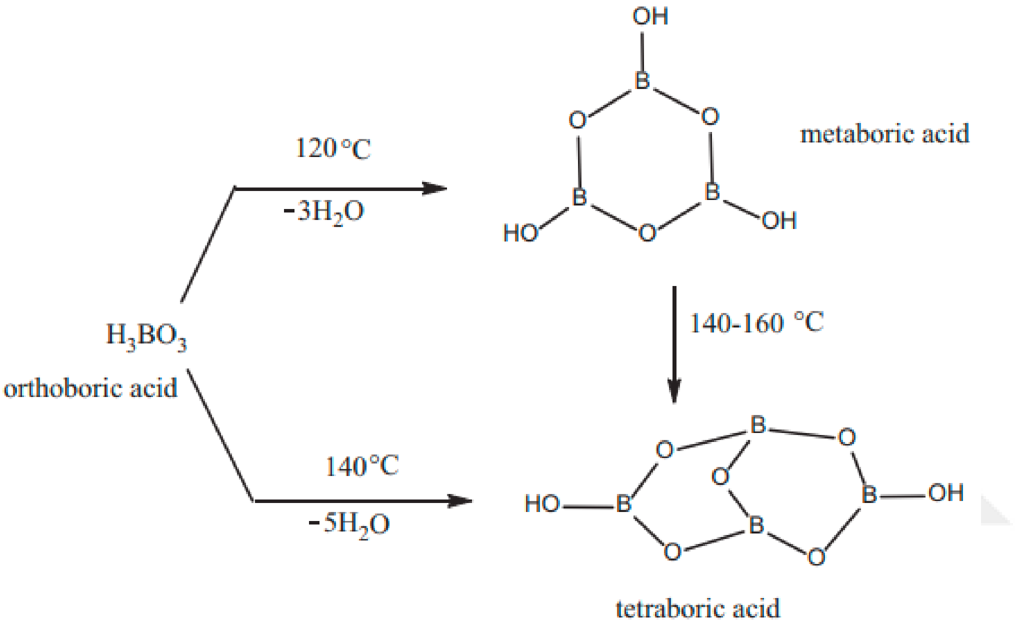


Figure 4.1 : Dehydration of boric acid to form metaboric acid and tetraboric acid.

Metaboric acid lost water by condensation reaction between –OH groups to give mainly tetraboric acid (bicyclic tetramer $(OH)_2B_4O_4$) by heating to about 140°C. Metaboric acid and tetraboric acid reacted with ammonium solution to result in PAB-1 and PAB-2. Their semi-quantitative element compositions were determined using SEM and SEM-electron dispersive spectroscopy (EDS). The results are shown in Figure 4.2. Boron, nitrogen and oxygen bond energies were 182–185 eV, 393–395 eV and 525–530 eV for PAB-1 and PAB-2 polyammonium borates. The approximate B, O, N atomic ratios of PAB-1 and PAB-2 were B/O/N = 3/4.2/ 1.3 and 3/4.3/1.2, respectively. These results showed that several boric acid molecules condensed to give cyclic and bicyclic structures and bridges between rings during heat treatment. Both

PAB-1 and PAB2 ground into a fine powder before being used in RPUF formulations. Figure 4.2 displays the SEM-EDX images of synthesized polyammonium borates:

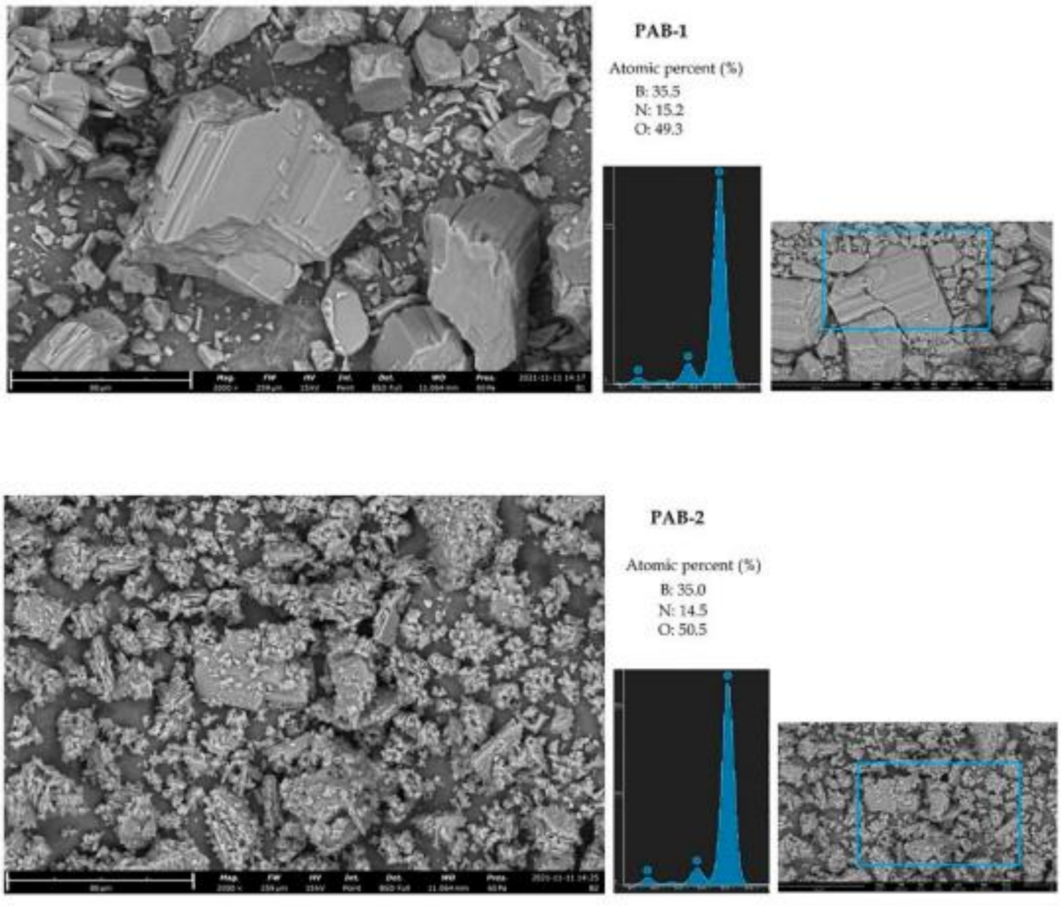


Figure 4.2 : SEM-EDX of polyammonium diborates PAB-1 and PAB-2 (bar: 80 mm).

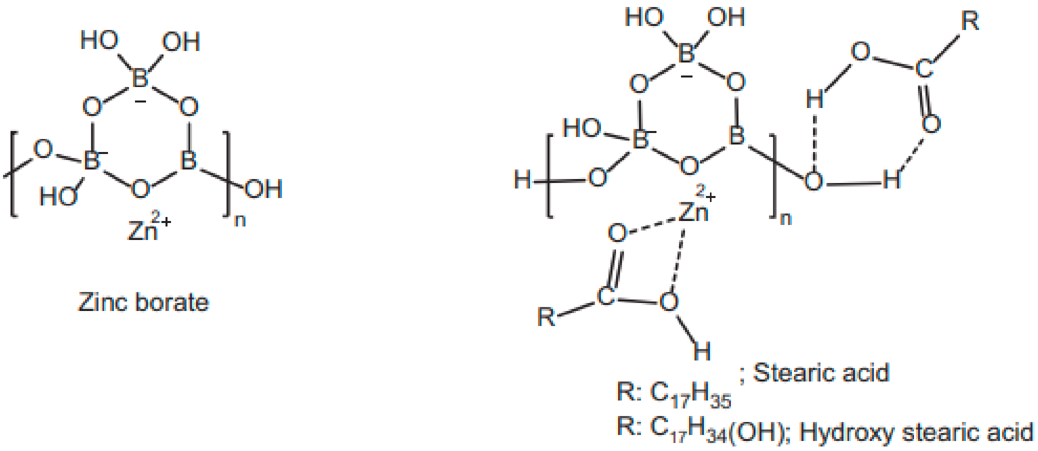
4.1.1.2 Complex of the zinc-pentaerythritol borate production

Pentaerythritol (0.25 mol), boric acid (0.25 mol) and water (500 mL) were put in a round-bottom flask equipped with a stirrer, condenser, thermometer pocket and gas bubbler. The mixture was heated to reflux under the nitrogen atmosphere with slow stirring. After about 45 min, zinc acetate solution in water was added slowly. The mixture was again heated to reflux for 2 h with slow stirring. On cooling to room temperature, a solid complex precipitated. It was washed with water and dried at 60°C for 48 h. These complexes were ground to a fine powder, sieved through (200 mesh BSS**)** and dried at 100°C for 24 h. The yield of these salts was 80–85 wt%.

Coating of the zinc borate particles with stearic acid or 12-hydroxy stearic acid

Zinc borate powder mixed with 12-hydroxy stearic acid or stearic acid (1.5 wt% of zinc borate) in a ball mill containing zircon beads for 1 h. The powder products were stearic acidcoated-zinc borate (SA-zinc borate) and 12-hydroxy stearic acid-coated zinc borate (HSA-zinc borate)

The surface of zinc borate powder was modified with stearic acid and hydroxy-stearic acid to obtain a hydrophobic surface. The amount of stearic acid was about 1.5 wt% of zinc borate powder. The structure of zinc borate and the purposed surface structure of stearic acid-coated zinc borate were in Figure 4.3. A strong bond occurred between the carboxylic acid group and Zn21 cations at the zinc borate particle surface. The stearic acid-coated zinc borate particles dispersed in polyol components easier than untreated zinc borate.



Zinc borate

R: $C_{17}H_{35}$; Stearic acid
R: $C_{17}H_{34}(OH)$; Hydroxy stearic acid

Figure 4.3 : Zinc borate structure and the surface modification with stearic acid and hydroxy stearic acid.

Reaction to fire results were investigated in 2 different group of formulations. First group of formulations (F1-F9) contain either Sb_2O_3 or PAB-1/PAB-2. Second set of formulations (F10 – F26) contain coated zinc borates.

UL-94 results

UL–94 test was applied 10 samples, which the first one was pristine PU foam. Formulations were reported in Table 4.1:

Table 4.1: PU foam experiments with synthesized borates.

	Pristine PU	F1	F2	F3	F4	F5	F6	F7	F8	F9
Polyol	100									
Zinc borate		15	20	35	15	15	15			5
ATH					50	50	40	50	50	40
Sb2O3			3	3	3					
PAB-1								10	20	
PAB-2										5
TCPP		10	10	10	10	10	8	10	20	8
Calculated density (kg/m3)	35	39	40	43	48	47	46	47	50	45
UL grade				HB	HB	HB	HB	HB	HB	HB
Ts	Burned	Burned	Burned	8	1	1	1	1	1	5

Pristine RPUF sample continued to burn at an increasing rate, and the flame at the front passed the 100 mm mark and burned completely. Formulation F6 - a combination of 15 wt% zinc borate, 40 wt% ATH and 8 wt% TCPP resulted in fire-retardant foam composites. Increasing ATH to 50 wt% did not improve fire-retardant properties as in formulation F5. TCPP acted as a fire-retardant additive in the gas phase, promoted barrier ash formation and also reduced the viscosity of the polyol component during the mixing of solid fire-retardants and the polyol component. The comparison F5 with F7 and F9 showed that both PAB-1 and PAB-2 were similar fire-retardant effects with zinc borate. When heated by a flame, the flame-retardant PAB-1 and PAB-2 compounds break down into acidic radicals that produce charring, and the nitrogen-containing radical also has a flame-retardant effect. In the second set of experiments polyol samples were prepared with the addition of SA-Zinc borate or HSA-Zinc borate.

When stearic acid or hydroxy stearic modified zinc borate was added into the polyol in place of zinc borate, the produced polyol component had much lower viscosity. In this case, a homogeneous mixture of polyol components formed without adding toxic liquid TCPP.

The burning time of FR-RPUF foam generally decreased with an increasing total content of fire-retardant additives. F3, F18 and F24 foams had slightly lower (48%–50 wt%) fire-retardant, and their burning times were about 3– 4 s. The type of fire-retardant also affected the burning time. F13, F14, F16, F17, F20, F22, F24 and F25 had 4–5 s of burning time. Formulations (F10-F26) were reported in Table 4.2:

Table 4.2: PU foam experiments with coated zinc borate.

	F10	F11	F12	F13	F14	F15	F16	F17	F18	F19	F20	F21	F22	F23	F24	F25	F26
SA-Zinc borate	30	15	15	15	15	10	15	15						10			
HSA-Zinc borate										15	15	15	15		10	10	10
PAB-1						5	5	10	10			5	10				
ATH		50	50	40	40	50	40	30	30	40	50	30	30	40	40	40	40
TCPP	3		8	8	5	10	5	10	10	10	8	10	5	8		8	10
UL grade		HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB	HB
Ts	Burned	7	8	4	5	3	5	5	3	7	4	6	4	3	4	5	6

As an outcome of the first study, it can be commented that synthesized polyammonium borates were better fire-retardants and smoke-suppressant than zinc borate. Stearic acid and hydroxy stearic acid-coated zinc borates dispersed in polyol easier than zinc borate. In this case, TCPP was not necessary for good dispersion of the fire-retardant mixtures in the polyol. The combination of cooling (ATH), smoke suppressant (zinc borate), barrier-forming and gas-phase inhibition (TCPP) type fire retardants resulted in the FR-RPUF composites. Liquid TCPP helped the dispersion of fire-retardant particles in the polyol during mixing. The densities of the FR-RPUF foams containing the combination of ATH, zinc borate and polyammonium borates were much higher than pristine RPUF foam. The density of FR-RPUF decreased if the stearic acid or hydroxy stearic acid-coated zinc borate were used instead of zinc borate.

4.1.2 Polyurethane foam containing alternative combustion modifiers

In this part, the target is the incorporation of commercially available combustion modifiers that are alternative to TCPP and synthesized/coated zinc borate. Different loadings of CMs in PUR foam and their results will be presented using DIN 4102 method.

4.1.2.1 Polyurethane foam with 14.7%wt of combustion modifiers addition

6 different CMs were selected as an alternative to TCPP and TEP; and free rise foams were prepared. As molecular weight of each CM is quiet different (which includes N, P and ZB), approach is to incorporate same amount by means of weight in the polyol blend.

For each formulation, an FR package of 14.7% by weight of polyol was inserted and rigid foams were prepared (Table 4.3).

Formulations are numbered with the donations of ´PUR´ based on the chemistry they are representing which is then followed by the experimental number. Additionally, a reference formulation was prepared which does not include any combustion modifier. It is coded as PUR Ref.

Table 4.3 : First set of polyurethane formulations with 14.7% wt of CM loading.

	PUR Ref	**PUR1**	**PUR2**	**PUR3**	**PUR4**	**PUR5**	**PUR6**	**PUR7**	**PUR8**
Polyol	100	85.3	85.3	85.3	85.3	85.3	85.3	85.3	85.3
TCPP		14.7							
TEP			14.7						
FB ZB				14.7					
APP					14.7				
APB						14.7			
Boric acid							14.7		
ASTD								14.7	
ATH									14.7
FRD (kg/m^3)		42	42	45	44	38	39	38	45

After the completion of curing, a lower free rise density and more friable structure were obtained with below foams:

- PUR5 containing ammonium pentaborate tetrahydrate
- PUR6 containing boric acid
- PUR7 containing sodium tetraborate decahydrate (Borax)

In order to understand the root cause of this behavior, reactivity profile of reference formulation (PUR Reg) was checked with Foamat. Figure 4.4 shows reactivity profile in black, as % of final growth, its derivative in blue (mm/s) and temperature change in first 120 seconds during polymerization reaction:

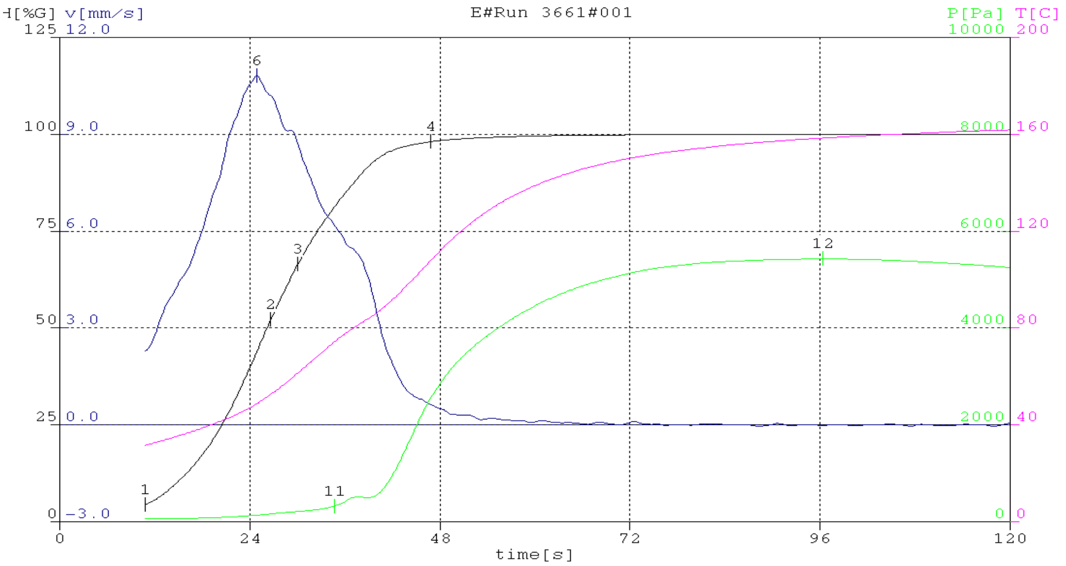


Figure 4.4 : Reaction profile of reference (PUR Ref) formulation.

In the Figure 4.4, green line represents the pressure created during polymerization reaction, purple line the change in temperature in the foam core, blue line polymerization reaction rate and black line as % of final growth.

Temperature in PU foam core reached up to 160°C in 45 seconds which is also denoting gel time of the product. This may indicate that, combustion modifiers Borax, boric acid and ammonium pentaborate tetrahydrate probably lose water of crystallization during polymerization which then leads to a lower free rise density thanks to the reaction between water and isocyanate.

This may be considered an undesirable effect as it's a superficial effect that depends on the morphological properties of the solid suspended in the liquid and it will change overtime. A possibility to override this effect would be to dry these CMs in a hot oven prior to polymerization reaction which means that it will not be possible to take the advantage of cooling effect of dehydration water during combustion or when designing rigid PU formulations.

DIN 4102 results for first set of Polyurethane formulations

DIN 4102 small flame height test was applied to all the specimens cut from free rise foams. It was not possible to measure the flame height for none of the foams since all burned vigorously.

It is observed that with 14.7% of flame retardants incorporation in rigid PU formulations comprised only of polyether polyols, it is not possible to achieve a B2 fire performance.

A new set of formulation was needed to be prepared with higher loading of Combustion Modifiers.

4.1.2.2 Polyurethane foam with 35% wt of combustion modifiers addition

In the second experimental campaign; borax, boric acid and ammonium pentaborate tetrahydrate were removed from further screening. As a next step, combustion modifiers were inserted at a total amount of 35% with respect to polyol blend weight.

While the target is to evaluate the performance of each CMs alone in rigid PU foam, some formulations containing two different CMs were also prepared in order to highlight whether a synergy can be observed in reaction to fire properties. Table 4.4 displays full set of PU formulations:

Table 4.4: Second set Polyurethane formulations (35% CM loading by total polyol wt).

	PUR9	**PUR10**	**PUR11**	**PUR12**	**PUR13**	**PUR14**	**PUR15**	**PUR16**
Polyol blend	65	65	65	65	65	65	65	65
TCPP	35	0	0	0	0	0	0	0
Triethyl Phosphate	0	35	0	0	0	20.3	0	0
Firebrake ZB	0	0	35	0	0	14.7	20.3	14.7
APP	0	0	0	35	0	0	0	20.3
DEEP	0	0	0	0	35	0	14.7	0
Sum	100	100	100	100	100	100	100	100

After the curing of the foams, cut samples were subjected to DIN 4102 test.

For the following experiments, in order to analyze the data with a statistical approach, JMP statical tool is used. Tukey Kramer HSD method was chosen for the analysis which were replicated 3 times and require a comparison that statistically provides the difference. DIN 4102 threshold 150 mm height was set as a reference for flame height results and displayed with red discontinuous lines. Flame height results were shown in circles that cover the bottom and top results of each specimen. For NBS smoke opacity results, as there is no threshold, the performance of formulations were compared with the same methodology excluding the limit (red discontinuous line).

DIN 4102 results for second set of Polyurethane formulations

Foams produced of formulations PUR11 (containing only FB ZB), PUR12 (containing only APP) and PUR16 (containing combination of FB ZB and APP) burned vigorously. It was not possible to measure the flame height; which indicates a poor reaction to fire performance of Firebrake ZB, APP and the combination of APP & ZB.

Zinc borate can be considered as a non-effective flame retardant when used alone.

Despite being a high phosphorus containing FR; APP, did not provide a good performance either in case when inserted as a sole CM.

In parallel PUR16 formulation, the combination of APP & ZB did not provide a synergic effect.

For the remaining foams, flame height of 3 samples from each formulation was measured and results are reported in Figure 4.5:

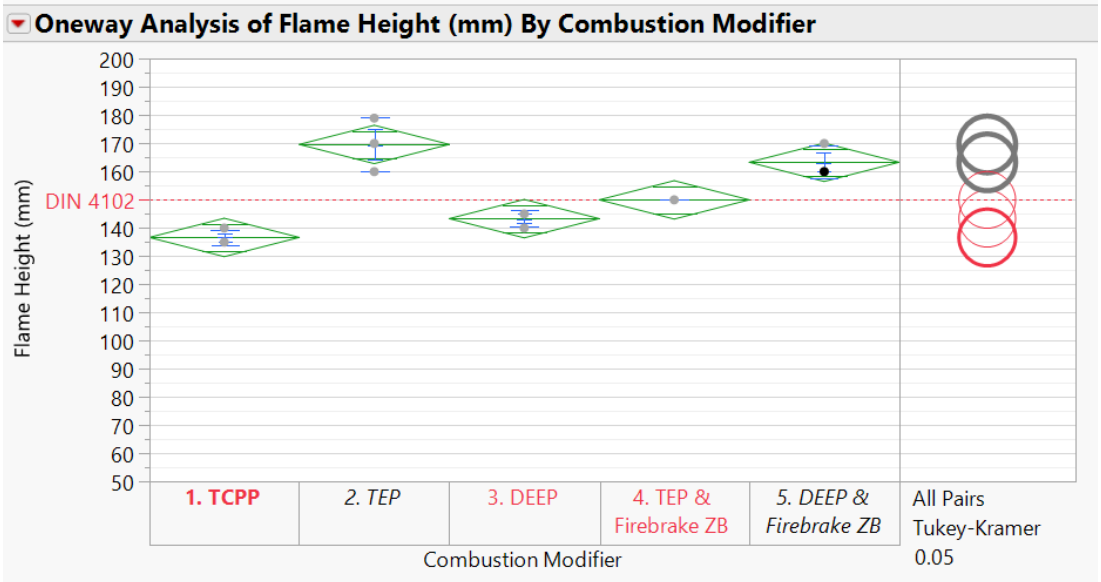


Figure 4.5 : DIN 4102 test results of second set formulations (35% CM loading by polyol wt).

There is no statistical in the data comparison between TCPP (PUR9), DEEP (PUR13) and TEP&ZB (PUR14) containing formulations according to Tukey-Kramer HSD (honestly significant difference) test, however, considering the fact that 150 mm flame height is the threshold of DIN 4102 B2 performance, formulation of TEP&ZB (PUR14) is not meeting this criteria due to one specimen’s exceeding the threshold value.

TEP (PUR10) and DEEP & Firebrake ZB (PUR15) formulations can not be classified as B2.

When compared to PUR10, a synergy might be noticed in formulation PUR14 which contains TEP and Firebrake ZB. While PUR10 alone displayed a performance of 17 cm average and PUR11 alone burned vigorously, PUR14-combination of said combustion modifiers confirmed an improved reaction to fire performance.

Reversely, while PUR13 (DEEP alone) was a B2 performing formulation, likewise in PUR15 (when used in conjunction with ZB), shows an antagonism behavior.

4.2 Polyisocyanurate Formulations

Experiments with PIR formulations were prepared based on:

1. Outcome of rigid Polyurethane foam experimentals: this led the elimination of some combustion modifiers from the list which are not suitable to validate in such formulations.
2. Distinction of combustion modifiers according to
    - Being reactive or inert towards isocyanates.
    - Phosphorus based or not.
    - Monomeric-oligomeric-polimeric. This classification is especially important for emission properties of the foams.

In the first part of PIR study (4.2.1); the interactions between non-reactive phosphorous CMs with ZB were investigated, indicated with red boxes shown in Figure 4.6:

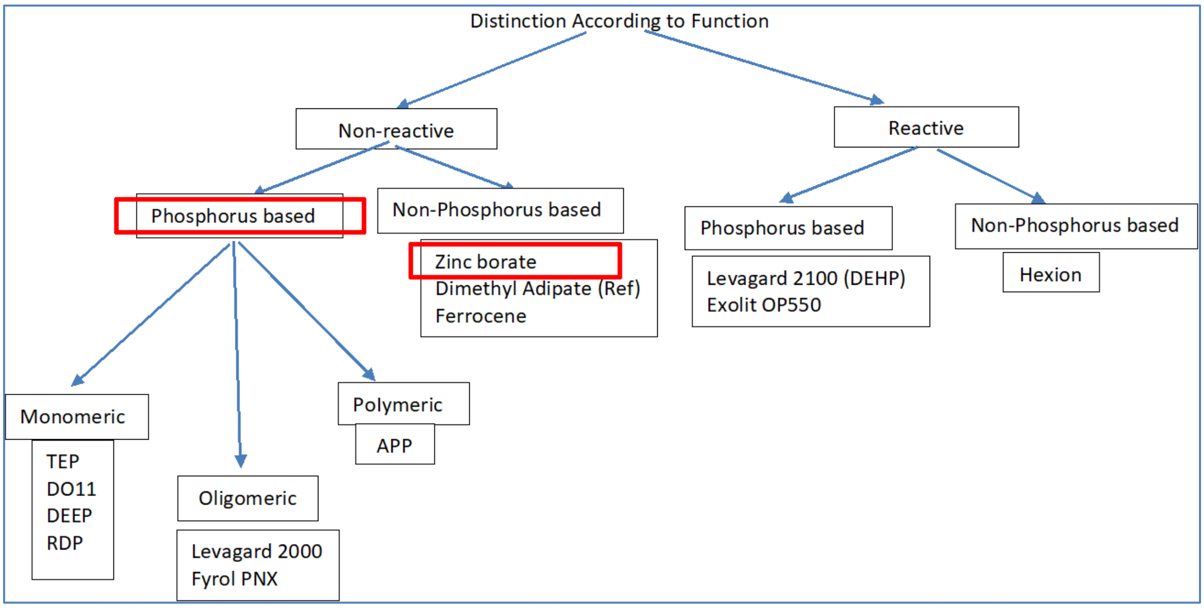


Figure 4.6 : Classification of CMs used for PIR applications.

In each part of this study, examined combustion modifiers group will be indicated in red boxes in the above scheme. Additionally, the type of combinations such as mono component, two component or three compound combustion modifiers definition will be included in the headings of the relevant part.

4.2.1 Non-reactive flame retardant and Zinc borate combinations

4.2.1.1 One and two combustion modifier combinations

Reference formulation, PIR1; was set as TEP containing formulation.

Formulation coding is done as:

- If the formulation contains only one combustion modifier then first number after word PIR is 1 such as PIR 1.1, PIR 1.2 etc. Second number, instead, indicates a different type of combustion modifier in the system.
- If the formulation contains two or three combustion modifier in the system, then the first number after word PIR is 2 or 3, depending on the amount of CM present.

In the first set of experimentals, a total of 35g (24.3%) of CMs were inserted in PIR formulations as in Table 4.5. When the formulations were prepared, the target was to insert either a single CM of 35 grams or a combination of 2 combustion modifiers, in which Zinc borate is always present at a weight of 14.6 grams (10.2%) and 20.27 grams (14.1%) of one flame retardant. This strategy was chosen to confirm the synergism of zinc borate with different flame retardants.

Table 4.5 : One and two combustion modifier combinations Polyisocyanurate formulations (35 gr by wt).

	PIR1.1	PIR1.2	PIR1.3	PIR1.4	PIR2.1	PIR2.2	PIR2.3	PIR2.4	PIR2.5	PIR2.6
Polyol	96	96	96	96	96	96	96	96	96	96
TEP	35	0	0	0	20.27	20.27	0	0	0	0
Firebrake ZB	0	35	0	0	0	14.67	14.67	14.67	14.67	14.67
APP	0	0	35	0	0	0	20.27	0	0	0
DEEP	0	0	0	35	0	0	0	20.27	0	0
Levagard 2000	0	0	0	0	0	0	0	0	20.27	0
DO11	0	0	0	0	0	0	0	0	0	20.27
Dimethyl adipate	0	0	0	0	14.67	0	0	0	0	0

Reaction to fire performance analysis

DIN 4102 flame height results

Figure 4.7 represents DIN 4102 test performance of one and two combustion modifier combinations performance in Polyisocyanurate foams:

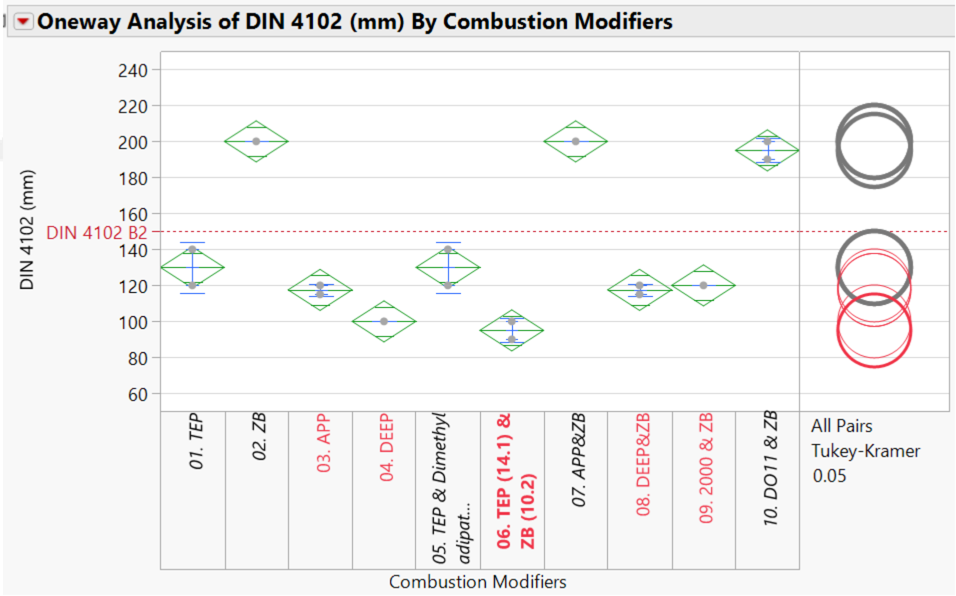


Figure 4.7 : DIN 4102 test performance.

3 formulations out of 10 formulations of table 4.5, confirmed that they are not in compliance with DIN 4102 B2 performance criteria (flame spread < 150 mm): PIR1.2 (ZB), PIR2.3 (APP&ZB), PIR2.6 (DO11&ZB). These foams were excluded from smoke density (smoke opacity) test.

Interesting result was obtained with PIR2.3. While PIR1.3, APP containing foam, displayed a very low flame spread performance, addition of Zinc borate as in PIR2.3

formulation, has impacted fire performance negatively.

PIR2.2, the combination of TEP&ZB, is a great example of synergism. PIR1.1 and PIR1.2 are the formulations that contain only TEP or ZB as a combustion modifier. Instead, when they used together at a lower amount but together as in PIR2.2 formulation, the synergy is confirmed.

On the other side, incorporation of Zinc borate on DEEP as in formula PIR2.4 with respect to PIR1.4, did not affect the performance neither positive nor negatively.

Smoke density

Smoke opacity performance of the 10 formulations are displayed in Figure 4.8:

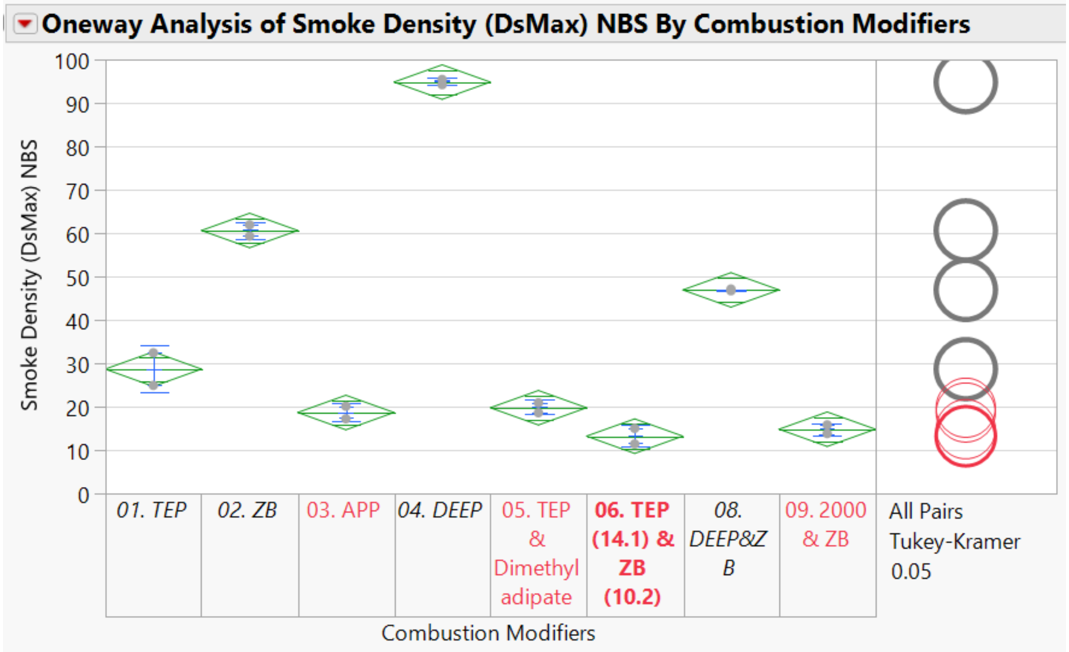


Figure 4.8 : Smoke opacity performance via ASTM D662.

Formulations based on ZB (nr 2), DEEP (nr 4), and DEEP&ZB (nr 8) displayed the worst performances, while the ones including APP (nr 3), TEP and dimethyl adipate (nr 5), TEP and ZB (nr 6), Levagard 2000 & ZB (nr 9) display very low values.

Overall evaluation of one and two compound combinations with an integrated approach

In order to investigate the root cause of diverse performance of the formulations; P% content, phosphorus type and molecular structures of CMs are presented in Table 4.6:

Table 4.6 : P (phosphorus) wt.-% in the foam vs type of oxidation state vs reaction to fire test results.

	PIR1.1	**PIR1.2**	**PIR1.3**	**PIR1.4**	**PIR2.1**	**PIR2.2**	**PIR2.3**	**PIR2.4**	**PIR2.5**	**PIR2.6**
P% in PU foam	1.7	0	3	1.87	1	1	1.76	1.09	0.96	0.83
Phosphorus type	P.ester	NA	P. ester	Phosphonate	P. ester	P. ester	P. ester	Phosphonate	P. ester	Phosphinate
Molecular structure	Monomeric	NA	Polymeric	Monomeric	Monomeric	Monomeric	Polymeric	Monomeric	Oligomeric	Monomeric
Average flame height (mm)	130	200	118	100	130	95	200	118	120	195
Average smoke density	29	60.7	19	95	20	13	NA	47	15	NA

The following observations arise:

- APP and DEEP, e.g. PIR2.3 and PIR2.4, when combined with Zinc Borate, do not allow passing the DIN 4102 B2 threshold; a worsening is instead highlighted, and there is no synergy.
- Both phosphate esters and phosphonates are effective combustion modifiers for PIR foams. The only tested phosphinate, PIR2.6, did not provide a positive performance.
- Monomeric, oligomeric or polymeric additives can all be used for an impactful reaction to fire performance (no clear dependence from the type of additive shows up).
- Synergism is confirmed for fire and smoke performance for PIR2.2 (TEP&ZB combination), in the sense that the values displayed for flame spread and smoke opacity are better than in the two cases when the CMs are used alone.
- Regarding the case of DEEP&ZB interaction (PIR2.4), the flame spread performance is in-between the performance of the foams using, respectively, DEEP (PIR1.4) and ZB (PIR1.2) alone, while for smoke density, a positive synergism is highlighted.
- Albeit not able to evaluate a possible synergism between Levagard® 2000 and ZB (PIR2.5) (the performance of a foam including Levagard® 2000 as the sole

CM has not been recorded), values displayed by the foam incorporating both as CMs is remarkable, in particular with very low values of smoke opacity (15 as DsMax when TEP & ZB -PIR2.2 is at 13)

- Based on conclusions of PIR1.2 formulation, ZB by itself can't be considered a combustion modifier acting both on flame spread and on smoke opacity.

4.2.1.2 Comparison of rigid PIR vs PUR foams results

When comes to a fair comparison between the results of rigid PUR and PIR foams, it would be convenient to use similar data set and combustion modifiers combinations in these 2 chemistries. For the evaluation, selected systems are 35% wt loading in rigid PUR system (second experimental campign of PU foam) vs 24.3% (35 g) of combustion modifiers loading in PIR system. Even though the total CM amount in PIR foam is inferior, still obtained results give a clear insight. Table 4.7 investigates the performance of certain CM´**s** in the 2 systems:

Table 4.7 : Performance comparison of combustion modifiers in PUR vs PIR system.

Chemistry	Combustion modifier	CM loading (%)	Foam	Av.flame height (mm)
PUR	TEP	35	PUR10	170
PIR		24.3	PIR1.1	130
PUR	ZB	35	PUR11	NA
PIR		24.3	PIR1.2	200
PUR	APP	35	PUR12	NA
PIR		24.3	PIR1.3	120
PUR	DEEP	35	PUR13	145
PIR		24.3	PIR1.4	100
PUR	TEP&ZB	35	PUR14	150
PIR		24.3	PIR2.2	90
PUR	DEEP&ZB	35	PUR15	165
PIR		24.3	PIR2.4	120

Despite a lower amount of CM incorporation, in all cases PIR foam exhibits a greater fire performance than rigid PUR foam, This can be explained with the existence of aromatic isocyanurate ring structure in PIR foams which was early described to increase the final material´s thermal stability as in Table 2.2 and represented as in Figure 4.9:

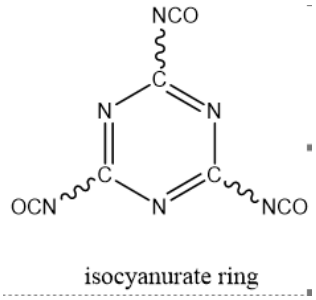


Figure 4.9 : Isocyanurate ring structure.

Another interesting finding is the validitiy of synergism between same flame retardants both in PUR and PIR systems. Zinc borate confirms the positive reaction with TEP and DEEP in both formulations. APP, instead provides a good fire performance in PIR differently than in rigid PUR foam.

Lastly, neither in PUR nor in PIR systems, Zinc borate functions as a flame retardant when incorporated alone. On the other hand, when combined with a right FR, it aids reducing the flame height as well as acting as a smoke suppressant.

4.2.1.3 Triethyl phosphate-zinc borate screening

From previous data, it became evident that best performance was reached thanks to TEP and ZB interaction. Therefore, a screening for different levels of TEP & ZB in PIR foam were performed as shown in Table 4.8. All the components are calculated to 100 parts by weight of fully formulated polyol.

Table 4.8 : Screening of various levels of TEP & ZB.

	PIR1.1	**PIR1.2**	**PIR2.2**	**PIR2.21 (1.5X(TEP & ZB))**	**PIR2.22 (TEP & 2XZB)**
Polyol	75.7	75.7	75.7	62.4	65.5
TEP	24.3	0	14.1	21.2	14.1
Firebrake ZB	0	24.3	10.2	16.4	20.4
Sum	100	100	100	100	100

Formulations PIR2.21 and PIR2.22 were prepared as follows:

PIR2.21 contains 1.5 times more of the total amount (weight in the polyol blend) of TEP&ZB combination present in PIR2.2.

PIR2.22 contains the same weight of TEP and 2 times more of weight of Zinc borate with respect to PIR2.2.

For the next analysis, PIR2.2 (TEP 14.1% & 10.25% wt combination) is used as a reference.

DIN 4102 flame height

Figure 4.10 displays flame spread changes with the increment in quantity of TEP-ZB.

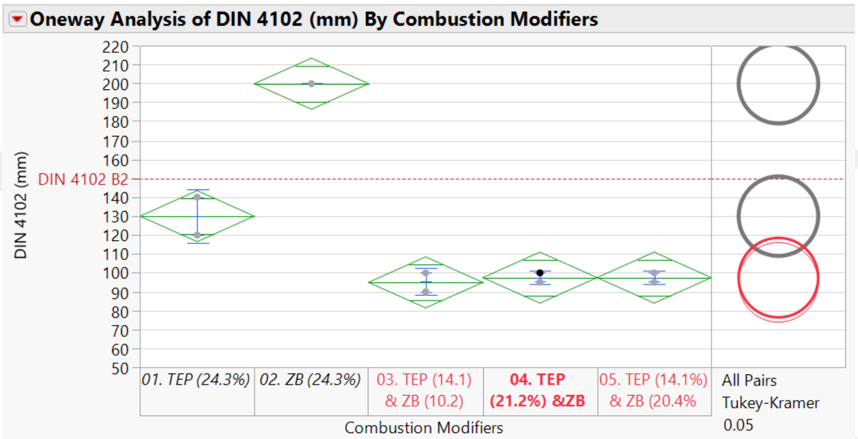


Figure 4.10 : DIN 4102 performance of TEP&ZB screening.

This screening exercise puts forward that increasing the amount of Zinc Borate and/or TEP are not favoring further synergy, which might indicate that the maximum level that can be obtained through this interaction is close to the levels tried initially as in PIR2.2 (14.1 wt.-% TEP, 10.2 wt.-% ZB).

Smoke density

Results of smoke density is reported in Figure 4.11:

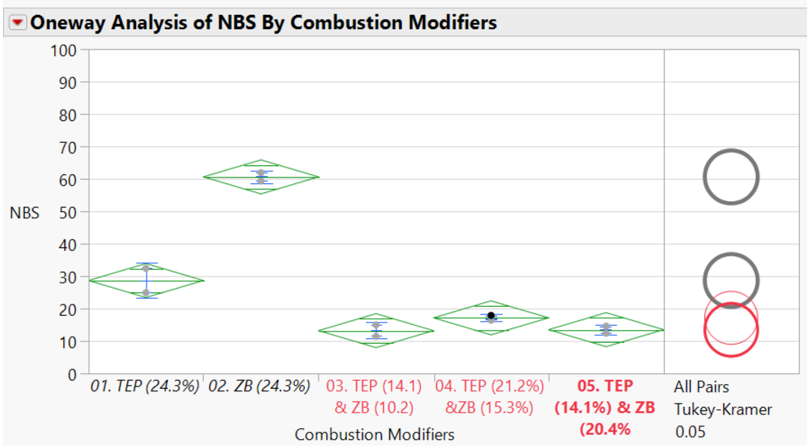


Figure 4.11 : Smoke density performance of TEP&ZB screening.

The same conclusion as of DIN 4102 fire performance can be drawn also for smoke generation. There is a threshold from a smoke performance point of view and it is not possible to further improvement in that performance by the increament of combustion modifiers amount in the reactive mixture. Therefore, it is convenient to keep initial limits as reference.

At this point, it might be also possible to reduce the level of loading (TEP & ZB) in the formulation while maintaining the same reaction to fire performance. In order to confirm this, additional studies should be carried out with a systematic Design of Experiment approach.

Thermal analysis

TEP & ZB interaction provides one of the most efficient CM combination in PIR foams on fire subject that is investigated in this study. Revealing the root cause of this behavior might be possible through various analysis such as TGA, DMA, open cell and SEM.

2 samples (PIR1.1 and PIR2.2) that were previously reported, were selected to proceed with further analysis. Thermal analysis of the reference foam incorporating TEP (PIR1.1) and the foam with TEP and ZB (PIR2.2) has been carried out. Weight loss data by means of temperature was obtained through TGA by running the analysis up to 700°C under air flow. Transitional behavior, e.g. measurement of the glass transition temperature (T_g), instead, was screened thanks to the Dynamic Mechanical Analyzer.

Thermo gravimetric analysis

TGA was carried out on both samples: PIR1.1 and PIR2.2 containing samples. Heating was applied from room temperature until 700 °C with a 10 °C/min sequence under air flow. Change of weight is illustrated in Figure 4.12.

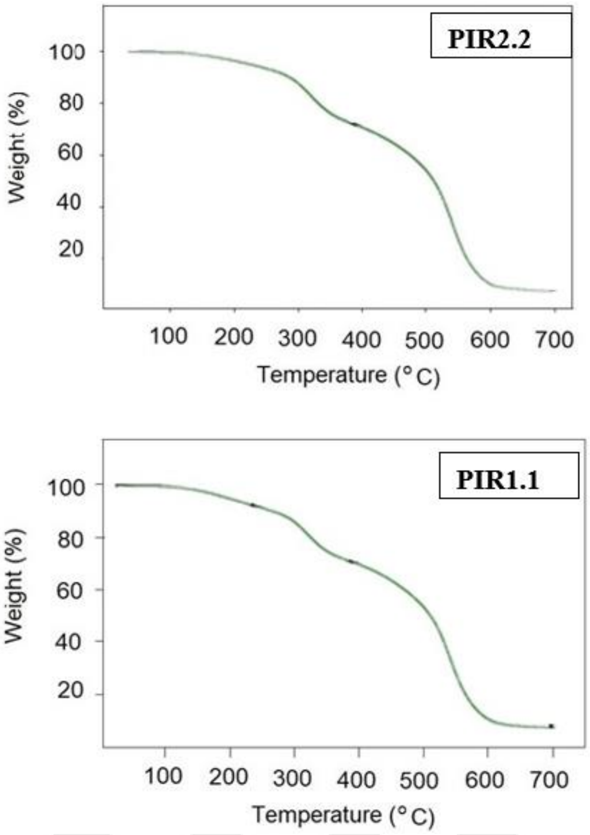


Figure 4.12 : TGA of PIR2.2 and PIR1.1 foams.

Once the samples were exposed to TGA, onset of decomposition occured between 250 and 300 °C for both. A step was indicated in the charts of yet its presence is rather questionable.

Sample in which Zinc borate was incorporated, approximately 28.4% of the foam's total weight was lost in the first decomposition step which took places between 300-400 °C, whereas for the sample without zinc borate this ratio was measured roughly as 29.6%. The two samples are substantially the same, even if in the analysis of Figure 4.9, a split of a decrease step in the range 150-200°C was attempted.

Zinc borate contains 20% of water of hydration in the structure and it should be lost quite before than 200 °C; however, no loss of water-step is highlighted at this level.

Dynamic mechanical analysis (DMA)

For PIR foams, glass transition temperature is expected to be between 120 and 180 °C. 2 foams (PIR1.1 and PIR2.2 combination) were exposed to dynamic mechanical analysis from room temperature up to 700 °C with a 10 °C/min sequence under air flow. Figure 4.13 indicates the results of PIR 2.2 and PIR 1.1:

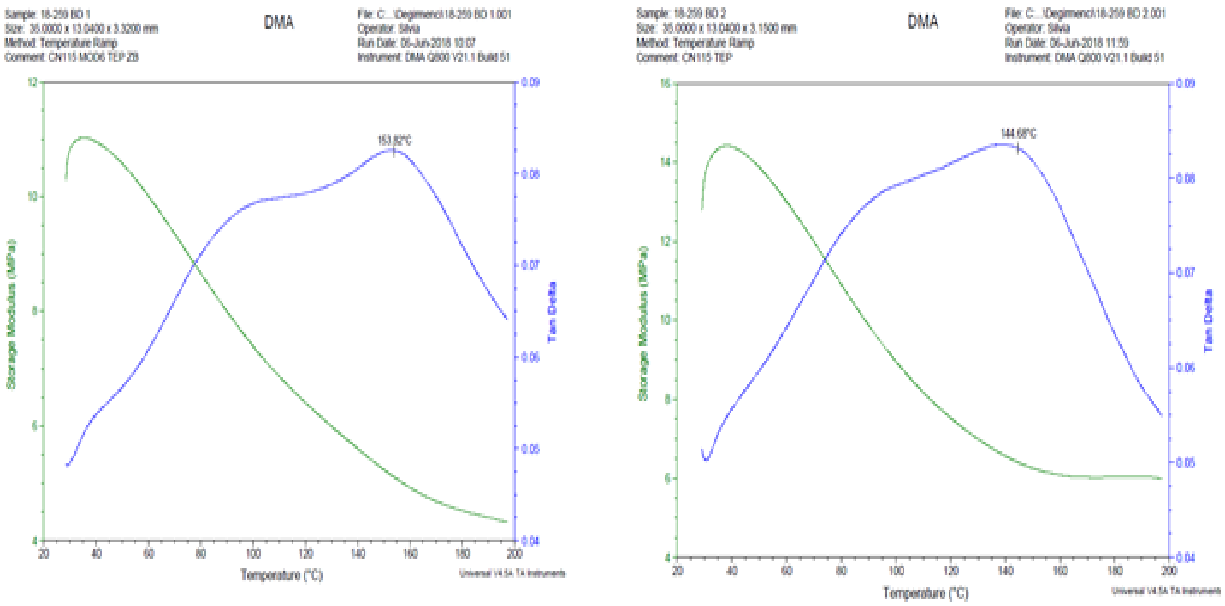


Figure 4.13 : DMA of (PIR2.2) and (PIR1.1) incorporated foams, respectively.

In the case of PIR2.2, the glass transition temperature was detected around 153 °C (tan delta peak), while for the PIR1.1 foam, a T_g of around 138-140 °C was reported. Even though, there is a small difference between T_g of 2 foams, it is not significant to indicate an increased thermal stability performance of the polymer contaning ZB.

Morphological analysis

Open cell content

Rigid foams are expected to have an open cell content between 5% and 15% in its structure. 2 foams (PIR1.1 and PIR2.2 combination) were tested to confirm whether the difference in fire performance arises from open cell content or not.

Table 4.9 : Open cell content comparison before fire testing.

Foam	Open Cell %
Including ZB + TEP	11.04
Including TEP	11.95

As reported in table 4.7, found values are in the range of expectation. Furthermore, there is not a significant OC content difference between the non-ignited foams; possible differences after the combustion will consequently depend on the kinetics of combustion itself and not on the initial morphology. Unluckily, though, OC content measurement can't be carried out on charred foams and visual analysis by means of SEM is necessary.

Scanning electron microscopy

The molecular structure of 2 specimens was characterized before and after the combustion as in Figure 4.14:

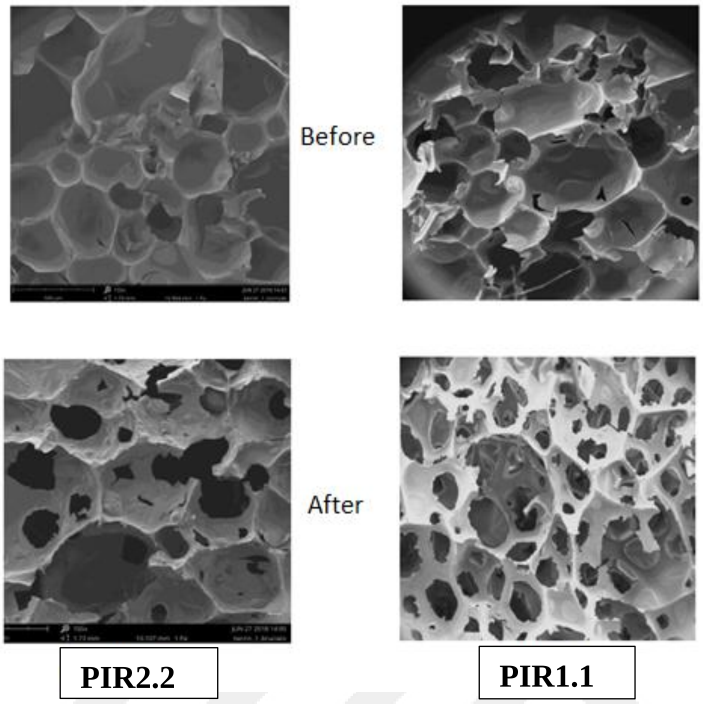


Figure 4.14 : SEM images of foam surface before/after combustion; left-hand side PIR2.2 (TEP&ZB-containing foam), right-hand side PIR1.1 (TEP-only foam).

While a similar type of morphology was displayed before the combustion, a certain difference was shown through SEM imaging after combustion. In particular, destruction of the cell windows in PIR1.1 foam occurred to a higher extent than in PIR2.2 foam, where a certain amount of cell windows remained close.

Based on the images of Figure 4.11, the sample incorporating PIR2.2 showed a greater consistency of maintaining the bigger portion of the interconnections between the cells after combustion.

TGA results and SEM pictures suggest that the synergy between PIR2.2 was due to physical and chemical interaction between them. During the mixing process of polyol and the combustion modifiers, some TEP may be adsorbed on the surface of ZB. The chemical interaction may start with the effect of heat produced during foam production or by fire.

4.2.1.4 Three combustion modifier combinations

As TEP & ZB combination is the best performing approach for PIR foams, 3rd degree interactions were tentatively derived based on this combination by reducing the amount of TEP and incorporating a 3rd CM in the formula as in Table 4.10, with CMs adding up to 35g in polyol blend.

Table 4.10 : Three components combination study (CMs 35gr in polyol blend).

Components	**PIR2.1**	**PIR2.3**	**PIR3.1**	**PIR3.2**	**PIR3.3**	**PIR3.4**	**PIR3.5**
Polyol	96	96	96	96	96	96	96
n-Pentane	12.85	12.85	12.85	12.85	12.85	12.85	12.85
TEP	20.27		10	10	10	10	10
APP		20.27				10.27	
Fyrol PNX			10.27				
RDP				10.27			
DO11					10.27		
Levagard 2000							10.27
Firebrake zinc borate	14.67	14.67	14.67	14.67	14.67	14.67	14.67

Preparation of the three component combustion modifiers in the selected formulation were done accordingly:

TEP (10g)+ ZB (14.67g) + CM (10.27g)

CM can be Fyrol PNX, RDP, DO11, APP, Levagard 2000 as denoted in table 4.7.

These 3 compound combinations are described with number 3 after ´PIR´ word.

Reaction to fire performance analysis

DIN 4102 flame height results

Figure 4.15 represents the results of 3 combustion modifiers combination study of DIN 4102 test.

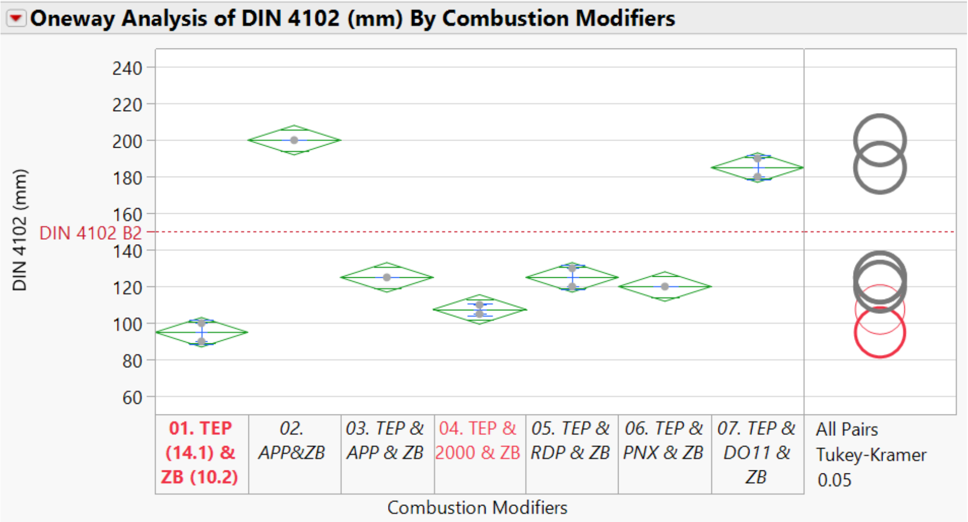


Figure 4.15 : 3 combustion modifiers combination – DIN 4102 results.

Best performance was achieved through the interaction between TEP & Levagard 2000 & ZB (PIR3.5), yet the result was not statistically different from the reference PIR2.2 as shown by the Tukey-Kramer HSD analysis.

Additionally, it was reported that incorporation of TEP in APP&ZB combination, significantly reduced the flame height (PIR2.3 and PIR3.4).

2 formulas were found to be not in compliance with DIN 4102 B2 criteria, that are PIR2.3 and PIR3.3 which were removed from smoke opacity exercise.

Smoke density results

6 samples were exposed to NBS smoke chamber analysis. Results are reported in Figure 4.16.

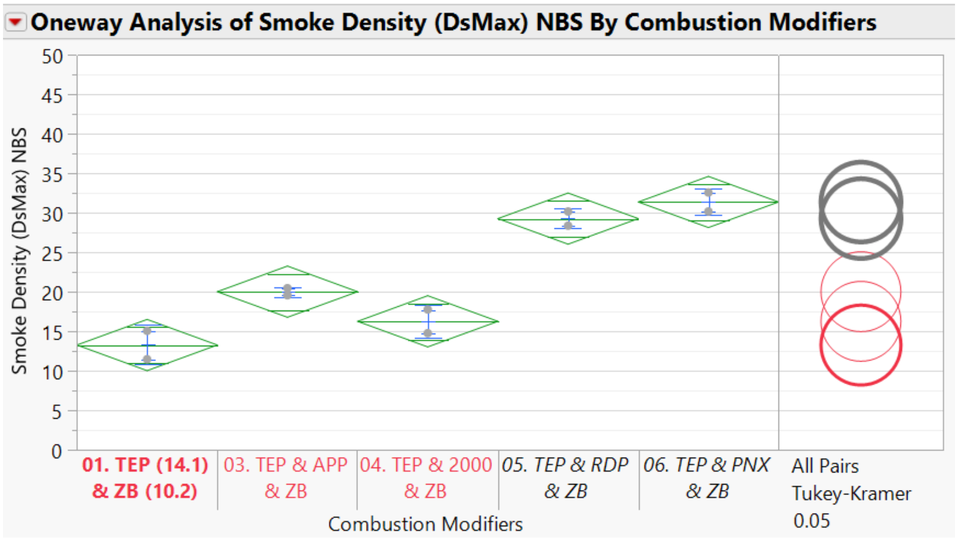


Figure 4.16 : 3 combustion modifiers combination – smoke performance.

The sample PIR3.5 (TEP&2000&ZB) performed well, and in a similar way to PIR3.4 (TEP & APP & ZB), yet in a non-distinctive way with respect to the reference PIR2.2 (TEP & ZB). Instead, PIR3.2 (TEP&RDP&ZB) as well as PIR3.1 (TEP&PNX&ZB) combinations were found to be performing significanlty lower than other combinations.

Overall evaluation of second and third-degree interactions with an integrated approach

Phosphorus based non reactive flame retardans and smoke suppressant zinc borate second and third level interactions in PIR foam revealed important results. These results were investigated together with the phosphorus family and molecular structure that is shown in Table 4.11:

Table 4.11 : 2 and 3 Combustion modifiers combination, summary of results.

	PIR2.2	**PIR2.3**	**PIR3.4**	**PIR3.1**	**PIR3.2**	**PIR3.5**	**PIR3.3**
	TEP&ZB	**APP&ZB**	**TEP&APPP&ZB**	**TEP&PNX&ZB**	**TEP&RDP&ZB**	**TEP&2000&ZB**	**TEP&DO11&ZB**
P% content in PU foam	1	1.76	1.40	1.10	0.82	1.04	0.92
Phosphorus family	Phosphate ester	Phosphate ester	Phosphate ester	Phosphate ester	Phosphate ester	Phosphate ester	Phosphate ester + Phosphinate
Molecular structure	Monomeric	Monomeric + Oligomeric	Monomeric + Polymeric	Monomeric + Oligomeric	Monomeric	Monomeric + Oligomeric	Monomeric
Average flame height (mm)	95	200	125	120	125	108	185
Average smoke density	13	NA	20	31	29	16	NA

The context of APP&ZB trial (PIR2.3) is to prove if a good reaction to fire performance can be achieved without any monomeric FRs. However, despite having the maximum P% content amongst all formulations, only the addition of a certain amount of TEP (PIR3.4) allows the attainment of a performance that is in compliance.

With the compounds RDP, PNX and DO11 no improvement/synergy was detected with respect to formulation PIR2.2.

The performance of PIR2.2 is similar to PIR3.5: nevertheless a significant difference was observed in fire performance, the change of monomeric substance amoun in the formulation might be impacting emission results of the final foam.

Evaluation of reaction to fire results together with substance´s phosphorus family and molecular structure puts forward that no clear dependence can be found between these facts.

4.2.2 Non-reactive flame retardant and Ferrocene combinations

Experiments completed in part 4.2 confirmed the most effective fire retardant and smoke suppressant combination as TEP&ZB in PIR foams (PIR2.2), which therefore was taken as a reference point for the next studies.

Ferrocene, that is alternative to Zinc borate for smoke suppression aspect in the polymers, was chosen to form new combinations with phosphorus flame retardants in the formulations. Figure 4.17 represents the selection of CMs for part 4.3:

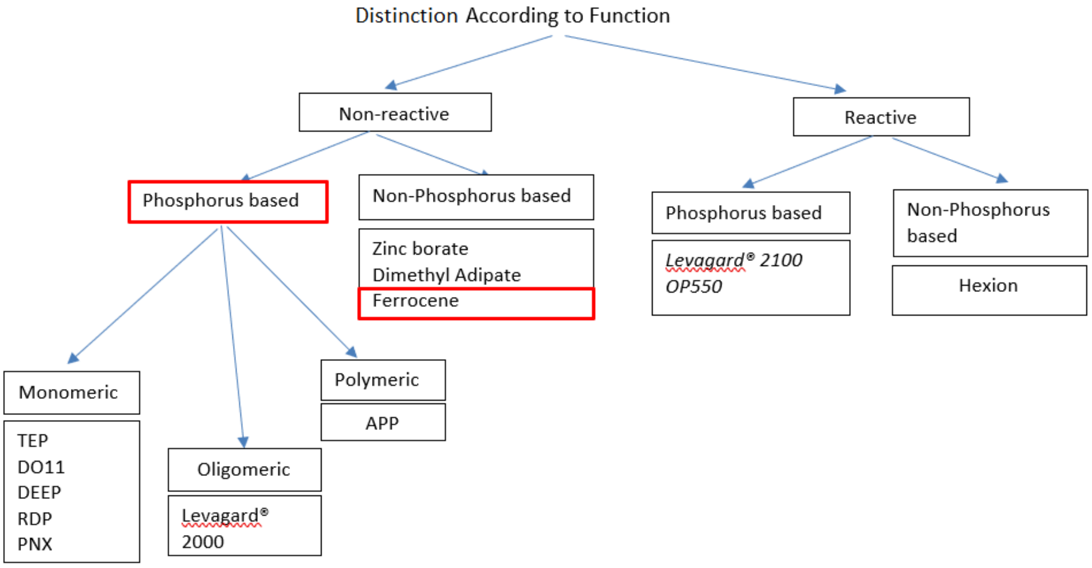


Figure 4.17 : Classification and selection of CMs for part 4.2.2.

First set of formulation with reference and Ferrocene

First exercise was completed by substuition of same weight of Zinc borate in the best performing formulation with Ferrocene. Formulations are re-scaled to 100% (Table 4.12).

Table 4.12 : Formulation re-scaled to 100%.

	PIR2.2	**PIR2.7**
Polyol blend	75.7	75.7
TEP	14.1	14.1
Firebrake ZB	10.2	0
Ferrocene	0	10.2
Sum	100	100

Reaction to fire performance analysis

DIN 4102 flame height results of first experiments with Fc

2 samples were compared with regards to flame height performance (Figure 4.18).

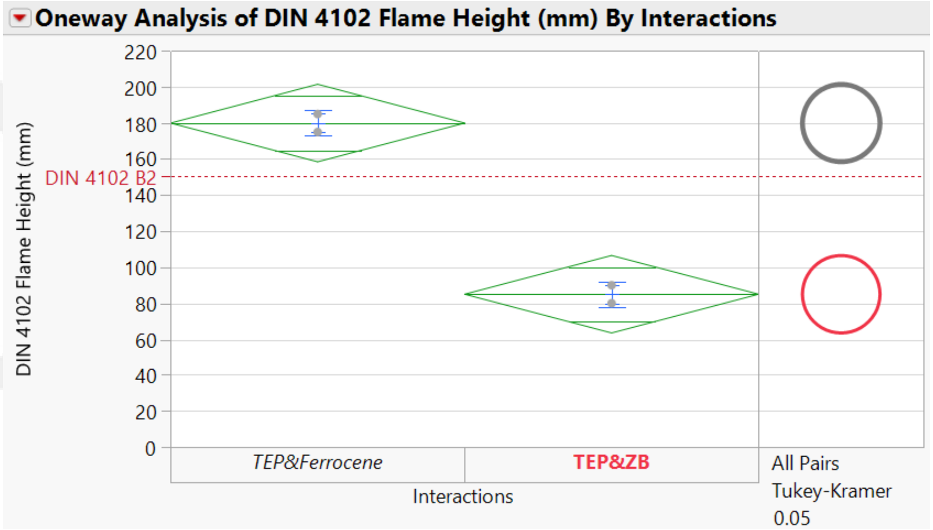


Figure 4.18 : DIN 4102 test results.

The foam incorporating Fc at the same wt.-% concentration of ZB burned vigorously. Consequently, a screening was carried by changing the Fc content in PIR formulation.

4.2.2.1 Ferrocene screening

In order to find the threshold for the flammability of PIR foam (compliance with DIN4102 test) when Ferrocene incorporated, a screening study should have been carried out with different levels of Fc loading. 5 identical polyol blend with same amount was prepared, and every time only Ferrocene loading was changed. The sum of polyol blend was re-sclaed to 100 as in Table 4.13. Formulations were coded from PIR2.71 to PIR2.75.

Table 4.13 : Same Polyisocyanurate formulation including different Fc loading (wt.% with respect to polyol blend).

	PIR2.71	**PIR2.72**	**PIR2.73**	**PIR2.74**	**PIR2.75**
Polyol	83.75	83.0	81.8	80.5	79.4
TEP	15.5	15.5	15.2	15.0	14.8
Ferrocene	0.75	1.5	3.0	4.5	5.8
Sum	100	100	100	100	100

DIN 4102 test was repeated with new samples obtained from these 5 formulations.

Reaction to fire performance analysis with Fc screening

DIN 4102 flame height

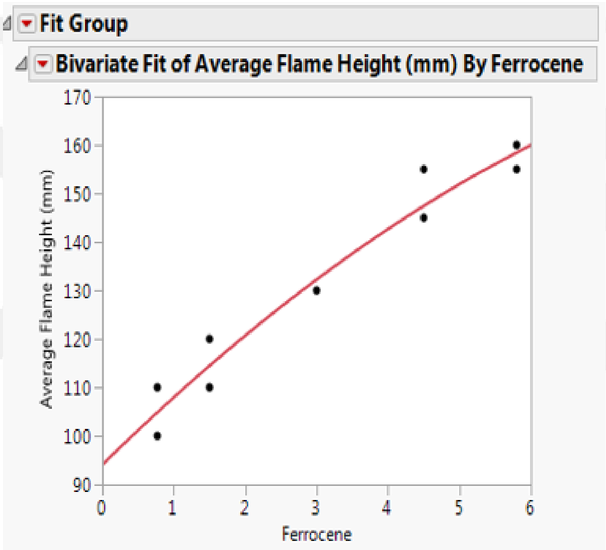


Figure 4.19 : DIN 4102 test results for different level of Fc incorporation (Fc% level-flame height mm).

A positive correlation was detected between the flame height and the amount of Ferrocene in PIR foam as illustrated in Figure 4.19. Introduction at a level higher than 5% of Fc, the selected system goes out of compliance to DIN 4102 B2 performance requirement of max. 150 mm flame height; values up to 4 wt.-% were used for further tests.

Smoke density

DsMax values, obtained in a ASTM E662 smoke chamber, are reported vs. the Fc load in the foam (wt.-%). Results are reported in Figure 4.20:

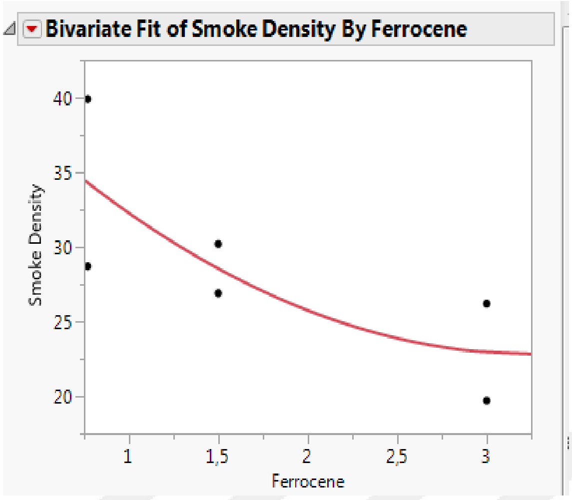


Figure 4.20 : Smoke opacity results for Fc (% by polyol wt) screening study.

On the contrary of what was observed with flame height increment, the higher the amount of Fc in the foam results in a lower smoke opacity value; this is a positive result confirming previous studies. With this finding, it can be concluded that the amount of Fc in the system should be limited to a maximum of 3% by polyol weight.

4.2.2.2 Two and three combustion modifier combinations

Aligned with the previous findings, below formulations were prepared (Table 4.14). The content of Ferrocene set at 4 parts by weight. Each compound is reported with its actual weight in grams:

Table 4.14 : Formulations and reactivity.

	PIR2.8	PIR2.9	PIR2.10	PIR2.11	PIR3.6	PIR3.7
Polyol	96	96	96	96	96	96
n-Pentane	12.85	12.85	12.85	12.85	12.85	12.85
TEP	20.27				10	10
APP		20.27				10.27
DO11			20.27			
Levagard 2000				20.27	10.27	
Ferrocene	4	4	4	4	4	4
Reactivity						
Cream time (s)	15-20	17-21	21-25	17-20	20-24	16-18
Gel time (s)	69-72	80-85	85-89	75-80	83-87	75-79
Free rise density (kg/m^3)	34.3	36.1	36.9	33.4	32.1	33.6

A significant deceleration in reactivity was detected for the formulations of:

- PIR2.9 (APP&Ferrocene)
- PIR2.10 (DO11&Ferrocene)
- PIR3.6 (TEP&Levagard 2000&Ferrocene)

No effects on the density were detected, with all the foams displaying values in the range of 34-37 g/L.

Regarding kinetics, a possible explanation of the experimental evidence of Table 4.14, is that TEP is a low-viscosity substance enhancing the mobility (and consequently reaction kinetics) of molecules in the polyol blend. This may explain well the decrease in reactivity going from PIR2.8 (TEP&Fc alone), to PIR3.7 (TEP&Fc&APP).

Reaction to fire performance analysis of two & three compound combinations

DIN 4102 flame height

6 foams were exposed to small scale flame test and results are shown in Figure 4.21:

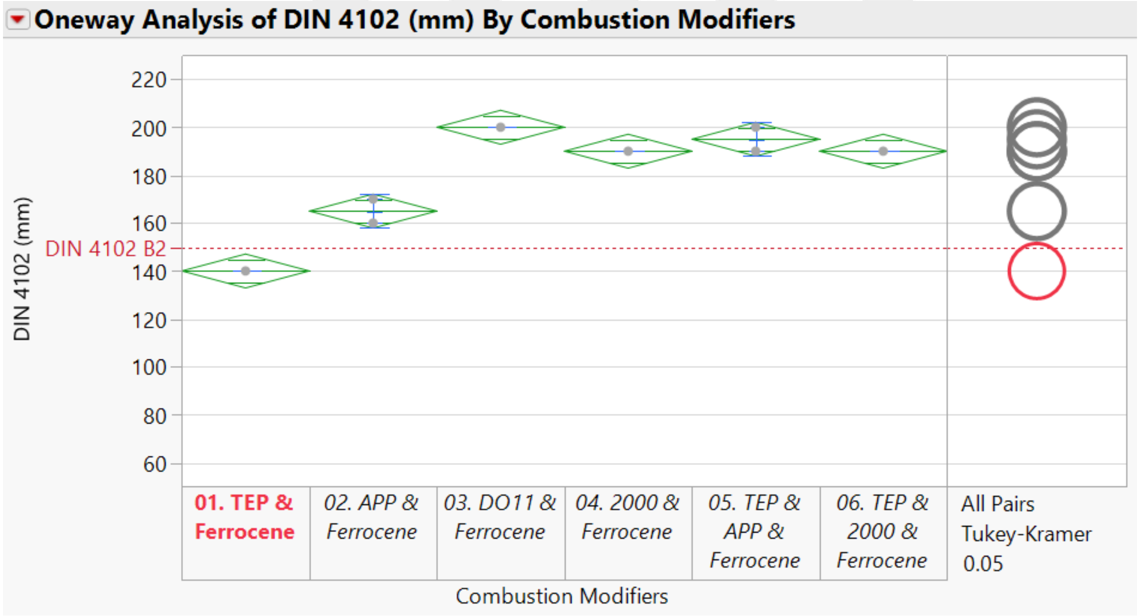


Figure 4.21 : DIN 4102 results for Fc incorporated formulations.

Found threshold value of Fc for PIR2.8 (TEP & Ferrocene combination) is not working for other combinations of CMs with regards to DIN 4102 B2 compliance requirement.

It is also verified that, reaction to fire performance cannot be only judged by P% content in final polymer but rather it is strongly impacted by the incurred synergism/antagonism of the selected CMs in the formulation. In order to find out workable Fc level, dedicated screenings (e.g. Design of Experiments) should be conducted for each interaction.

Comparative study for Triethyl phosphate-Zinc borate and Triethyl phosphate-Ferrocene

Obtained results proved that most effective combinations are PIR2.2 (TEP&ZB combination) and PIR2.8 (TEP&Ferrocene). In order to understand how addition of ZB as well as Fc in the polyol mixture is impacting the FRD and reactivity, a comparative study was carried out (Table 4.15):

Table 4.15 : Comparison PIR2.2 and PIR2.8 formulations; focus on reactivity.

	PIR1.1	**PIR2.2**	**PIR2.8**
	TEP	**TEP&ZB**	**TEP&Fc**
Polyol	96	96	96
n-pentane	12.85	12.85	12.85
TEP	34.64	20.27	20.27
Zinc Borate		14.67	
Ferrocene			4.00
Reactivity			
Cream time (s)	18-21	11-14	15-20
Gel time (s)	69-72	70-72	69-72
Free rise density (kg/m³)	32.7	36.1	34.3

Although the reactivity values are similar, there is a certain difference between the free rise density of the formulations. Incorporation of either ZB or Fc, in particular in absence of part of the TEP, leads to an increment of the FRD explained by the higher specific gravity of said solid compounds.

Reaction to fire performance

DIN 4102 flame height

Results of 3 foams were compared with JMP analysis in Figure 4.22:

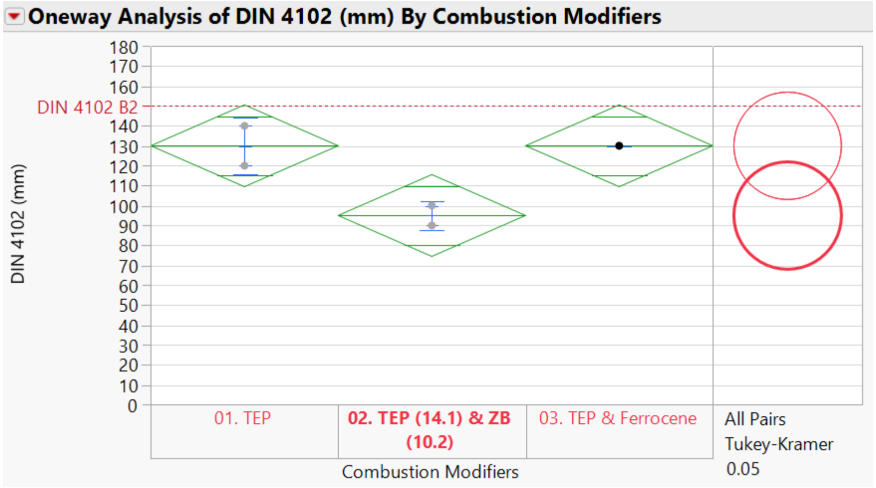


Figure 4.22 : DIN 4102 test results.

Statistically, no significant difference was reported between the flame height of the foams. Anyhow, foam PIR2.2 confirmed the lowest values.

Smoke opacity

Smoke opacity results are illustrated in Figure 4.23:

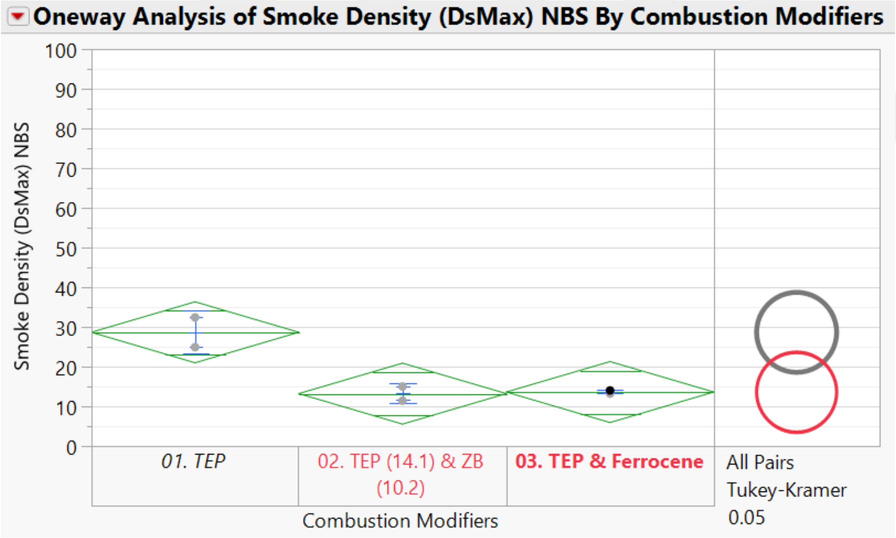


Figure 4.23 : Smoke opacity results via ASTM E662.

Both formulations that contain either ZB or ferrocene differentiated their performance significantly than the reference one, and are not statistically different from each other. As previously confirmed, reaction to fire performance is not a direct result of P% content in the formula; synergism also plays a role.

4.2.3 Reactive flame retardants and Zinc borate combinations

Previous parts of this study focused on highlighting the interactions between non-reactive CMs in the selected PIR system. This part, instead, reviews the synergism between reactive (either phosphorus or non-phosphorus based) combustion modifiers and smoke suppressants (ZB or Fc).

After a research of commercially available reactive CMs, 3 candidates were found to be suitable for the validation in rigid PIR/PUR formulations. Selected candidates are marked under the red box in Figure 4.24 (Reactive CMs).

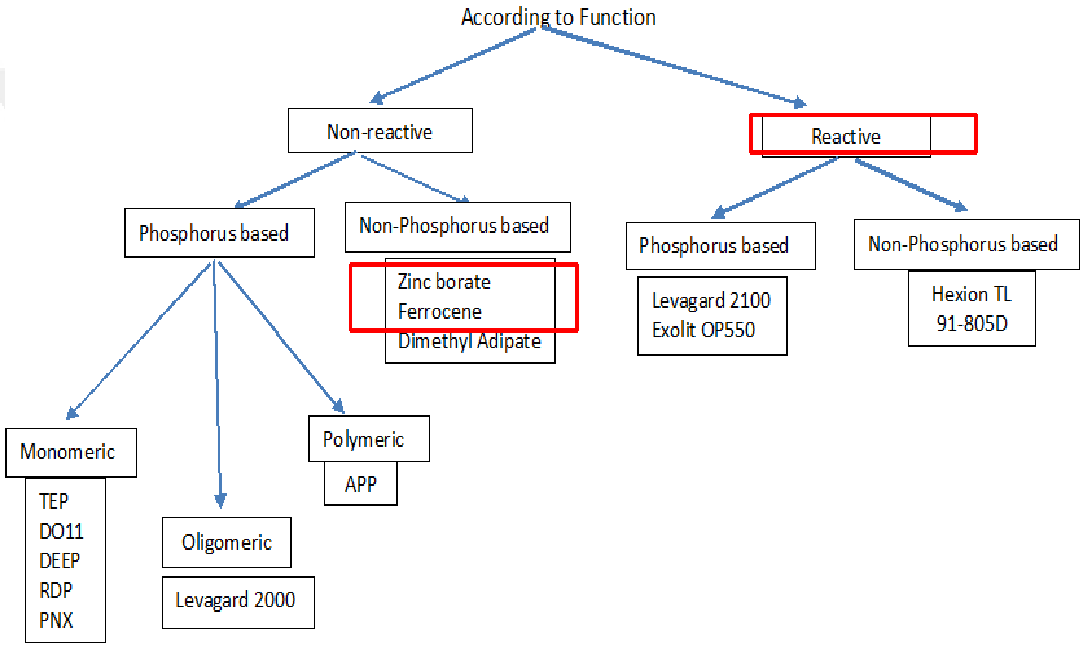


Figure 4.24 : Classification of CMs and selected ones for part 4.2.3.

In the first experimental campaign with reactive fire retardants, the target is to evaluate the same amount of FRs added to formulations including always the same amount of ZB in the reference formulation. This strategy was chosen as it is not possible to have the same P wt.-% or molar content due to Hexion TL 91-805D polyol non phosphorous structure. Table 4.16 summarizes first set of formulations.

Table 4.16 : First set of formulations with ZB (in gr).

Components	OH nr (Mg KOH/g)	PIR2.2 (ref)	PIR2R1	PIR3R1	PIR3R2	PIR3R3	PIR3R4
Polyol		96	96	96	96	96	96
n-pentane		12.85	12.85	12.85	12.85	12.85	12.85
TEP		20.27		10.00	10.00	10.00	
Levagard 2000							10.00
DEHP (Levagard 2100)	310		20.27	10.27			10.27
Exolit OP 550	170				10.27		
Hexion TL 91-805D	460					10.27	
FB ZB		14.67	14.67	14.67	14.67	14.67	14.67
Sum		144.00	144.00	144.00	144.00	144.00	144.00

The quantity of the components reported in Table 4.14 displays the exact weight (g) of the ingredients that was used to prepare free-rise foams. Additionally, index of each formulation was kept constant to avoid the impact of different trimer content in the final foam.

Reaction to fire performance analysis

DIN 4102 flame height results

Figure 4.25 compares the performance of reactive FRs when added together with Zinc Borate in the formulations.

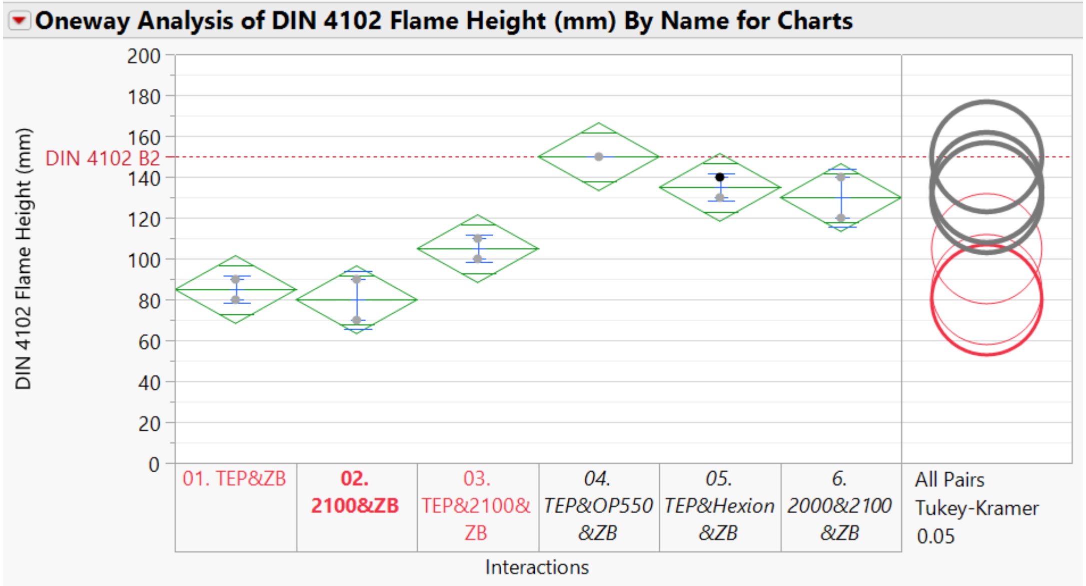


Figure 4.25 : DIN 4102 test results.

A similar result to the one of TEP / ZB combination (reference, PIR2.2) was obtained when DEHP (Levagard 2100) is used (PIR2R1 and PIR3R1).

Exolit OP550 (PIR3R2) and Hexion (PIR3R3) did not offer a competitive performance with respect to PIR2.2 and displayed borderline performance: below 15 cm of flame spread, the test is not considered as passed.

Albeit acceptable (< 150 mm flame spread), the substitution of TEP with Levagard® 2000 (PIR3R4) does not provide any benefit with respect to its reference (PIR2R1).

Smoke density

NBS results are reported in Figure 4.26:

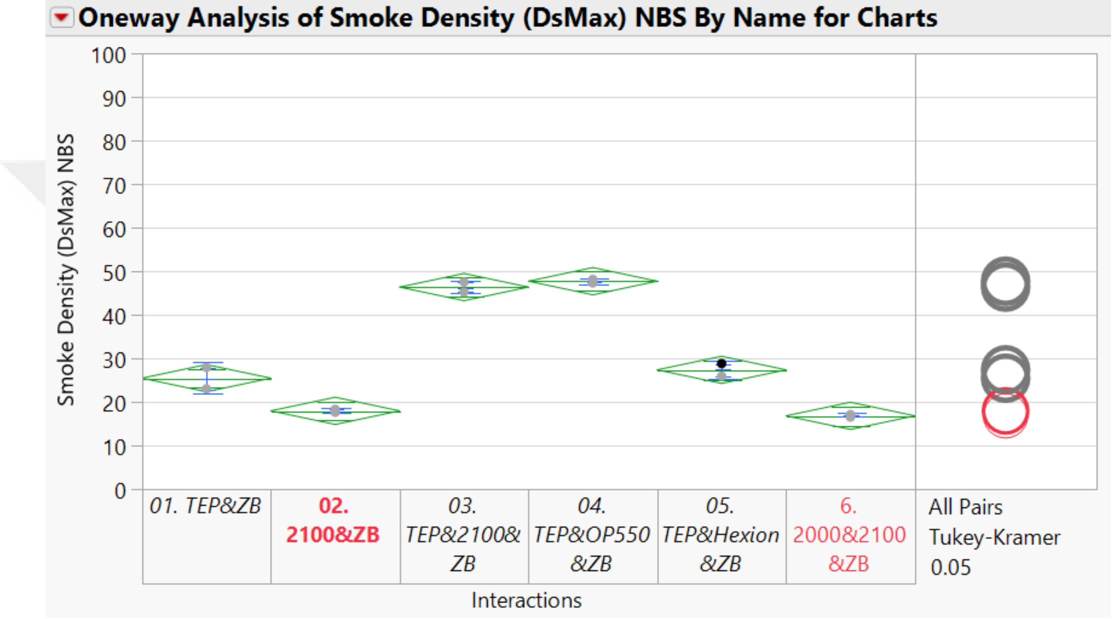


Figure 4.26 : NBS results.

Best performance was obtained with formulations PIR2R1 and PIR3R4 of Table 4.16, that is, Levagard® 2100 and mixture of Levagard 2100 with Levagard 2000.

However, the impact of the resulting foam density was not considered for this analysis and needs to be repeated in the next studies. Density is known to have a marked impact on the NBS chamber DsMax.

4.2.4 Reactive flame retardants and Ferrocene combinations

Previous screening exercise was repeated with Fc instead of ZB.

As previously reported, the increment in the amount of Fc in the formulation led a high degree of flammability (increase of flame spread during DIN 4102 test) and, at the same time, an improved smoke performance. Therefore, in the reference system, the quantity of Fc was set at the maximum possible to minimize the smoke generation while maintaining DIN 4102 B2 classification (<150 mm flame spread). The purpose was to start from the best possible result achievable with Fc. Starting formulations are reported in Table 4.17:

Table 4.17 : Second set of formulations with Fc (actual amount in grams).

Components	OH nr	PIR2.2 (ref)	PIR2R2	PIR3R5	PIR3R6	PIR3R7	PIR3R8
Polyol		96	96	96	96	96	96
n-pentane		12.85	12.85	12.85	12.85	12.85	12.85
TEP		20.27		10.00	10.00	10.00	
Levagard 2000							10.00
	310		20.27	10.27			10.27
Exolit OP 550	170				10.27		
Hexion TL 91-805D	460					10.27	
FB ZB Ferrocene		4.00	4.00	4.00	4.00	4.00	4.00
Sum		134	134	134	134	134	134

Total sum of the reactive mixture is minor due to the limited amount of use of Fc. Nevertheless, as the isocyanate-reactive groups amount remains constant, index and added isocyanate equivalent weight remains constant as well.

Reaction to fire performance analysis

DIN 4102 flame height results

Figure 4.27 displays the flame height results of reactive compounds in PIR foam:

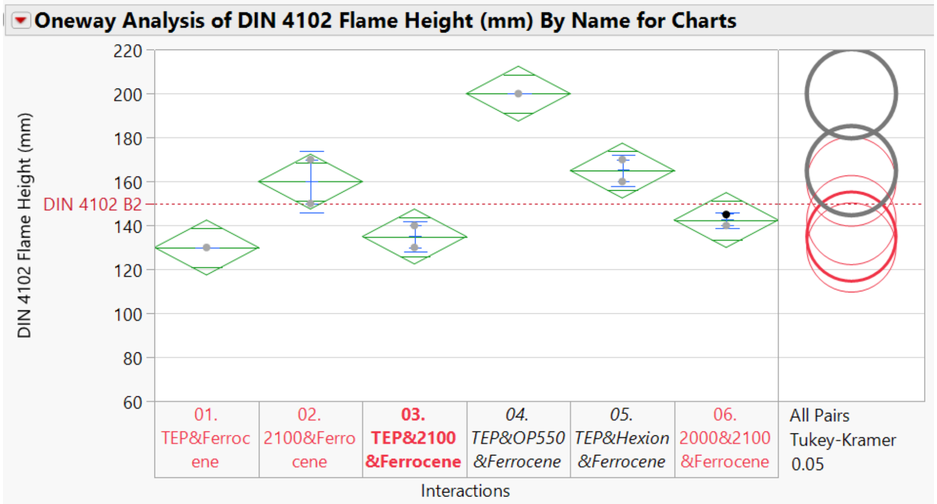


Figure 4.27 : DIN 4102 results for the second experimental campaign.

Only PIR3R5 and PIR3R8 combinations displayed less than 150 mm of flame spread in the DIN 4102 B2 test.

Exolit OP550 and Hexion TL91-805D were eliminated from further screening due to the poor reaction to fire performance in the selected PIR system.

Smoke density results

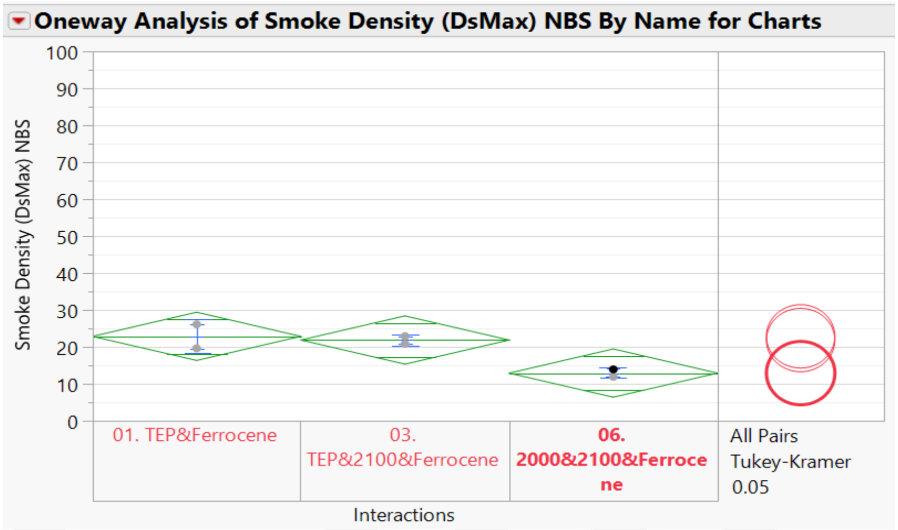


Figure 4.28 : NBS results for second set experiments.

While there is no statistical difference detected in the results, it was observed that PIR3R8 (a combination of 2000/2100/Fc) provided a certain improvement in the performance as seen in Figure 4.28.

In principle, the two formula PIR3R5 and PIR3R8 display a reaction to fire overall performance similar to the reference PIR2.2, with a possible advantage in terms of smoke opacity in the case of PIR3R8.

4.2.5 Replication study of best performing formulations

In the previous chapters of this study, most effective CMs were determined by hand-mix activities in a reference PIR system.

In this part, a replication study for the formulations that contain high performing CMs (red boxes in Figure 4.29) in at least one of the areas of reaction to fire performance criteria (flame height, smoke density) was carried out. Target is to draw a conclusion for the performance of candidates under same operation conditions, at the same time.

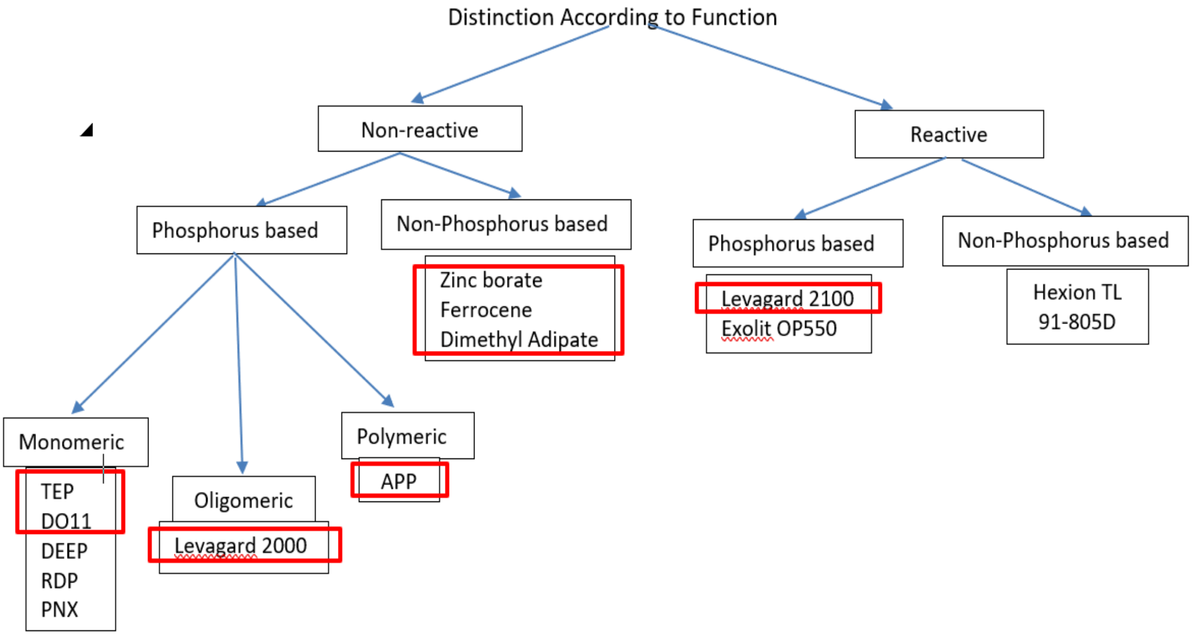


Figure 4.29 : Main classification of CMs used in study, red boxes are replications in this part.

In parallel to the reaction to fire performance screening, reactivity and free rise density of the foams were studied in details. Even if many considered CMs are not reactive towards isocyanate, some of the candidates are impacting reactivity profile and free rise density.

In order to deliver accurate and comparative results, below variables were maintained at the same level:

- Molded density (38-40 kg/m^3): aligned with previously proposed tolerance range: < 8%
- Fc% in final foam, when present
- P% in final foam

Prepared foams were lately shipped to external laboratory for cone calorimeter analysis.

4.2.5.1 Replication experiments with Zinc borate

The target of the first set of experiments was to highlight effects on reactivity and free rise density of foams incorporating the CMs under same conditions.

11 formulations were prepared using one, two and three compound combinations. A generic formulation that was used to prepare the blends with ZB was prepared as follows in Table 4.18:

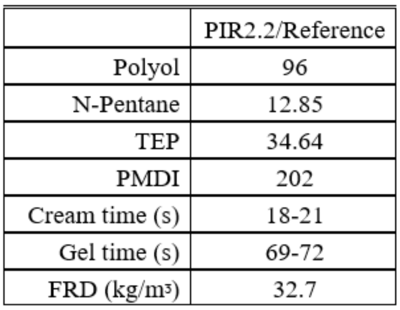
Table 4.18 : Formulations made with ZB (actual weight in grams).

Components	One CM addition	2 CM addition	3 CM addition
Polyol	96.00	96.00	96.00
n-pentane	12.85	12.85	12.85
CM-1	34.64	20.27	10.00
CM-2	-	-	10.27
Zinc borate	-	14.67	14.67
Sum	144	144	144

Full set of formulations can be found in appendix.

As a first activity, FRD and reactivity data were reported for the formulations in object (see in Table 4.19).

Table 4.19 : PIR2.2 (reference) reactivity and FRD.



	PIR2.2/Reference
Polyol	96
N-Pentane	12.85
TEP	34.64
PMDI	202
Cream time (s)	18-21
Gel time (s)	69-72
FRD (kg/m³)	32.7

In order to determine the impact of each single CM and their 2nd and 3rd degree interactions on reactivity as well as FRD of the resulting foam, deviations from the reference data points are proposed to be reported as in Table 4.20 for a meaningful and simplified outcome. Arrow directions represen the inclination or declination from the reference system.

Table 4.20 : Tolerance range for reactivity and FRD based on PIR2.2 reference system.

± 0-8%	± 8-15%	±15 - 25%	< 25% or > 25%
=	↑ or ↓	↑↑ or ↓↓	↑↑↑or ↓↓↓

Table 4.21 summarizes the impact of the interactions on reactivity and FRD of the formulations that contain Zinc borate as smoke suppressant:

Table 4.21 : Impact of 2 and 3 combustion modifier combination on foam reactivity and FRD.

	Formulations	Reactivity		Free Rise Density
Combinations		Cream time	Gel time	Free Rise Density
ZB	PIR1.2	↓	↑	↑↑
TEP/ZB	PIR2.2	↓↓	=	↑
TEP/ZB/APP	PIR3.4	=	↑↑	=
ZB/APP	PIR2.3	=	↑↑	=
ZB/2100	PIR2R1	↓↓	↓↓↓	↑↑↑
TEP/ZB/DO11	PIR3.3	↑↑	↑↑↑	↑↑↑
ZB/DO11	PIR2.6	↑↑	↑↑↑	↑↑↑
TEP/ZB/2000	PIR3.5	↓	=	↑↑
ZB/2000	PIR2.5	=	=	↑↑
ZB/2100/2000	PIR3R4	↓↓↓	↓↓	↑

- ✓ Introduction of ZB in PIR foams leads to a reduction in cream time, increase in gel time and an increment in FRD. This increase of FRD can be associated to ZB being an inert solid.
- ✓ APP presence causes a longer gel time (PIR3.4, PIR2.3). On the other side, it compensates the impact of the increase in FRD that is brought by ZB.
- ✓ Levagard 2100 (DEHP, PIR2R1) has a strong effect on the foam. While cream and gel times decrease significantly, free rise density increases.
- ✓ DO11 (PIR3.3, PIR2.6), leads to a decrease in reactivity and at the same time a remarkable increment in the FRD.
- ✓ Levagard 2000 (oligomeric TEP) (PIR3.5, PIR2.5, PIR3R4) has a minor impact on the cited properties compared to other CMs. When used together with Levagard® 2100, the effects of the latter prevail.

Reaction to fire analysis with Zinc borate interactions

DIN 4102 flame height

Figure 4.30 summarizes the performance of formulations containing ZB:

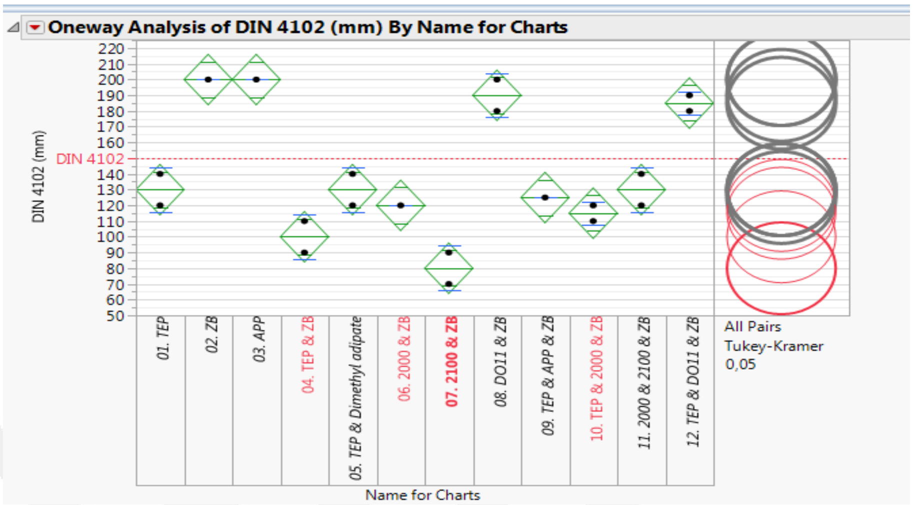


Figure 4.30 : DIN 4102 results, Zinc borate.

In this case, there are several formulations which respect the DIN 4102 B2 compliance. More significantly, there are 4 set of formulations that highlight a certain synergistic effect:

- PIR2.2 (TEP/ZB)
- PIR2.5 (Levagard 2000/ZB)
- PIR2R1 (Levagard 2100/ZB)
- PIR3.5 (TEP/Levagard 2000/ZB)

NBS smoke chamber analysis

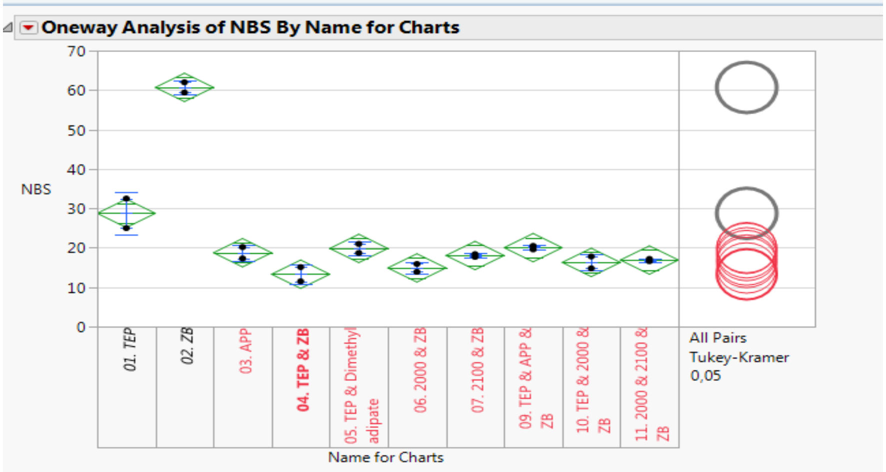


Figure 4.31 : Smoke density results, Zinc borate.

Figure 4.31 reports the smoke density results of the PIR formulations containing ZB. In terms of smoke density, results are very similar to each other excluding the reference (PIR2.2) and formulation based only on ZB (PIR1.2).

This is an additional confirmation that ZB itself is not providing an improvement for reaction to fire performance but when used in conjunction with other CMs, it is creating a synergistic impact.

4.2.5.2 Replication experiments with Ferrocene

In Table 4.22, the formulation approach with Fc is reported:

Table 4.22 : Formulations incorporating Fc (in grams).

Components	2 CM addition	3 CM addition
Polyol	96	96
n-pentane	12.85	12.85
CM-1	20.27	10
CM-2		10.27
Fc	4	4
Sum	134	134

Full set of formulations can be found in appendix.

Table 4.23 displays interactions with Fc and the outcome of reactivity and free rise density of the resulting foams:

Table 4.23 : Impact of 2 and 3 combustion modifier combination on foam reactivity and FRD.

Interactions	Formulations	Cream time	Gel time	Free Rise Density
TEP/dimethyl adipate	PIR2.1	=	=	↑
TEP/Fc	PIR2.8	↓	=	=
Fc/APP	PIR2.9	=	↑↑	↑
Fc/2100	PIR2R2	↓↓↓	↓↓↓	↑
Fc/DO11	PIR2.10	↑↑	↑↑	↑↑↑
TEP/Fc/2100	PIR3R5	=	↑	=
Fc/2000	PIR2.11	=	↑	=
TEP/Fc/2000	PIR3.6	↑	↑↑	=
TEP/Fc/APP	PIR3.7	=	↑	=
Fc/2100/2000	PIR3R8	↓↓	↓↓↓	↑

- ✓ Introduction of Fc at this quantity (PIR2.8) has little to no impact on reactivity parameters nor density.
- ✓ Ferrocene and APP dual interaction lengthens gel time as well as increases FRD (PIR2.9 and PIR3.7).
- ✓ Ferrocene is almost able to compensate for the density increase that is brought by Levagard 2100, but not the delay in reactivity (PIR2R2 and PIR3R8 together with Levagard® 2000 display very long cream and gel time).

Reaction to fire analysis with Ferrocene interactions

DIN 4102 flame height

Figure 4.32 represents the flame height results of the PIR foams containing Fc.

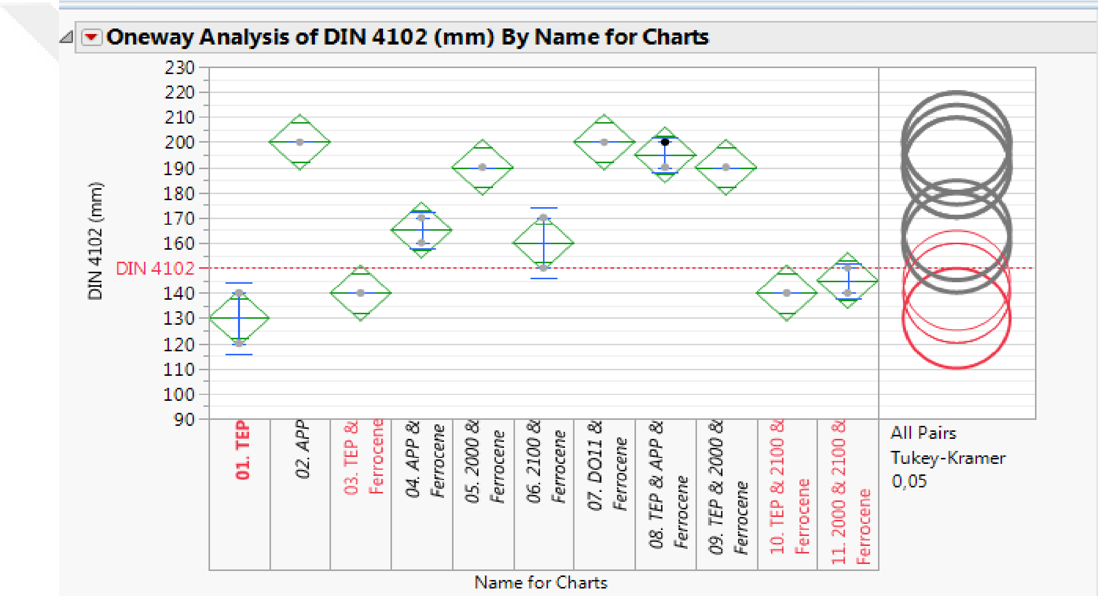


Figure 4.32 : DIN 4202 B2 results on Ferrocene-embedding foams.

As confirmed in previous exercises, a high amount of Fc makes foams more prone to ignition.

Nevertheless, for this study, the quantity was determined as 4 pbw since it was to some degree lower than the threshold for DIN 4102 B2 performance for the reference – mod1.

Results show that this quantity would be even higher for the majority of the formulations in which it is added as a second or third CM. Only four foams are compliant with the 150 mm requirement of the small scale flame test.

For each formulation, a dedicated study of Fc incorporated amount should be carried out.

NBS smoke chamber results

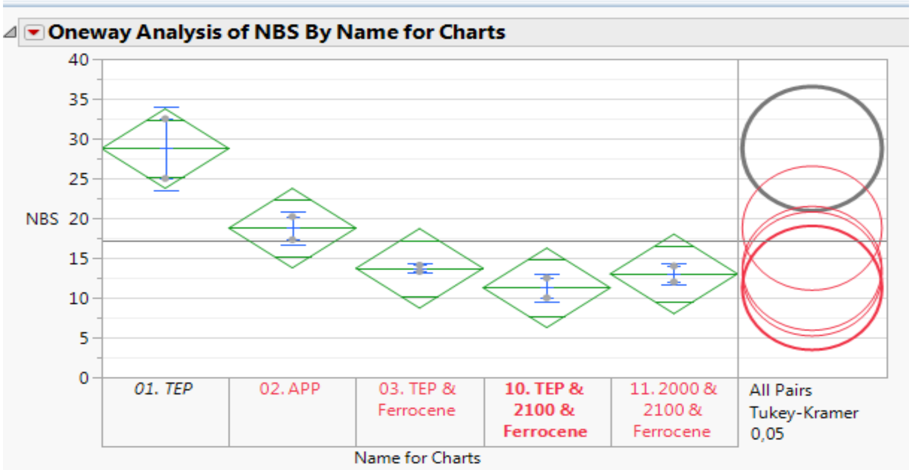


Figure 4.33 : NBS results, Fc.

For the foams that are in compliance with DIN 4102 B2 requisitions, NBS smoke analysis was performed and results are displayed in Figure 4.33.

Despite its highly flammable character, Fc provided a significant improvement in smoke reduction.

In parallel to the comparison of the same amount of CMs in the formula, a new approach was prepared based on equal P% content in the foam; this new approach is is described in the part of cone calorimeter studies.

4.2.5.3 Overall evaluation of Zinc borate and Ferrocene replication study

Impact on reactivity and free rise density

For a better understanding of the impact of ZB and Fc interactions in the foam, a comparative table is prepared as below (Table 4.24):

Table 4.24 : ZB and Fc behavior characterization with respect to reference (only TEP containing foam-PIR1.1).

	ZB			Fc		
	Cream time	**Gel time**	**FRD**	**Cream time**	**Gel time**	**FRD**
TEP	↓↓	=	↑	↓	=	=
APP	=	↑↑	=	=	↑↑	↑
2100	↓↓	↓↓↓	↑↑↑	↓↓	↓↓	↑
DO11	↑↑	↑↑	↑↑↑	↑↑	↑↑	↑↑↑
2000	=	=	↑↑	=	↑	=
TEP/APP	=	↑↑	=	=	↑	=
TEP/2000	↓	=	↑↑	↑	↑↑	=
2100/2000	↓↓↓	↓↓	↑	↓↓	↓↓↓	↑

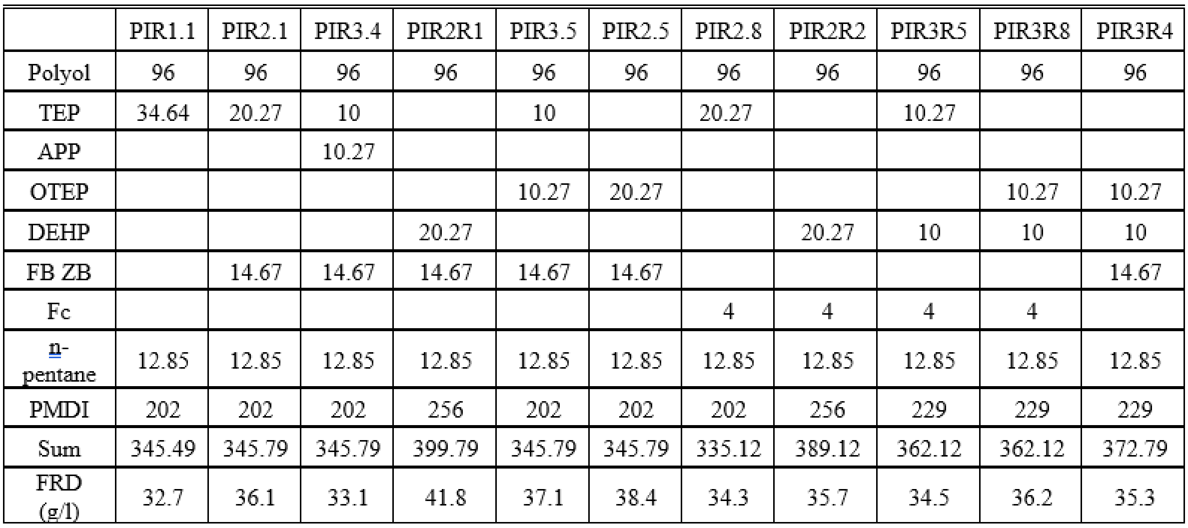
Levagard® 2000 behaves differently in presence of ZB (reactivity remains substantially the same) and Fc (gelation occurs later). In any case, both with ZB and Fc, when Levagard® 2000 is used jointly with Levagard® 2100, the accelerating effect of the latter additive prevails and the foam is much faster in reactivity. It may be possible that some interaction in the liquid phase between the two reactants (2000 and Fc) occurs, such as a complexation effect.

With regards to the density increment thanks to the incorporation of solid combustion modifiers, a study from the author revealed a similar outcome. A possible explanation for this situation might be that during the formation of FR-RPUF foam cells, solid additive particles may act as heterogeneous nucleation sites, resulting in foam cell size decrease and density increase. The addition of solid inorganic fire-retardant partly inherited the expansion of the foam. The physical and chemical interaction between the surface of solid fire-retardants with the additives in the polyol was possible. Inorganic fire retardants may adsorb a part of the catalysts and the water during the mixing. The generated heat during foam formation may also be adsorbed by the inorganic fire-retardant and rise in the internal temperature of foam comparable lower; thus, the expansion rate of the foam is lower [86]. Therefore, it would be convenient to expect an increment in the free rise density of RPUF when working with solid FRs. In this study, the only FR that is proving a reverse conclusion is Ammonium Polyphosphate. In the formulations where APP is present, a reduction in the density is detected. This finding should be investigated in deeper in the next studies.

4.3 Sample Preparation for Cone Calorimeter

Replication studies were completed to confirm the performance of previously found laboratory results with regards to reaction to fire performance. For cone calorimeter analysis, best formulations among replication studies were selected to continue. 10 formulations proved to perform better than the reference PIR1.1 (based on only TEP as a CM). Table 4.25 summarizes best formulations obtained with replication studies.

Table 4.25 : Best formulations obtained from replication studies (actual weight in grams).



	PIR1.1	PIR2.1	PIR3.4	PIR2R1	PIR3.5	PIR2.5	PIR2.8	PIR2R2	PIR3R5	PIR3R8	PIR3R4
Polyol	96	96	96	96	96	96	96	96	96	96	96
TEP	34.64	20.27	10		10		20.27		10.27		
APP			10.27								
OTEP					10.27	20.27				10.27	10.27
DEHP				20.27				20.27	10	10	10
FB ZB		14.67	14.67	14.67	14.67	14.67					14.67
Fc							4	4	4	4	
n-pentane	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85
PMDI	202	202	202	256	202	202	202	256	229	229	229
Sum	345.49	345.79	345.79	399.79	345.79	345.79	335.12	389.12	362.12	362.12	372.79
FRD (g/l)	32.7	36.1	33.1	41.8	37.1	38.4	34.3	35.7	34.5	36.2	35.3

As previously indicated, despite having the same amount of blowing agent in the formulations, free rise density of the foams are quite different. In the part 2, it was explained that foam density has an impact of smoke generation therefore this difference between foams should be minimized.

Additionally, until now, all the conducted studies were done based on same amount of combustion modifier in the formulation. At this point, it is substituted with P% in the foam as this will be a more valid point when comparing the final performance of the foams.

In order to make a fair comparison, 2 further studies were carried out:

- Equalizing molded density of the best performing formulations to avoid misleading smoke density results
- Equalizing total P% content in the foam to reveal the most effective interactions

4.3.1 Molded density adjustment

For cone calorimeter studies, a new nomination was selected which starts with mod1 and the rest was coded with mod and a code. Using reference formulation PIR1.1 (based on TEP) which is coded as mod1, an exercise was carried out to determine the reduction in free rise density through the addition of 1 g of extra blowing agent – (n-pentane, Figure 4.34):

	Mod1
Polyol blend	96
n-Pentane	12.85
TEP	34.64
PMDI	202
FRD (kg/m^3)	32.7

	Mod1 rev.
Polyol blend	96
n-Pentane	13.85
TEP	34.64
PMDI	202
FRD (kg/m^3)	31.3

Figure 4.34 : – n-pentane modification on the reference Mod1 formula.

1g of n-pentane addition leads approximately 1.35 kg/m^3 reduction in the FRD of the reference foam.

This information is used for the preparation of similar density foams.

4.3.2 P% adjustment in the foam

For what it concerns P% adjustment of the final foam, there are 3 variables to be considered:

- Quantity of total blowing agent present in the final foam – which is the most challenging as FRDs of each foam is different; nevertheless, above finding will be used as a reference for the first adjustment, and in case of big differences, exercise will be repeated with a required quantity of BA to achieve the right density.
- P% in the CMs – as there are 4 phosphorus-based FRs, in order to set a similar P quantity, an equation delivered below is to be used as in Table 4.26:

Table 4.26 : Equation used for the equivalent weight of P% in the foam.

	Mw	**P% content**	**Equalized P%**
TEP	182	17.0	x
APP		30.0	0.566x
Levagard 2100	168	18.4	0.924x
Levagard 2000		16.4	1.037x

- PMDI amount – For the formulations that contain reactive CM (in particular: Levagard 2100 (DEHP)), a higher amount of PMDI must be used to maintain the same index. In order to incorporate at the same time the same P%, a higher quantity of CM must be accordingly incorporated in the reaction mixture.

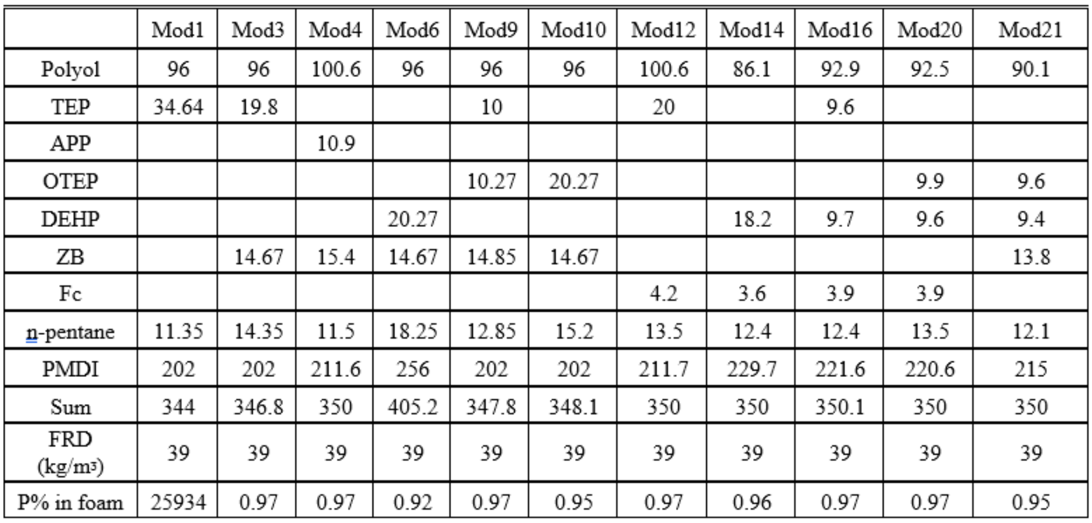
  With regards to P% content of reference formulation mod1, based on TEP, it was left as it is to demonstrate the impact of synergism of other formulations.

  Additionally, ZB% amount in the formulations is not adjusted as it is not flammable and to simplify the calculation and hand-mix process.

  Ferrocene amount is equalized in the foams as its real quantity is relevant to determine reaction to fire performance.

A complete data set for the selected formulations is shown in Table 4.27:

Table 4.27 : Re-organized formulations for cone calorimeter (actual weight in grams).



	Mod1	Mod3	Mod4	Mod6	Mod9	Mod10	Mod12	Mod14	Mod16	Mod20	Mod21
Polyol	96	96	100.6	96	96	96	100.6	86.1	92.9	92.5	90.1
TEP	34.64	19.8			10		20		9.6		
APP			10.9								
OTEP					10.27	20.27				9.9	9.6
DEHP				20.27				18.2	9.7	9.6	9.4
ZB		14.67	15.4	14.67	14.85	14.67					13.8
Fc							4.2	3.6	3.9	3.9	
n-pentane	11.35	14.35	11.5	18.25	12.85	15.2	13.5	12.4	12.4	13.5	12.1
PMDI	202	202	211.6	256	202	202	211.7	229.7	221.6	220.6	215
Sum	344	346.8	350	405.2	347.8	348.1	350	350	350.1	350	350
FRD (kg/m^3)	39	39	39	39	39	39	39	39	39	39	39
P% in foam	25934	0.97	0.97	0.92	0.97	0.95	0.97	0.96	0.97	0.97	0.95

For the preparation of the foams described in table 4.24, principles that were set at the beginning were respected:

- Molded density: 39 kg/m^3
- Fc% in final foam
- P% in final foam

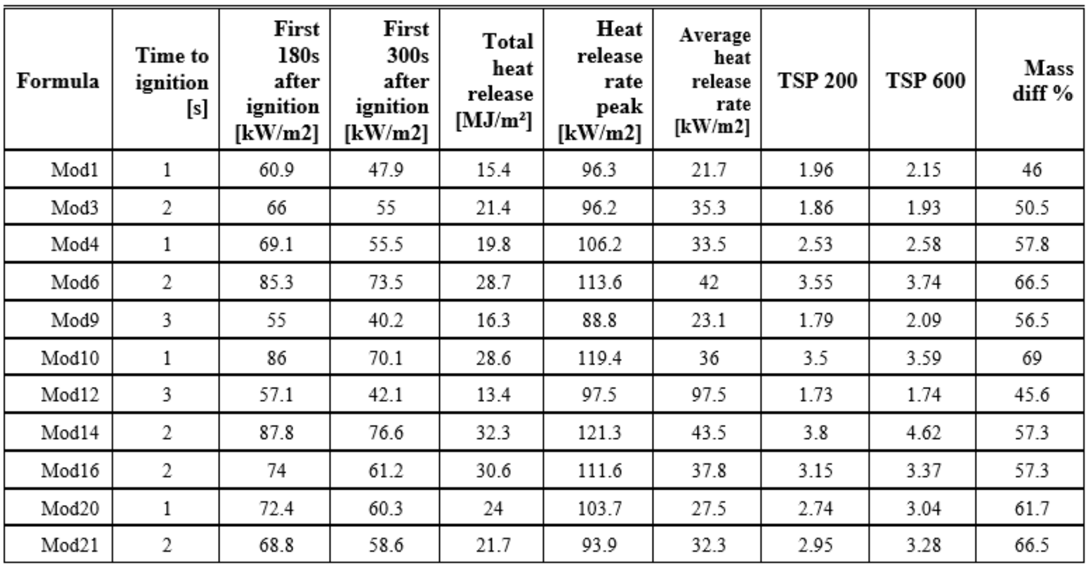
Selection Criteria is aligned with Combustion Modifiers Evolution Strategy which was described in a previous chapter (Figure 4.35).

Figure 4.35 : Combustion modifiers evolution strategy.

4.4 Cone Calorimeter Results

Cone calorimeter provided output for time to ignition, total heat release, heat release rate peak, average heat release, TSP 200, TSP 600 and mass difference. In Table 4.28, all the results are reported.

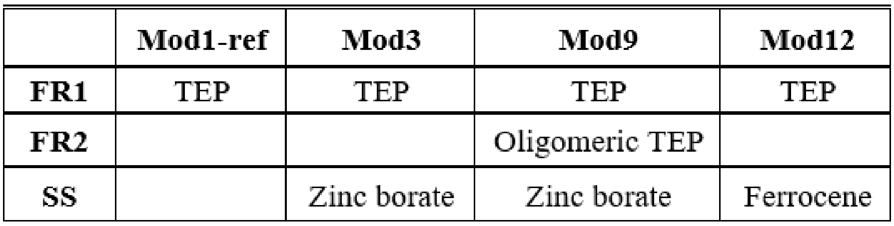
Table 4.28 : Cone calorimeter results for 11 formulations.



Formula	Time to ignition [s]	First 180s after ignition [kW/m2]	First 300s after ignition [kW/m2]	Total heat release $[MJ/m^2]$	Heat release rate peak [kW/m2]	Average heat release rate [kW/m2]	TSP 200	TSP 600	Mass diff %
Mod1	1	60.9	47.9	15.4	96.3	21.7	1.96	2.15	46
Mod3	2	66	55	21.4	96.2	35.3	1.86	1.93	50.5
Mod4	1	69.1	55.5	19.8	106.2	33.5	2.53	2.58	57.8
Mod6	2	85.3	73.5	28.7	113.6	42	3.55	3.74	66.5
Mod9	3	55	40.2	16.3	88.8	23.1	1.79	2.09	56.5
Mod10	1	86	70.1	28.6	119.4	36	3.5	3.59	69
Mod12	3	57.1	42.1	13.4	97.5	97.5	1.73	1.74	45.6
Mod14	2	87.8	76.6	32.3	121.3	43.5	3.8	4.62	57.3
Mod16	2	74	61.2	30.6	111.6	37.8	3.15	3.37	57.3
Mod20	1	72.4	60.3	24	103.7	27.5	2.74	3.04	61.7
Mod21	2	68.8	58.6	21.7	93.9	32.3	2.95	3.28	66.5

- ❖ Excluding reference mod1, although all the foams have a similar content of P% and molded density, there are 3 formulations that are performing better than reference at least in 3 criteria: mod3, mod9, mod12. That explains the fact that, apart from P% content, there are other factors that impact reaction to fire performance (e.g. synergism).
- ❖ Mod12 is confirming the best performance in almost all measures while it is the same for Mod14 on the negative edge of the bar.
- ❖ It is found that still not likely to fully replace TEP but a partial substitution is possible. Table 4.29 presents best performing formulations along with the reference (mod1)

Table 4.29 : CM composition of best performing formulations.



	Mod1-ref	**Mod3**	**Mod9**	**Mod12**
FR1	TEP	TEP	TEP	TEP
FR2			Oligomeric TEP	
SS		Zinc borate	Zinc borate	Ferrocene

- ❖ Mod 3 and mod 12 which contain only monomeric type of FR – TEP – likewise reference mod 1, confirmed a superior performance than mod1, which can be only explained by the synergic impact that was brought by smoke suppressants Zinc borate (ZB) and Ferrocene (Fc) with TEP. In particular, Mod12 is the only formulation that displays a lower THR than the reference, and also a lower smoke production overtime.
- ❖ Foams that contain polymeric or reactive type of FRs, are not able to exceed performance of the reference foam (e.g. mod4, mod6). On the other hand, while they do not display comparable results when used alone (mod10), oligomeric FR demonstrated a significant synergy when used with monomeric FR and TEP (mod9).

Reaction to fire performance comparison of the most effective approaches

Parameters such as heat release rate, total heat release, smoke production rate and mass loss versus time were investigated in details for the most effective formulations. Figure 4.33 displays the change in heat release rate versus time for 4 formulations; mod 1, mod 3, mod 9, mod 12.

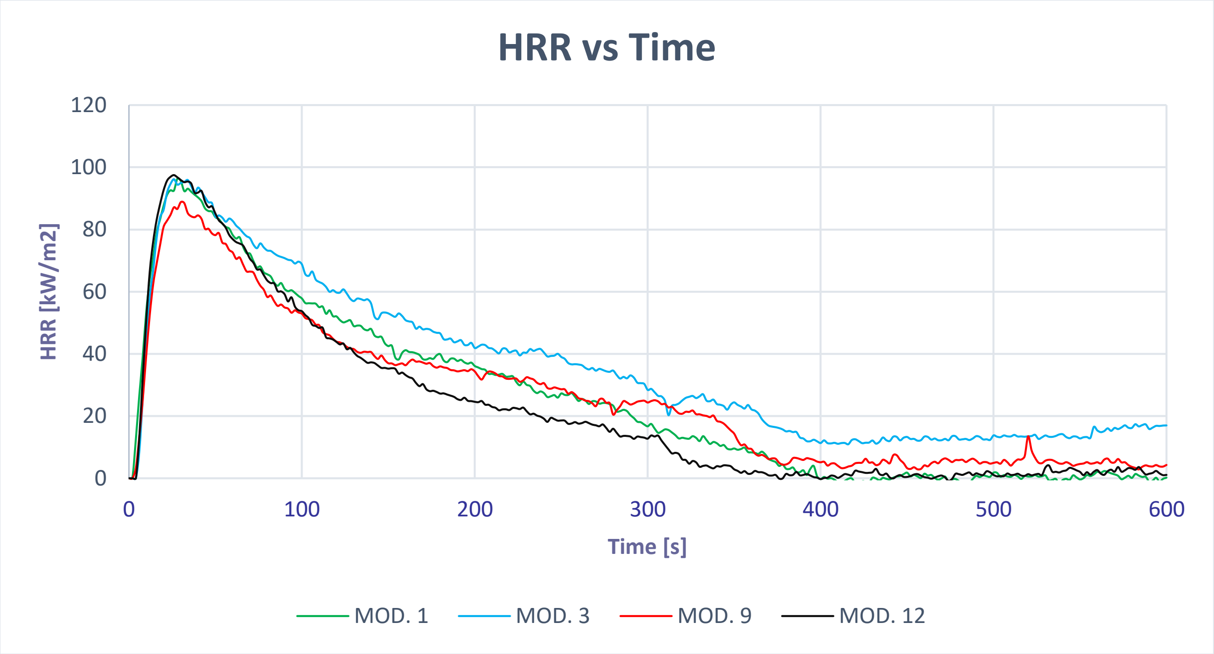


Figure 4.36 : Heat release rate vs time.

The heat release rate (HRR) value changed with time as in Figure 4.36. Mod 3, mod 9, and mod 21 had lower PHHR values than mod 1 and their HRR decreasing trends were similar. PHRR value is important in terms of the intensity of a fire. After about 30 seconds, the HRR value of all PIR foams started to decrease and reached to lowest values of about 0-10 kW/m^2 at about 400 seconds.

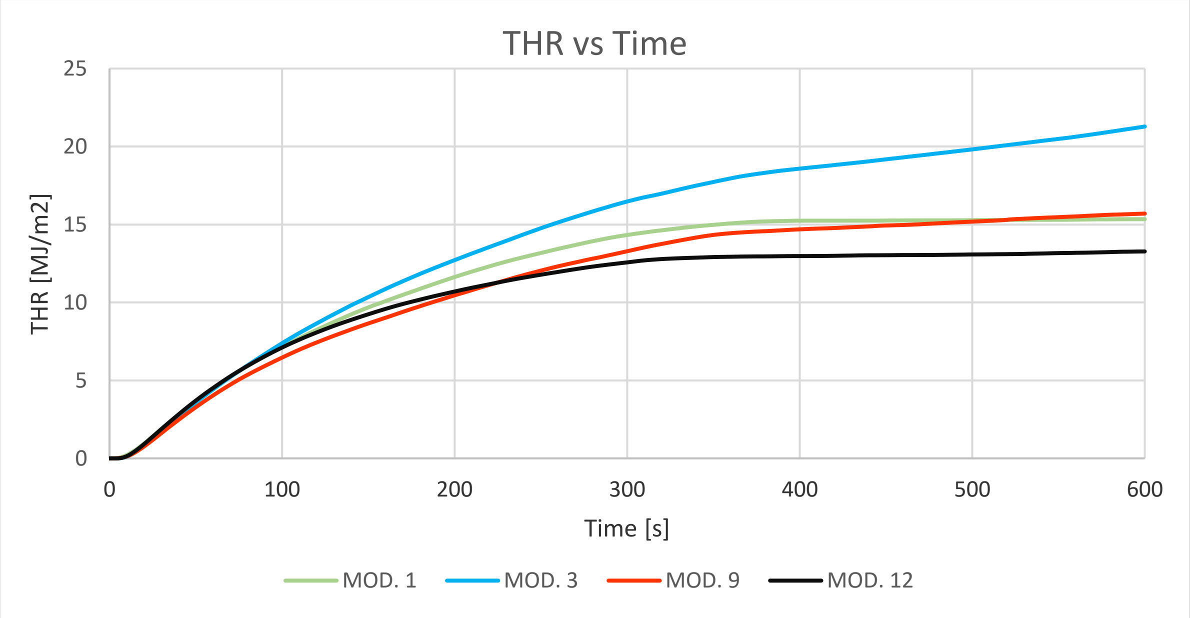


Figure 4.37 : Total heat release vs time.

The trends of THR changes were in Figure 4.37. Mod 1 and mod 9 had THR values of about 15-16 MJ/m^2 at 600 seconds. The THR value of mod 9 foam increased to 13.3

MJ/m^2 in 300 s and then with a slight increase reached 15 MJ/m^2 in a total time of 600 seconds. The combination of TEP/OTEP/ZB (mod 9) resulted in the lowest total heat release (THR) value among the fire retardant combinations.

Additionally, ferrocene has a remarkable impact on both heat release rate and total heat release value. It is the unique formulation that provides better values than the reference in this space.

Another important finding is that while Zinc Borate is not improving heat release, oligomeric TEP aids to reduce this value when used jointly with TEP and ZB.

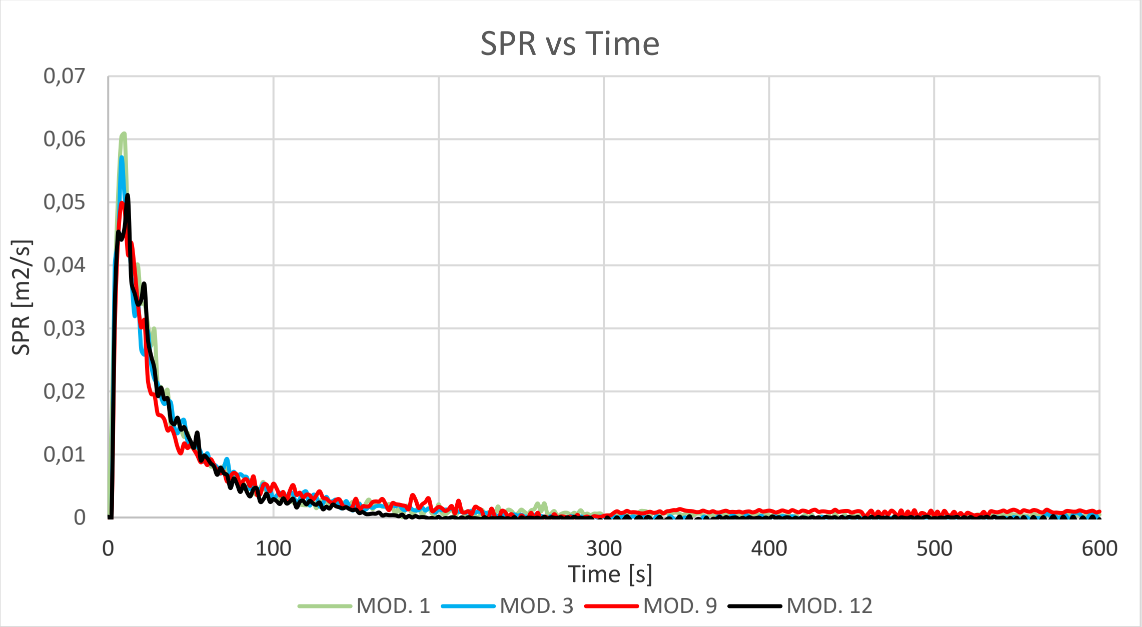


Figure 4.38 : Smoke production rate vs time.

The peak smoke production rate (SPR) value of mod 12 was the lowest, followed by mod 9 (about 0.05 m^2/s) and mod 3 (0.058 m^2/s) as shown in Figure 4.38.

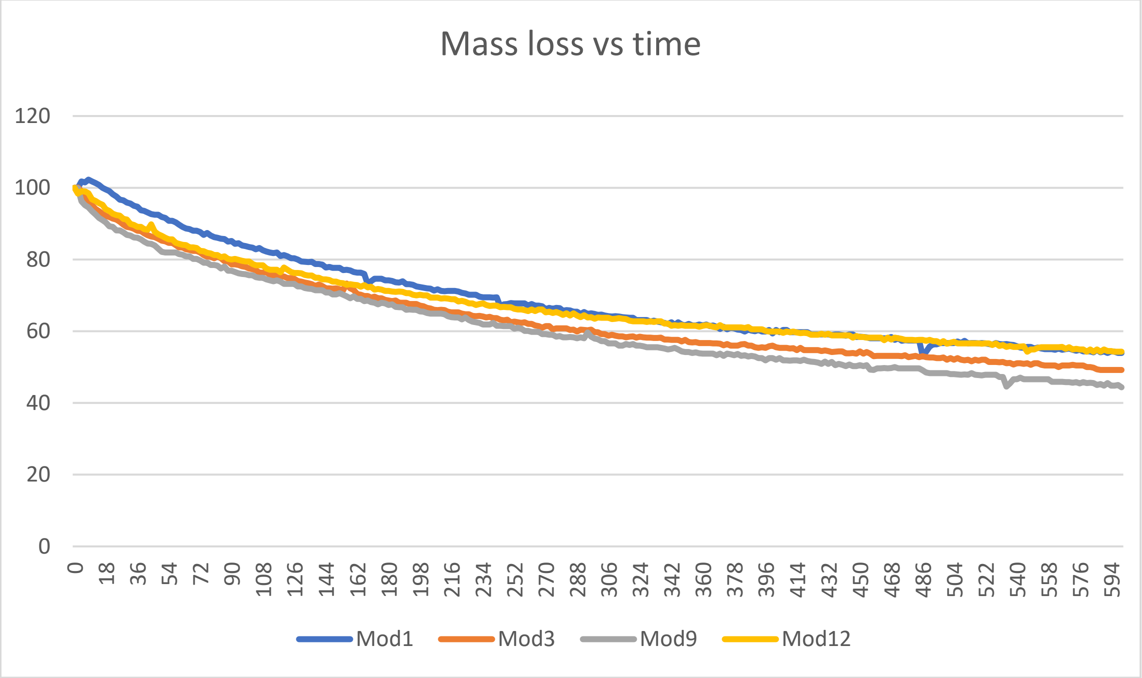


Figure 4.39 : Mass loss % vs time.

The comparison of the mass change of PIR foams (mod1, mod 3, mod 9 and mod 12) with time showed that the total residue of the foams are correlated inversely with the pentane amount (Figure 4.39). This was expected since pentane evaporated and burned during the burning of PIR foam.

It is evident that ZB as well as Fc are effective smoke suppressants when combined with right flame retardants.

With regards to delay in combustion/ignition, the impact of ZB and Fc is confirmed as in Table 4.30.

Table 4.30 : Time to ignition.

	Mod1-ref	**Mod3**	**Mod9**	**Mod12**
Seconds	1	2	3	3

4.5 Emission Analysis Results

Results of cone calorimeter analysis, highlighted that three formulations (Mod3, Mod9, Mod12) performed well against the reference Mod1.

The headspace-GC-MS analysis of these four foams is reported below in Figure 4.40. The reported chromatograms are of Mod1 (reference), Mod12, Mod3 and Mod9 in descending order. Emission analysis results are displaying the VOC´s occuring under

150 °C after 15 minutes. It is providing the VOC performance of formulated polyisocyanurate foam during its life cycle in an accelerated way.

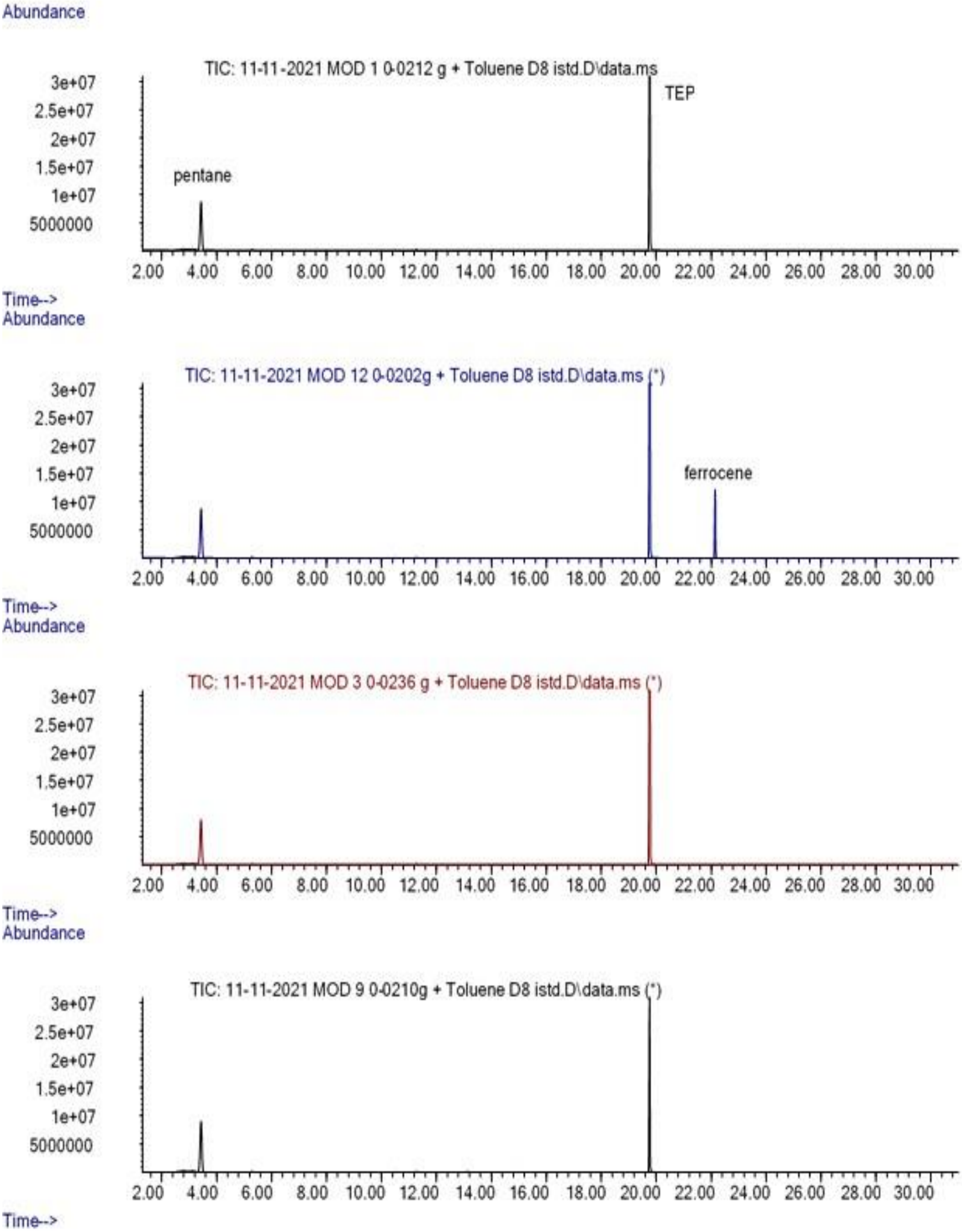
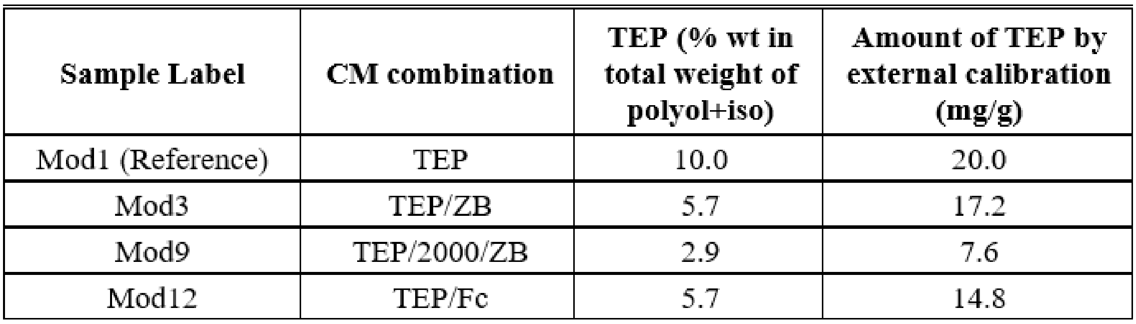


Figure 4.40 : Stacked HS-GC-MS chromatograms (150°C, 15 min) of the 4 foam samples.

Triethyl phosphate is clearly visible in the different samples, at quite elevated levels for this technique. Levels are comparable for the 4 samples, with only Mod9 showing significantly lower levels of TEP (roughly two-fold). Mod12 shows the additional presence of the ferrocene peak.

Amounts of TEP quantified by external calibration are shown in Table 4.31:

Table 4.31 : Quantified TEP by external calibration.



Sample Label	CM combination	TEP (% wt in total weight of polyol+iso)	Amount of TEP by external calibration (mg/g)
Mod1 (Reference)	TEP	10.0	20.0
Mod3	TEP/ZB	5.7	17.2
Mod9	TEP/2000/ZB	2.9	7.6
Mod12	TEP/Fc	5.7	14.8

While Mod12 exhibit an outstanding reaction to fire performance, emission analysis proves that ferrocene (Fc) can migrate from the foam and might cause indoor air pollution. Considering the amount of Fc incorporated in the foam, however, the absolute concentration value by weight is expected to be found much inferior with respect to the one of TEP.

Assuming that there might be some deviation between the measurements, anyhow, reported TEP values of Mod3 and Mod12, displays notably different level of emissions (17.2 mg/g vs 14.8 mg/g).

In any case, the EH&S profile of Fc is worse than the one of TEP or n-pentane. A comparison of the hazard phrases of the three volatile organic compounds found in these chromatograms (n-pentane, TEP and Fc) is proposed along with the CLP CMR category (carcinogenic, mutagenic, reprotoxic) in 4.30. CMR-rated compounds (ranking 1A, 1B or 2) are often banned or severely limited in terms of presence in foams when said foams are in use in the automotive industry. In the future, possibly, rules will apply also to the rigid foam insulation industry, and these considerations may result in a selection of appropriate CMs; for example, the AgBB evaluation schemes aready include C1A and C1B (Carcinogenic 1A and Carcinogenic 1B) substances in a ban list.

Table 4.32 : Analysis of the H-phrases and CMR classification of the VOC found in the HS-GC-MS tests.

n-pentane	**Triethyl phosphate**	**Ferrocene**
Hazard Phrases		
H225 (highly flam. liquid)	H302 (harmful if swallowed)	H228 (flam. solid)
H304 (fatal if swallowed)	H319 (causes serious eye irrit.)	H302+332 (harmful sw. or inh.)
H336 (may cause dizziness)		H360FD (damage fert.)
H411 (tox to aquatic life)		H410 (very tox to aquatic life)
CLP CMR classification		
Not applicable	Not applicable	Reprotoxic 1B

Table 4.32 demonstrated the analysis of H-phrases and CMR classification of the found VOC´s in the analysis. Levagard® 2000 (oligomeric TEP) is an interesting candidate for assessment. Oligomeric TEP was not detected in the chromotographic analysis (see Mod9 in Figure 4.37), this is a positive outcome in terms of emission performance. Found value confirms the possibility to partially substitute TEP in the formulations.

5. CONCLUSIONS

This study on rigid polyurethane and polyisocyanurate foams provided useful insights on the selection of combustion modifiers.

During the literature search it was reported that, while it is possible to find and use a broad type of experimental reactive FRs, only very few number of these substances are commercially available which limits the researchers to evaluate them at an industrial scale. More specifically, it is easier to retrieve phosphorus based fire retardants while there is a limited number of choice for substances based on nitrogen and boron.

Among commercially available phosphorus-based CMs, phosphate esters have a wider offering. In terms of molecular structure, monomeric types are found to be more common.

At earlier stages of the study, selected flame retardant candidates proved to have some obstacles for their use in PUR/PIR applications. Low onset decomposition temperature of some combustion modifiers such as ammonium pentaborate, sodium tetraborate decahydrate as well as boric acid makes it difficult to use said CMs in rigid polyurethane foam applications as, during the polymerization reaction, temperature in the foam core may reach up to 180 °C, which causes the release of hydration water present in molecule structure. This results a lower free rise density and a brittle foam. Therefore,

- Either combustion modifiers that are thermally stable up to at least 180°C should be selected
- Or said combustion modifiers should be exposed to a pre-drying step before the use.

With regards to reaction to fire performance of rigid PUR foams that is prepared with polyether polyols, in order not to exceed a certain level of flame height (max. 15 cm), compliance to DIN 4102 B2 fire rating is achievable only with high loading of combustion modifiers (35% per polyol blend weight) which might lead to a significant worsening in physical mechanical properties. With these amount of CM incorporation in free rise foams, shrinkage was observed after 24 hours.

Studies proved that while it is still not possible to attain the fire performance of TCPP, next best alternatives such as a combination of Triethyl phosphate and Firebrake Zinc borate improves the reaction to fire performance is of rigid PUR foams. This is a proof of synergistic impact as non of the said CMs alone were able to reach this fire performance.

First set of experiments with polyisocyanurate formulations confirmed the superior fire behaviour of this chemistry when compared to rigid polyurethane foam. 24.3% of combustion modifiers incorporation in the system allowed to pass polyurethane formulations including 35% of the same flame retardants. This is a proof of the positive impact of highly thermally stable aromatic isocyanurate structure present in PIR foams.

Same FR combinations that functioned in PUR formulations proved their synergic impact also in PIR formulations such as Triethyl phosphate-Zinc borate and Diethyl ethylphosphonate-Zinc borate combinations. During these studies, Zinc borate confirmed to act as an effective agent to reduce the flame height and suppress the smoke formation. Having said that, increasing the amount of Zinc borate more than a certain limit is not improving the performance further.

Another interesting finding came out when Ferrocene was evaluated in PIR formulations. Introduction of a small amount of Ferrocene into TEP containing polyol blend was reported to be surpassing the performance of Triethyl phosphate-Zinc borate combination incorporated foams. However, there is a threshold of the minimum reachable flame height and minimum smoke density value. Further loading of Ferrocene is worsening the flame height and smoke opacity values reach a plateau, therefore amount of this substance should be optimized for each different formulation.

Besides measuring the reaction to fire properties of PUR/PIR formulations, other tested key parameters cover reactivity profile and free rise density of formulations. First outcome is that the densities of the FR-RPUF foams containing the combination of ATH, zinc borate and polyammonium borates were much higher than pristine RPUF foam. This result was obtained also with PIR experimentals. Results displayed that, almost all solid combustion modifiers increase free rise density while accelerating the gel time. Only exception from this case is Ammonium polyphosphate which led to a reduction in the density and decelerated gel time.

Another method that was used to examine fire behaviour of PIR formulations was cone calorimeter. This analysis gave an opportunity to confirm the previous findings in the laboratory experiments. It provided a broad range of data including heat release rate, total heat release, total smoke production rate and mass loss for 11 formulations. When compared to the performance of reference PIR foam that contains only TEP as a CM, 3 formula proved an improved fire performance in PIR foams thanks to the synergism occurred between the interactions of

- TEP&ZB,
- TEP&Fc,
- TEP&Levagard® 2000&ZB.

Best performance was achieved with TEP&Fc combination. Ferrocene greatly aided to the reduction in total heat release and heat release peak. Performance of Zinc borate was also confirmed especially on total smoke production aspect in which together with oligomeric TEP, they created a synergic impact.

On the emission aspect, Levagard® 2000 (oligomeric TEP) confirms the research hypothesis that the incorporation of oligomeric CMs improves emission performance of the system, thus reducing the migration of molecules from the final product. Oligomeric TEP was not detected in emission analysis at least in the tested conditions of HS-GC-MS. It should be also included that, tested foams did not include any reactive combustion modifiers as they did not perform well during cone calorimeter analysis.

Albeit useful for a good reaction to fire performance, Ferrocene is a volatile compound and it’s reprotoxic class 1B; it is detected easily in the HS-GC-MS experiment carried out on foams, and it will likely be detected in larger scale emission tests. Consequently, in the context of emission testing, its use should be limited or strategies of incorporation in the primary structure should be elaborated.

For the future studies, to improve the reaction to fire performance and emission performance in rigid polyurethane/polyisocyanurate foams, below path is suggested:

- Incorporation or partially substitution of current polyether polyols with polyester polyols in rigid PU/PIR foams.
- Investigation of the incorporation of different oligomeric and reactive combustion modifiers.

- Lowering the amount of Combustion Modifiers in final Polyisocyanurate formulations.

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APPENDIX A: Tables and Figures

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Table A.1 : Impact of CM´s on reactivity and FRD in PIR foams.

	Mod1	**Mod2**	**Mod3**	**Mod4**	**Mod5**	**Mod6**	**Mod7**	**Mod8**	**Mod9**	**Mod10**	**Mod21**
Polyol blend	96	96	96	96	96	96	96	96	96	96	96
n-pentane	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85
TEP	34.64		20.27	10			10		10		
ZB			14.67	14.67	14.67	14.67	14.67	14.67	14.67	14.67	14.67
Dimethyl adipate											
APP				10.27	20.27						
Lev 2100						20.27	10.27				10.27
DO11								20.27			
Lev 2000									10.27	20.27	10
Reactivity											
Cream time (s)	18-21		11-14	16-19	18-20	12-15	20-23	20-23	15-18	17-20	8-12
Gel time (s)	69-72		70-72	80-85	83-87	54-57	90-93	88-90	67-71	71-74	52-56
Free rise density (kg/m3)	32.7		36.1	33.1	32.4	41.8	41.1	41.3	37.1	38.4	35.3

Table A.2 : Impact of CM´s on reactivity and FRD in PIR foams.

	Mod1	**Mod12**	**Mod13**	**Mod14**	**Mod15**	**Mod16**	**Mod17**	**Mod18**	**Mod19**	**Mod20**
Polyol	96	96	96	96	96	96	96	96	96	96
n-pentane	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85	12.85
TEP	34.64	20.27				10		10	10	
Ferrocene		4	4	4	4	4	4	4	4	4
APP			20.27						10.27	
Lev 2100				20.27		10.27				10.27
DO11					20.27					
Lev 2000							20.27	10.27		10
Reactivity										
Cream time (s)	18-21	15-18	17-20	41913	41548	18-21	17-20	20-24	16-18	42705
Gel time (s)	69-72	69-72	80-85	58-60	80-84	75-79	75-79	83-87	75-79	58-62
FRD (kg/m3)	32.7	34.3	36.1	35.7	41.5	34.5	33.4	32.1	33.6	36.2

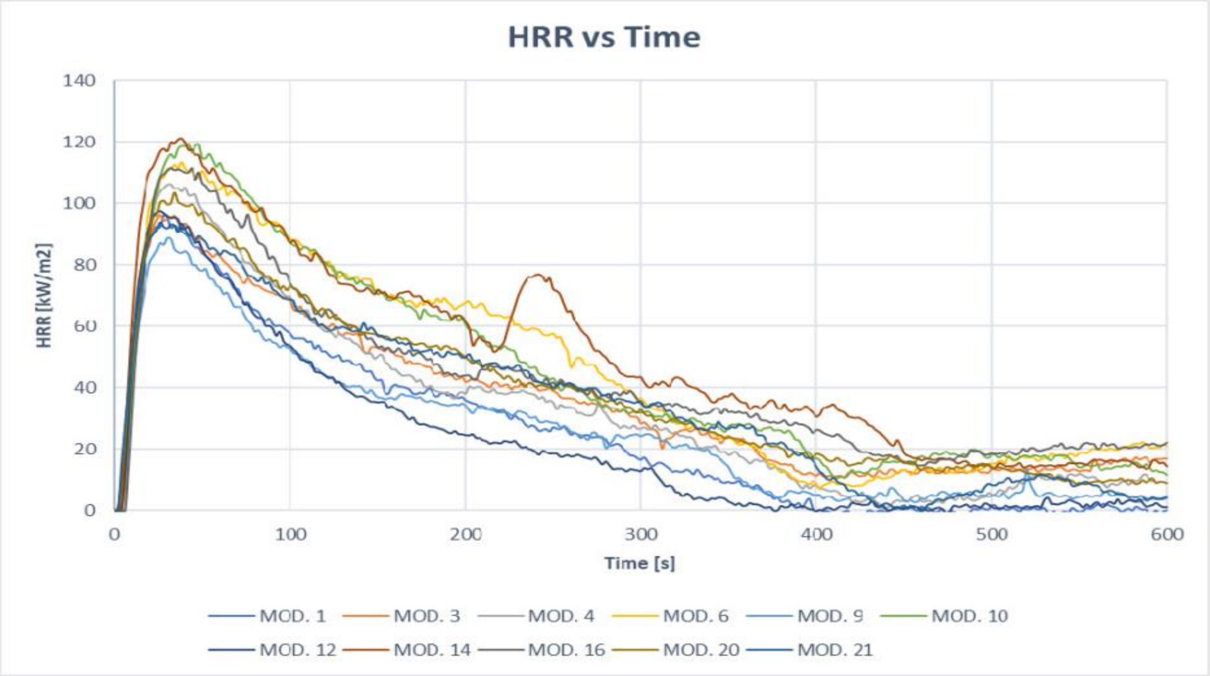

Figure A.1 : Cone calorimeter results - Heat release rate vs time.

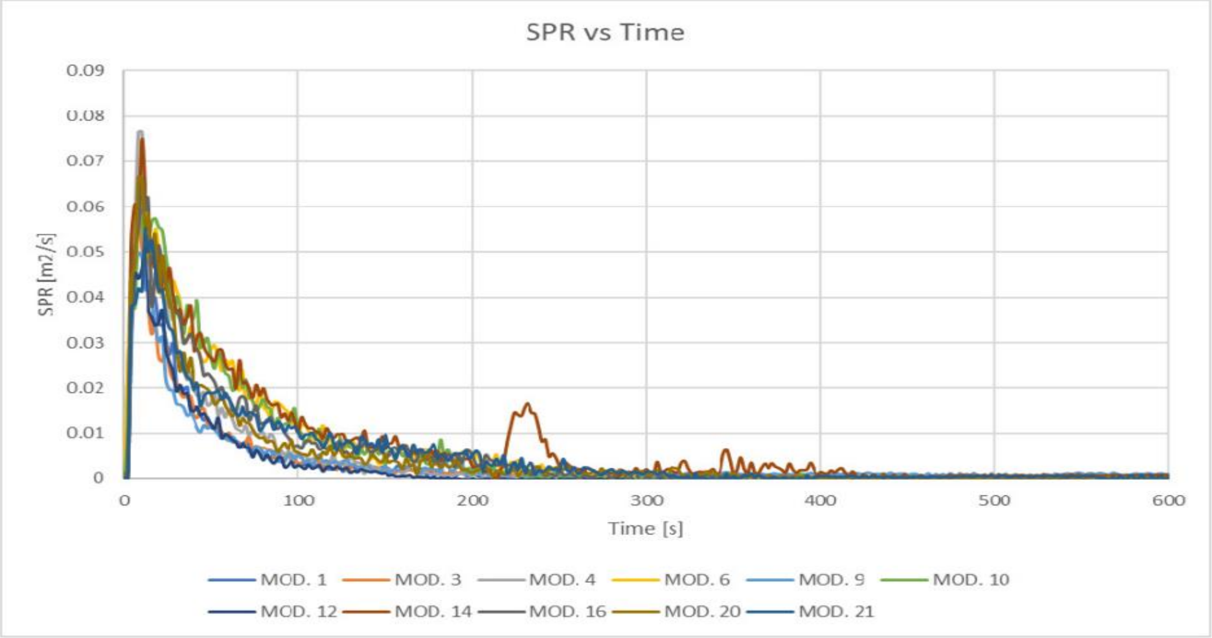

Figure A.2 : Cone calorimeter results – Smoke production rate vs time.

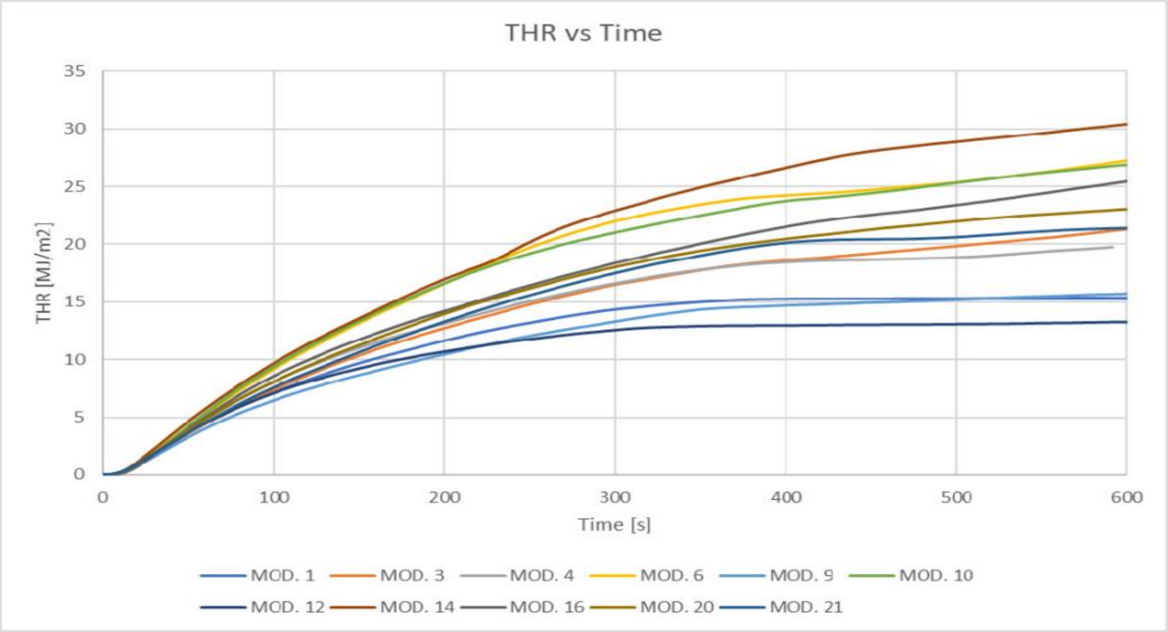

Figure A.3 : Cone calorimeter results – Total heat release vs time.

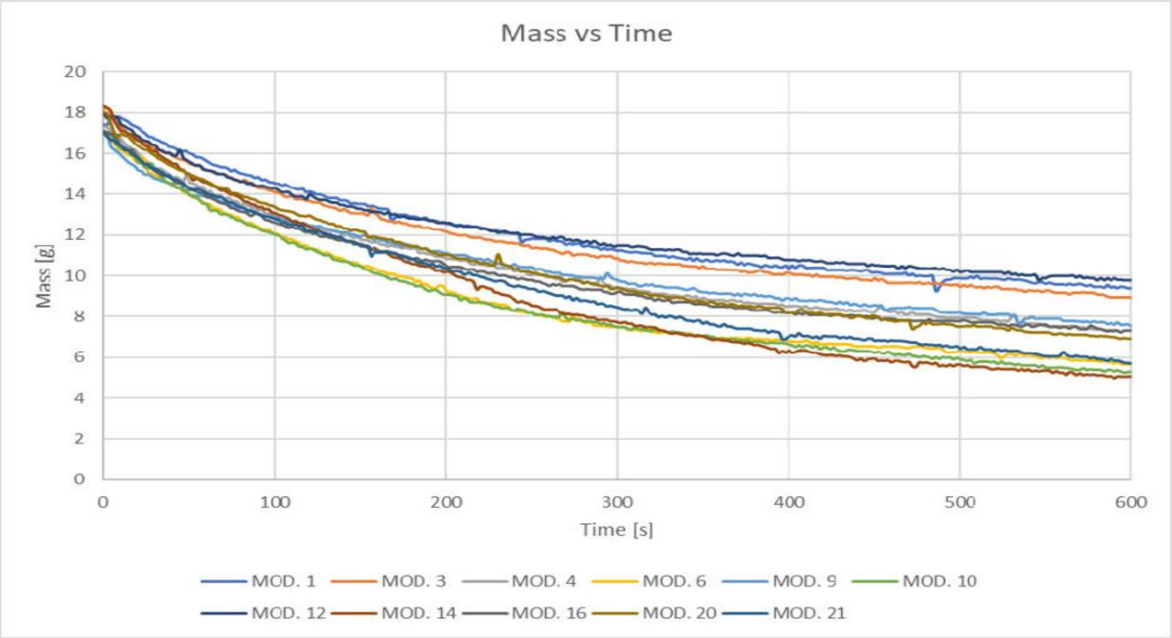

Figure A.4 : Cone calorimeter results – Mass loss vs time.

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PUBLICATIONS AND PRESENTATIONS ON THE THESIS:

1. Akar, A., **Değirmenci, B.,** & Köken, N. (2023). Fire-retardant and smoke-suppressant rigid polyurethane foam composites. *Pigment & Resin Technology*, *52*(2), 237-245.
2. **Degirmenci B.,** Koken, N., & Akar, A. (2022) Ferrocene containing fire retardant Polyisocyanurate Foam, *2nd International Congress on Multidisciplinary Natural Sciences and Engineering*.