FLAME RETARDANCY OF POLYMERIC COATINGS

SHEHRYAR ALI MALIK

Master's Thesis

Supervisors: Prof. Carl-Erik Wilén, Melanie Aubert and Teija Tirri

Laboratory of Polymer Technology

Department of Chemical and Process Engineering

Åbo Akademi University, April 2019

Abstract

This Master's Thesis was done at the Laboratory of Polymer Technology (TPK) at Åbo Akademi University as a commissioned work for Walki Oy between November 2018 and April 2019. The study and experimentation were performed under the supervision of Prof. Carl-Erik Wilén, Senior Researcher Melanie Aubert and Lab Engineer Teija Tirri.

The aim of this study is to prepare Flame Retarded Polymeric Coatings to be used in packaging and construction materials. The increasing usage of polymers in our daily life makes the issue of safety a significant factor. Polymers are known to be highly combustible under normal circumstances and this issue needs to be addressed. The concept of introducing flame retardants in the polymers has gained much attention in recent years. An overview of the concept of flame retardancy and the testing methods used for this purpose has been described in this study.

The experimental part of this study consists of testing the polymeric coatings on the pilot scale. Several FRs and their combinations were tested in the laboratory and the promising combinations were chosen for the pilot scale testing. A paper substrate was used and LDPE containing FRs was coated on the substrate which was further evaluated using DIN-4102 fire testing standard. The results showed that the processing temperature is playing a great role in the adhesion of LDPE on the substrate and also for the degradation of the FRs. The adhesion between the layers and efficient flame retardation are both equally important concerns which require a borderline temperature to be used. Further study is required to synthesize or obtain FRs which can withstand higher temperatures without degrading and in that way both concerns can be addressed.

Keywords: low-density polyethylene (LDPE), flame retardants, fire testing standards, extrusion coating, oxidation in polymers.

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Acknowledgments

I would like to express my gratitude to Prof. Carl-Erik Wilén for providing me with an opportunity to work in the Laboratory of Polymer Chemistry and to gain extensive knowledge with practical work.

I would like to acknowledge Senior Researcher Melanie Aubert and Lab Engineer Teija Tirri for their guidance on each and every step during my stay at TPK. Their teaching made it very convenient for me to learn all the instruments and the whole procedure of this research. I would also like to thank the staff at Walki oy Pietarsaari who helped and guided us during our visits to the industry.

Finally, I would like to dedicate my work to my family and friends who were always there to support me in pursuing the Master's Degree in Chemical Engineering at Åbo Akademi University, Finland. It has been an amazing experience to study in Finland and especially to be working in the Laboratory of Polymer Technology (TPK).

Thank you!

List of abbreviations

FR	Flame Retardant
FR	Flame Retardants
MHs	Metal Hydroxides
LDPE	Low-Density Polyethylene
PP	Polypropylene
UL	Underwriters' Laboratories
THR	Total Heat Release
HRR	Heat Release Rate
TTI	Time to Ignition
TSR	Total Smoke Release
LOI	Limiting Oxygen Index
DSC	Differential Scanning Calorimeter
OIT	Oxygen Induction Time
XPS	X-ray Photon Spectroscopy
NFR	Nitrogen based FR
N.C	Non-Classified
L+W	Length+Width

1. Introduction

The usage of polymeric materials in our everyday life has increased exponentially over the past few decades. The polymer materials are everywhere around us from construction materials, vehicles, home interiors to the packaging materials and many more. The increased consumption of these materials also has raised questions concerning the fire hazard that these polymeric materials may cause. In general, polymers are composed of carbon and hydrogen atoms which is the reason they are highly combustible under normal circumstances. Consequently, it is very important to address this shortcoming of polymers by developing efficient fire retardants that drastically reduce the potential of fire hazards of polymeric products in the 21st century. [22]

The modern flame retardants must be very effective in order for polymeric materials to meet today's stringent fire safety regulations. Moreover, the flame retardants need to be inexpensive, effective at low loadings and toxicity of these compounds as well as adverse environmental impact should be as low as possible. Owing to this, the research on the FRs has taken its course towards ensuring that new flame retardants provide the required fire protection, recyclability together with environmental and human safety. Thus, it is our hope that these FR materials will continue to contribute to the safety of human life in a cost-effective and efficient manner and by making the environment safe for everyone.

2. Flame retardation

The general mechanism of the combustion of polymers includes four steps: 1) preheating, 2) pyrolysis (volatilization/decomposition) due to bond scission and emission of flammable gases by the burning material, 3) combustion and 4) propagation. The radical generation during the process in combination with oxygen is as follows: [24]

$$H^* + O_2 \rightarrow OH^* + O^* \tag{1}$$

$$O^* + H_2 \rightarrow OH^* + H^* \tag{2}$$

The exothermic reaction keeping the flame active is:

$$OH^* + CO \rightarrow CO_2 + H^* \tag{3}$$

If the evolved heat is enough to cause further pyrolysis of the polymer then a self-sustaining reaction will propagate. Here, the need for an FR becomes inevitable as this process has to be quenched or controlled by either reducing the flammable volatiles or isolating the burning material from the constant supply of oxygen. [3, 24] The FR materials make the polymers and other combustible materials more resistant to fire. If an object is already on fire then the FR will help to prevent the spread of fire to the other combustible materials around that object. The importance of FR materials has significantly increased over the past decades in parallel with the increasing use of polymer-based appliances.
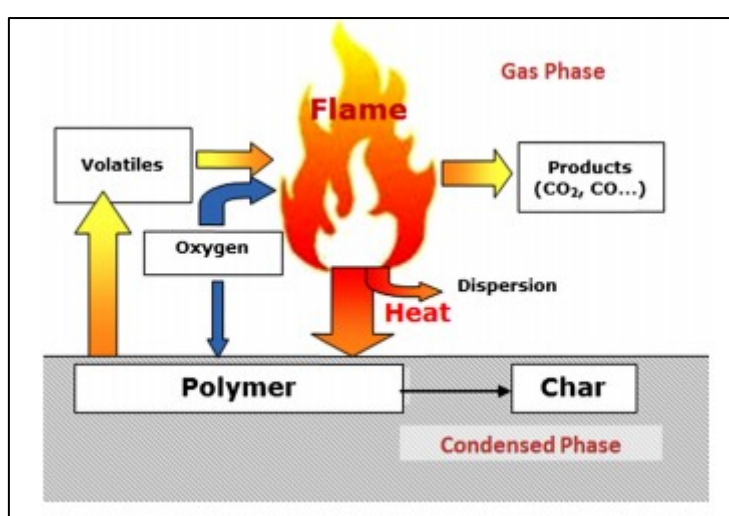

Figure 1: Polymer combustion cycle [1]

The combustion cycle is shown in Figure 1 where the ignition source heats the combustible material, the release of energy causes further degradation of material whereby more volatile fractions diffuse into the air and in some cases also a char (in some cases) is formed. These volatile fractions create flammable gases in the presence of oxygen and the auto-ignition point is attained due to the constant increase in temperature. Hence, the activation energy required for ignition of the flammable gases is acquired causing the heat release and the start of a fire. The process of burning is exothermic and this heat is further utilized in enhanced burning of the combustible material. The aim is to prevent this situation of fire with the addition of FRs to combustible materials and this area is an ongoing area of interest in the whole world.

2.1 Action of flame retardants

As described in Figure 2, there are several points in the combustion cycle where the action of an FR could be implemented. The FR can enhance the decomposition temperature causing a significant delay in the ignition or it can release non-combustible gases around the material. The diluting gases will prevent the fire spread to the nearby combustible materials and will reduce the supply of oxygen to the burning material. [7]
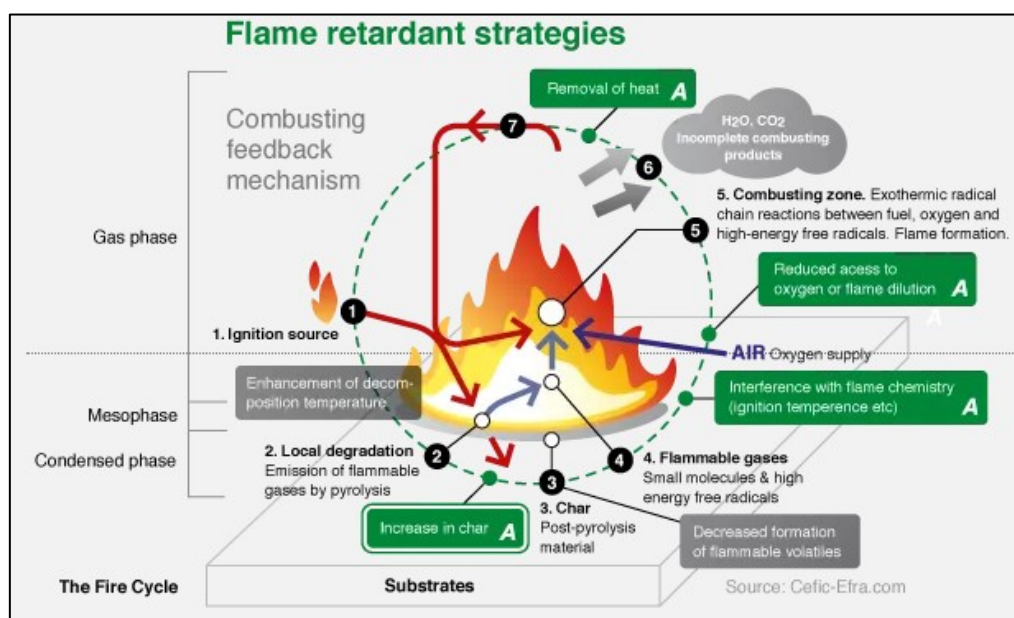
Figure 2: Fire cycle and FR action points [29]

The proper blending of FR with the polymeric or any combustible material is necessary in order to achieve the desired fire retardancy. After blending there should be no leaching of FR from the polymer. In many cases, the FRs are also used with synergists which can help trigger and enhance the action of the FR. There are certain halogenated compounds which can decompose endothermically inside the combustion zone and thereby are helpful for removal of heat. [3] Recently, the FRs are either blended with the material, reacted or pasted on the surface for the inhibition of fire spread. The best possible solution in the future would be an FR compound that has been incorporated inside the polymer chain and causes the material to self-extinguish after ignition. [3]

3. Types of FRs and mechanisms

The FRs are based on a variety of compounds which can contain halogens, nitrogen, phosphorus, and inorganic compounds. Every class of the FRs has its own advantages as well as drawbacks. The main factors that are needed to be considered are the compatibility with the combustible material, the toxicity of the FR, treatment methods, price, and way of disposal. The most problematic is related to the toxicity of the certain FRs especially halogen based FRs.

3.1 Halogenated FRs

FRs normally act in the gas phase or the condensed phase by physical or chemical reaction during the combustion cycle. The halogenated compounds, mostly brominated or chlorinated compounds particularly act by a radical mechanism in the vapor phase by suppressing flame propagation. They scavenge the high energy OH* and H* radicals generated during the combustion hence decreasing the heat in the process. [22, 24] The halogenated FRs are commonly used due to their low cost, good efficacy, miscibility, and the fact that they easily liberate the halogens during the process. Over the years many of these compounds have been banned or restricted because of the toxicity of the halogens but still they are used as new brominated FRs are also still in the development phases.

The trapping efficacy of halogenated FRs depends on the group to which halogen atoms are attached. The ratio of carbon-halogen atoms and their bond energy is determined from this and also the number of halogens that will be released during the combustion. [22] The aromatic halogen compounds have higher carbon-halogen bond energies than aliphatic or alicyclic halogen compounds which makes the latter a better choice. However, the toxic emissions by the halogenated-compounds have caused the restriction of their usage in many countries around the world. The compounds such as polybromodiphenyl ethers (PBDPE), brominated epoxy resin (BEP), hexabromocyclododecane (HBCD), tetrabromobisphenol A (TBBPA), and decabromodiphenyl ether (DBDPE) are very efficient flame retardants but they are either banned or under consideration due to the issue of toxicity. [22]

3.2 Metal Hydroxides

The most popular metal hydroxides that can be used as FRs are magnesium hydroxide [Mg $(OH)_2$] (MDH) and aluminum hydroxide [Al $(OH)_3$] (ATH) for a variety of polymeric materials. Metal oxides and hydroxides have lesser toxicity than brominated FRs, low cost, low emissions during the combustion process and some have anti-corrosion properties especially magnesium hydroxide. [22] The metal hydroxides decompose endothermically by liberating water and oxides during the burning process.

MHs are more suitable when used in the polymers with higher stability as some MH such as aluminum monohydrate [AlOOH] has a decomposition temperature of 340-350 ^{0}C. [24] A general disadvantage of ATH and MDH is their requirement of a very high loading (40 to 60 wt. %) to achieve the desired level of efficiency. This, in turn, leads to a drastic change in the physical properties of the polymeric material. In addition, the poor dispersion and miscibility of metal hydroxides in the polymer may reduce significantly the strength of the polymeric product. [24]

3.3 Phosphorus-based FRs

Phosphorus-based compounds are widely available in the market as a replacement of halogenated FRs. Most used phosphorus-based FRs include phosphonates, red phosphorus, phosphonium compounds, and phosphates. [22, 24] The compounds having a high oxidation number of phosphor atom act in the condensed phase by dehydration and char formation resulting in the reduction of the flammable gases during combustion. In most cases, these phosphorus compounds are converted to phosphoric acid while the thermal decomposition takes place and produce pyrophosphate or polyphosphate structures. They cause the elimination of water molecules at the polymer end chains and trigger the formation of char. Whereas, P compounds with low oxidation state act as scavenging agents for H* and OH* radicals by active radical generation (PO_2*, PO* and HPO*). [24]

The challenge in phosphorus-based FRs is to prepare such compounds which only volatilize during the combustion and not during the polymer processing. Phosphorus-based FRs such as red phosphorus is used in combination with other FRs for the synergistic effect. [22] Most of the phosphorus-based FRs are biodegradable and have better UV stability than the halogenated

FRs. On the other hand, these FRs have a very low efficiency unless a charring agent is used with them in polyolefins. They are hydrophilic and the uptake of moisture can cause problems in the processing conditions especially in the case of red phosphorus. [25] The future perspectives include a universal range of phosphorus-based FRs which are not only active in highly charring polymers but also have more diverse applications. [25]

3.4 Nitrogen based FRs

Nitrogen-based FRs are one of the main replacements for halogenated FRs. These compounds are used alone and in synergistic combination with phosphorus compounds for efficient flame retardancy of the polymers. Mainly nitrogen based FRs are derived from ammonia and melamine but some compounds derived from urea are also known. [26] The mode of action of nitrogen-based FRs is based on endothermic decomposition in the combustion zone whereby inflammable gases such as ammonia and nitrogen will be released. Most used FRs belonging to this category are melamine in polyurethane foams, ammonium polyphosphate-pentaerythritol or ethylene-urea formaldehyde in polyolefins, melamine phosphates, and guanidine phosphates. [26] Another mode of action of nitrogen-based FRs is a strong interaction with the polymer matrix. The reaction of these FRs leads to intense charring or decomposition of the polymer matrix.

Nitrogen-based FRs have many advantages including the non-toxicity of the base compounds (melamine, ammonium polyphosphate and guanidine) and their derivatives along with the gases evolved during combustion. [29] Low smoke production in fire conditions and emission of less corrosive gases are also the advantages of NFRs. These FRs exhibit a higher degradation temperature and can be processed several times without losing the flame retardancy. The disposal of NFRs is very convenient because they act as fertilizers in landfill applications and this phenomenon can be enhanced using methods for faster degradation of the waste products. [29]

4. Extrusion coating on paper

4.1 Introduction

A polymer can be coated on a paper substrate by extrusion coating. The process was used in this study for manufacturing of flame retarded LDPE coated paper. The FR additives were added in both the polymer and paper parts. A thin layer from 10-80 g/m² was coated on a paper in the process and our coating target of LDPE was 25 g/m² in pilot runs. [13] The procedure involved preparation of the flame retarded LDPE pellets and feeding them to the extruder screws as shown in Figure 3. A series of heaters are placed on the line used to melt and heat LDPE to the desired temperature for paper coating. The coated paper was then passed through a chill roll at 10 °C and a pressure roll for the successful adhesion between the paper and the LDPE coating.
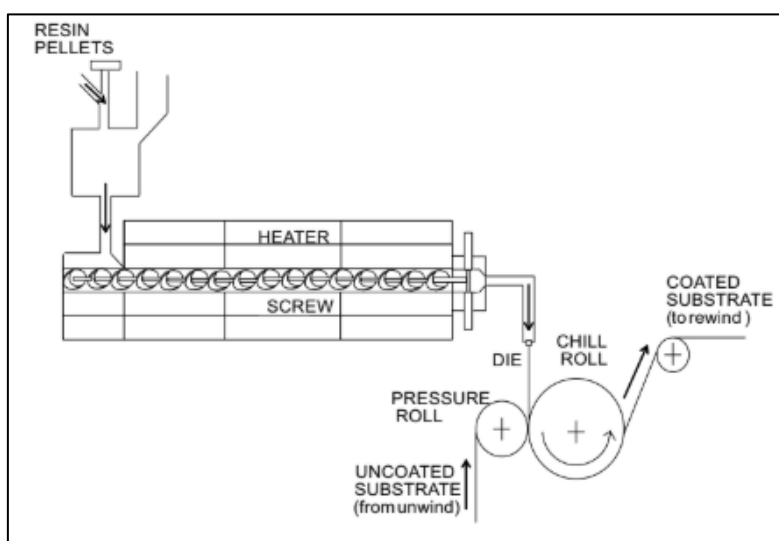
Figure 3: Schematic diagram for extrusion coating of LDPE on paper [13]

The paper coating process is used to enhance the surface properties of paper along with water resistance, wet strength, oxygen permeability, and particularly in our study the flame retardancy. [13] On the other hand, the FRs added to these coatings must be capable of performing at low loadings, ensure good runnability, disperse well in the polymer matrix, and be safe to the humans and environment. Some of our FR added LDPE formulations depicted

good adhesion properties while others had good flame retardancy. The problem lies with the high extrusion temperature to the best of our knowledge and the aim is to find a sustainable FR or alternative method for good adhesion at a lower temperature than 300 °C. [13]

4.2 Preparation of the polymer

Most polymer pellets need drying before extrusion as the moisture from the atmosphere and the previous treatments may cause problems during the extrusion process. Especially, resins such as nylon, polyester, and polycarbonate are very hydrophobic and must be dried. [16] Even if the polymer is kept under controlled moisture and temperature conditions the residual moisture should always be removed in order to avoid degradation during processing. In addition, moisture in the polymer can evaporate during the extrusion process and cause problems in the surface of the final product. One of the suitable drying procedure is through a dehumidifying dryer with a dew point temperature of -40 °C while another option is vacuum drying at room temperature for the removal of moisture. [16]

The size of the polymer pellets is important to ensure the proper flow into the feeder screw as the different sizes can cause larger pellets to deposit on the surface and smaller ones at the bottom. This problem particularly arises when additives such as FRs are being added to the polymer before extrusion. In the start, the coating will become richer with the additive and later the polymer will be in a greater quantity. [17] In order to avoid this condition, the additives should be premixed with the polymer and pelletized so that the process of extrusion is run smoothly and the coated layer has homogeneous additives.

4.3 Coating procedure

The basic principle of extrusion coating is to apply a molten polymer film continuously on a paper substrate. Thus, the molten polymer is being deposited on a paper substrate using an extruder as shown in Figure 4. [4] The polymer curtain falls in between the pressure roll and the chill roll under the force of gravity and adhesion of the two layers takes place between the two rolls. Multiple polymer layers can also be used in this process. A suitable speed for the rolls needs to be selected keeping in view the desired thickness (coating weight) of the deposited layer. The slower running will result in a thicker layer and vice versa.
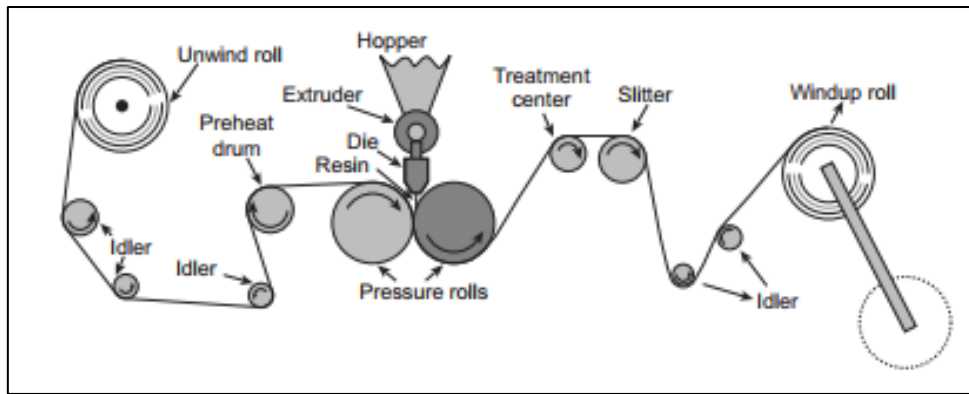
Figure 4: Extrusion coating schematic diagram. [15]

The process of adhesion may take place due to the chemical or physical linkages between the paper and the polymer. The physical adhesion process requires force and the ability of the substrate to have enough surface energy so that it attracts the molten polymer and surface area enough to contain the polymer in the solidification phase. [4] On the other hand, the chemical linkages require special treatments such as corona treatment and application of primers to the substrate to ensure the molten polymer will wet the paper fibers. [4] Moreover, a rough surface provides better adhesion than a smooth surface in case of an untreated substrate. [15]

4.4 Adhesion troubleshooting

The successful adhesion between the substrate and the LDPE coating is of paramount importance. A number of factors may contribute to poor adhesion of the coating on the paper substrate. [18]

1. If the melt temperature is inadequate, the polymer has too high viscosity to flow and stick to the paper substrate. To solve this problem either the temperature of the extruder zones can be increased or pressure inside the die zone can be increased.
2. Too high temperature can cause degradation of the polymer and consequently poor adhesion. The extruder barrel temperature can be lowered or the speed of the screw can be slightly increased to counter this issue.
3. If the melt curtain is very near to the extrusion coating nip then the polymer will not have sufficient surface oxidation to adhere to the paper substrate.
4. If the polymer cools down before reaching the substrate or if the chill roll temperature is too low then the adhesion will be poor.

5. The surface of the substrate must have enough roughness and fibres so that they support the coating to be deposited by making bonds with it. [18]

Among all the above-mentioned challenges, the case of lower melt temperature seems to cause problems when the polymers with additives are coated on paper. The additives such as FRs have lower degradation temperatures (around 250 ℃) and their efficiency is lost if we use high enough temperature for ensuring excellent adhesion. The sufficient temperatures used for LDPE coating on paper lies between 300-330 ℃. [19] Moreover, the thickness of the deposited layer plays an important role in the adhesion process. Experiments have shown that a thicker layer has more time to cool down on the substrate resulting in more interaction between the fibres and the polymer which results in better adhesion. [19]

4.5 Polymer degradation

Polyethylene has significant use in packaging and construction materials prepared via sheet extrusion, film blowing and by extrusion coating on a paper substrate. During thermal processing, the polymer may degrade due to high mechanical and thermal stresses. Degradation can cause bad odor or decolorization. Severe degradation is not favorable for the use of PE in any of the above-mentioned applications.

Degradation of any polymer can be countered or reduced by various antioxidants. [21] Antioxidants can be added in the polymer to scavenge the free radical generated by polymer degradation cycle. The main oxidation occurs when the film is exposed to the air at the extruder outlet but some degradation also occurs inside the extruder barrel. The experiments have shown that the oxidation index of LDPE during extrusion coating is a function of the air gap between the extruder outlet and substrate. [21] Many of these newly formed compounds on the polymer surface enhance adhesion to paper. However, some of the oxidation products may have a characteristic taste and smell even at very low concentrations which may interact with the final products inside the packaging.

It is evident that more exposure time to air at the extruder outlet causes more degradation as more oxygen interacts with the polymer melt. The thicker films take more time to cool before quenching and hence emit more smoke containing volatile compounds. [20]

5. Fire testing methods and standards

The polymeric materials are altered chemically or physically in order to make them more fire resistant. The addition of an FR can change the properties of the material. In order to use an FR commercially in any given material, the altered material needs to be tested in accordance with the international fire testing standards.

5.1 DIN 4102 B2

The DIN 4102 B2 test is performed inside a burning chamber without any interference of outside air as it can cause distortion of the flame. The methane flame is calibrated by testing the time for it to reach from 100 °C to 700 °C within 40-50 seconds. The height of the sample holder and burner once adjusted should not be changed during the testing. The specimen is hung vertically inside the chamber with the help of a holding clamp. The sample size should be 190 mm x 90 mm and thickness may vary up to 80 mm. A reference mark is made at 150 mm from the bottom edge of the sample to check the damage length according to the standard.
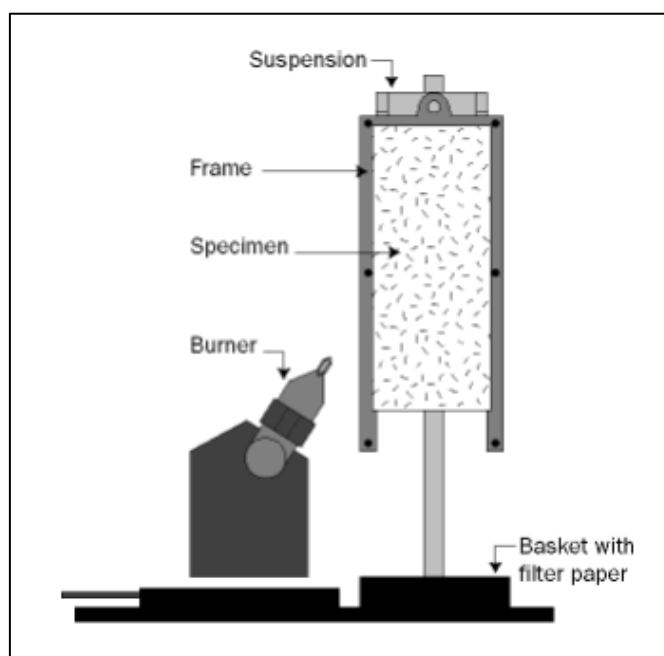

Figure 5: DIN 4102 test apparatus [30]

The 20 mm flame is applied at the lower end of the specimen at an angle of 45 degrees for 15 seconds only once and then removed. Even if the sample ignites during this time the flame

should not be removed. In order to pass the B2 criteria, the flame should not reach the reference mark within 20 seconds after the flame is removed. A filter paper is placed below the specimen to check if it drips and ignites the filter paper during the test. Three to five samples are tested with the same procedure and all of them must pass the test for the material to be classified as B2 according to the DIN 4102 standard. After each sample, the combustion gases must be removed from the chamber by ventilation so that there is no alteration in the results for the next samples.

5.2 UL94 vertical test

The UL test for the plastics has been approved by the 'Underwriters' Laboratories' and is frequently used in preliminary testing of the flame retarded plastics. The test is referred to as (IEC 60695-11-10) standard specified for small flames (50W). [7] The test has a subclass UL94 which is commonly used to test the ignitability of the plastics in bulk and the progression of fire can be observed as well. The test is performed inside a closed chamber without any outside interference of air with 20 mm flame placed below the specimen.
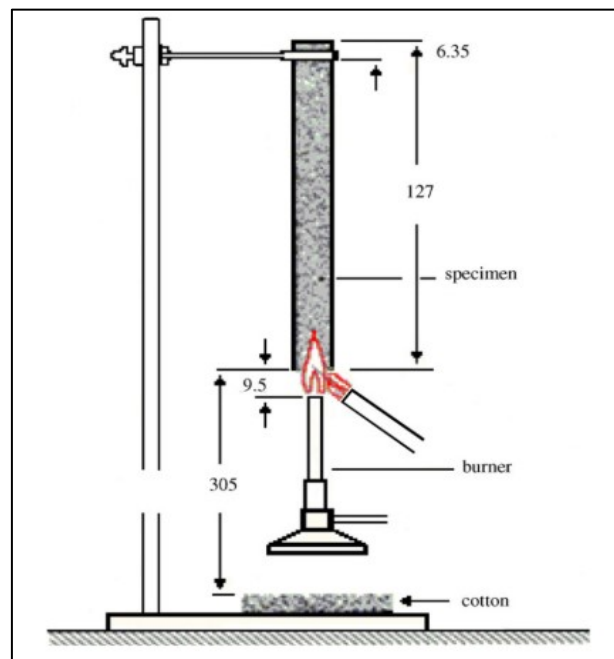

Figure 6: UL94 test apparatus [7]

The specimen is clamped vertically and dry surgical cotton is placed 305 mm below the specimen to observe the dripping during the combustion process. During the test, the flame is

applied at the lower end of the specimen for 10 s keeping the top of the burner at a distance of 10 mm from the specimen. The first ignition time is noted until the specimen extinguishes and called as after-flame time t_1. After that, the flame is again applied from the same distance to the remaining sample and the second after-flame time t_2 is noted. The time for the after-glow of the sample is referred to as t_3 which is often calculated with t_2 or separately as well. After each sample, the chamber must be cleared using the room extraction system so that the next sample is tested in clean air supply. A total of five samples for each specimen are tested and evaluated as V-0, V-1, or V-2. The evaluation criteria are described in Table 1. [7]

Table 1: UL94 test criterion [7]

UL94 V-0	After-flame times ≤ 10 s for each sample Sum of AF time ≤ 50 s for all five samples Sum of AF time and after-glow time ≤ 30 s for any sample No complete burning up to the holding clamp No dripping that ignites the dry cotton
UL94 V-1	After-flame times ≤ 30 s for each sample Sum of AF time ≤ 250 s for all five samples Sum of AF time and after-glow time ≤ 60 s for any sample No complete burning up to the holding clamp No dripping that ignites the dry cotton
UL94 V-2	After-flame times ≤ 30 s for each sample Sum of AF time ≤ 250 s for all five samples Sum of AF time and after-glow time ≤ 60 s for any sample No complete burning up to the holding clamp Dripping that ignites the dry cotton is allowed

5.3 Cone calorimeter

The cone calorimeter is referred to as ISO 5660-1 standard and is used effectively in testing a wide range of materials to determine their burning behavior. The testing is used in product development phases and also for the classification of products on the basis of their resistance to fire conditions and the emissions during the burning phases. A standardized calibration is required each time before the test run and all the attributes are adjusted according to the requirements. The test apparatus is shown in Figure 7.
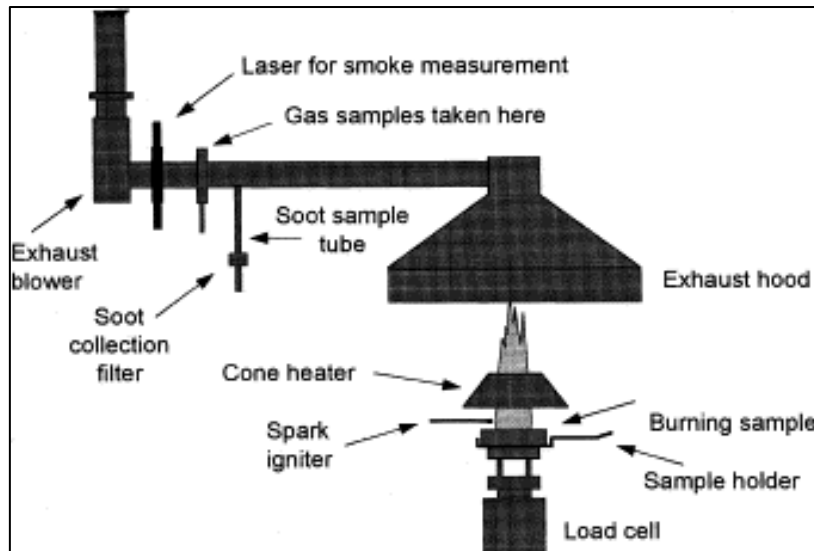
Figure 7: Cone calorimeter schematic diagram [31]

The samples for cone calorimeter are prepared with dimensions of 100 mm x 100 mm maximum and the thickness may vary from 3 mm to 50 mm as desired. The weathering of samples is done if required. The heat from the cone hood is delivered to the specimen by a radiation source called 'cone heater'. The required level of heat flux from the cone is selected and the system will ask to adjust the temperature for that required heat flux. The range of heat flux lies from 0-100 kW/m². The sample is placed inside a sample holder and the holder is placed on a load cell which is used to measure the mass loss of the sample during the combustion. The fumes and combustion gases reach the analyzers through the fume hood and then released to the ventilation system.

The results from cone calorimeter determine the total heat released (THR) in kJ/m^2, heat release rate (HRR) in kW/m^2, time to ignition (TTI), total smoke release (TSR), and the ratio of some of the combustion gases produced. Any unusual event occurred during the testing can also be recorded manually in the apparatus for further classification of the event. [6] The above parameters define the efficiency of the flame retardant in the polymer material

5.4 Limiting oxygen index (LOI)

The limiting oxygen index test is used to evaluate the flammability of the test specimen at different oxygen-nitrogen mixtures. The test results give the minimum amount of oxygen that is required to sustain the combustion process. Higher oxygen index values are better as it

indicates that the material can resist the combustion even at higher oxygen concentrations. [27] A step increase or decrease of 0.2% in oxygen concentration is done after observing the behavior of the test specimen once it ignites. Air has about 21% oxygen content so a specimen burning at a higher concentration of oxygen in the LOI test will likely to some extent resist combustion in air. After a rough estimation of the oxygen ratio, the results are evaluated using the US standard ASTM D 2863-77 for very precise result up to three significant figures. [27] The apparatus for the LOI test is shown in Figure 8.
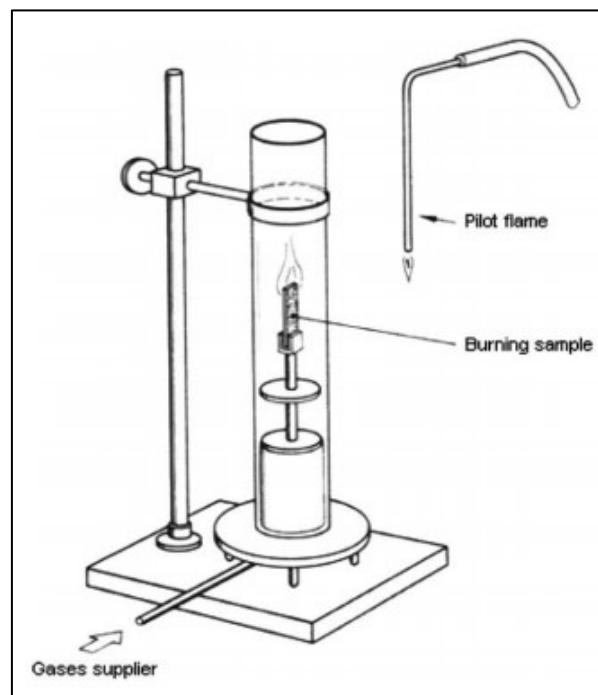
Figure 8: Limiting oxygen index apparatus [27]

The vertical test specimen is ignited by a pilot flame inside a test chimney by just touching the top surface of the specimen. A nitrogen-oxygen mixture is released inside the chimney from the bottom to provide the required oxygen concentration for burning. The dimensions of the test specimen should be between 70 and 150 mm in length, 6.5 mm in width, and 3 mm in thickness. [28] The flame is applied for 30 seconds by removing it every 5 seconds to check if the specimen has ignited and then applied again in case of no ignition. The time is noted until the flame has extinguished after the removal of the flame. LOI is a simple and reproducible test which gives a single figure result that can be used to rank the flammability of the material. [28]

6. Oxidation study methods

6.1 DSC for OIT and OIT*

Different polymers are frequently stabilized to withstand environmental conditions. The determination of oxygen induction time (OIT) is an efficient method to check the oxidation stability and the efficiency of the additives used in polymers. [8] OIT calculation is referred to as EN 728 standard and is calculated using a differential scanning calorimetry (DSC) apparatus. It is one of the most precise methods available for the oxidation state testing as the sample weight is very small in order to keep the precision at the highest level. The gases used are an inert gas preferably nitrogen and pure oxygen or air can be used as required for the oxidation step.

At the start of the test, the sample of the polymer weighing approximately 15-20 mg is placed inside the apparatus. The sample is then heated in an inert atmosphere with a step increase in temperature of about 20 ^{o}C/min to the desired temperature for oxidation study. When the required point is achieved the isothermal part begins and lasts for 3 minutes. As soon as the isothermal part ends, the gas is switched to pure oxygen or air as desired and the atmosphere is created for oxidation step. The OIT time is then measured to the point when the apparatus gets an oxidation signal and decomposition starts. The standard EN 728 defines the level of input gases to be 50 ml/min throughout the test. [8] The graphical representation of the procedure is presented in Figure 9.
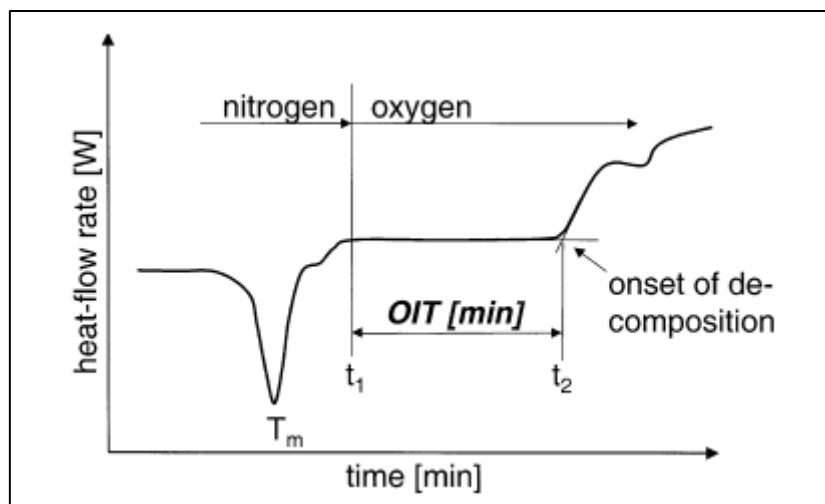
Figure 9: Principle of calculating OIT using DSC [8]

For the FR additives, it is expected that they will decrease the oxidation time. Alternatively, the sample can be tested for the same results under different test conditions of heating at 10 °C/min to the desired temperature and the input gas is always pure oxygen or air. This method is known as 'Oxidation induction temperature (OIT*)' and it is only yet accepted as a standard in Finland. [8] The test principle is shown in Figure 10.
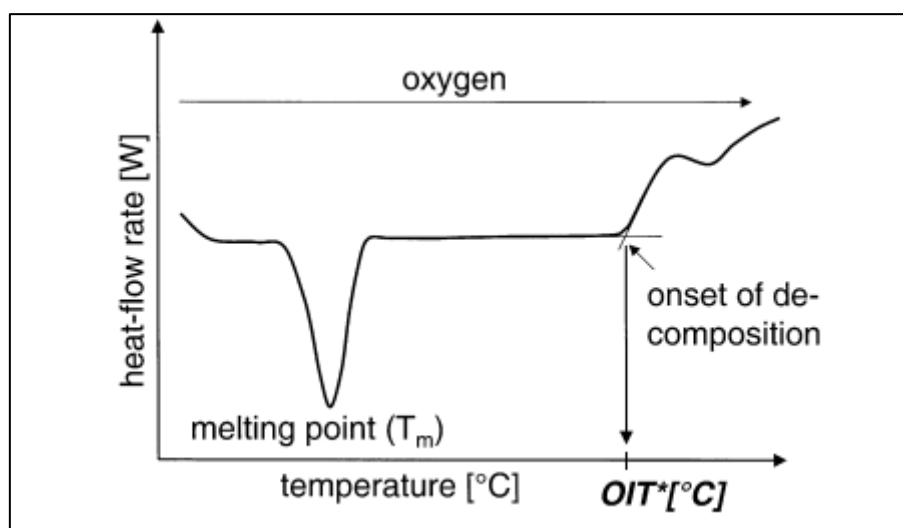
Figure 10: Principle of calculating OIT* using DSC [8]

This is a dynamic test unlike the OIT which is static and in OIT* there is no switching of input gas which eliminates a source of error. The oxidation signal is easier to identify for the apparatus in the case of OIT*. This method is rather suitable in the case where oxidation happens instantly due to a very high temperature and the graphical representation makes it difficult to pinpoint the exact oxidation time. [8]

6.2 XPS for surface study

X-ray photon spectroscopy is an analytical method involving the measurement of energies of photo-electrons being emitted from the atoms upon irradiating them with X-ray photons. [11] The method is used to study the structures chemically and also for the elemental analysis. The physical structure can be examined with high accuracy if desired. The energy emitted by the photo-electrons can be used to identify the atoms to which they were bound to and had the same energy used as 'binding energy'. XPS for solid involves the study of atoms only close to the surface of the material and if the surface is homogeneous then the chemical composition can also be estimated with fair accuracy. [11] The elemental analysis can be performed using the binding energies to identify the atoms and then calculating the frequency of the emitted photo-electrons. The frequencies will reveal the number of each kind of atoms under consideration.
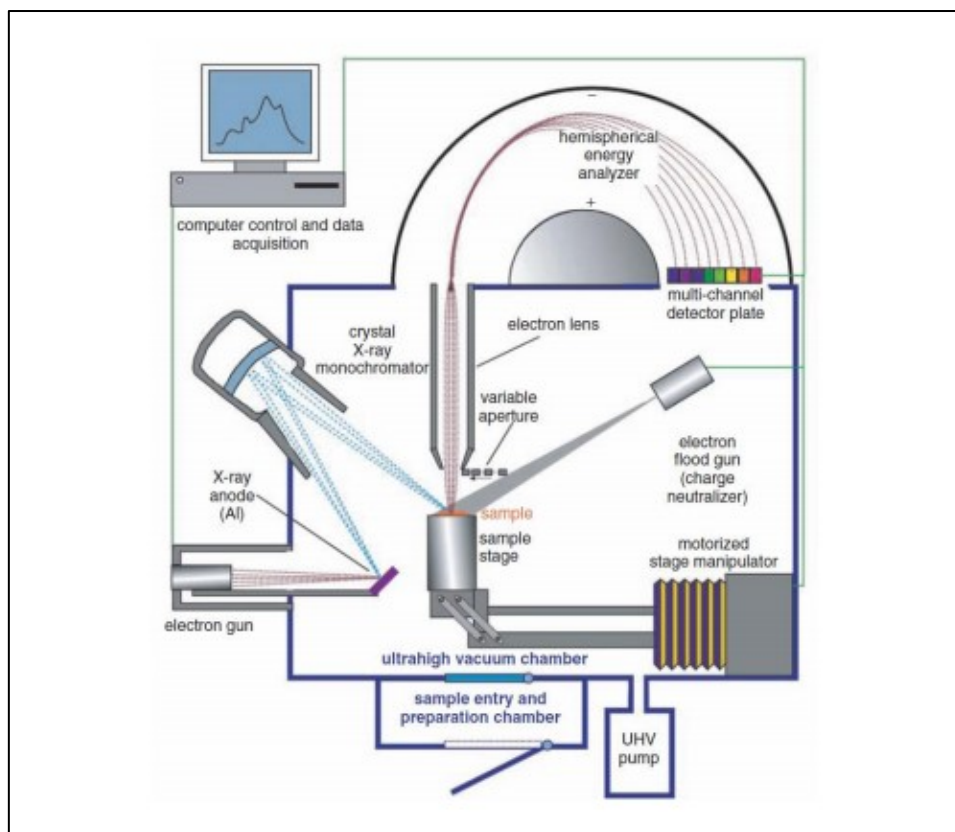
Figure 11: Schematic view of the XPS instrument. [12]

In case of polymers added with FRs XPS can be used to study the surface of the pure and flame-retarded polymer in order to check the effect of the FR on the polymer surface composition. In case of multilayer XPS study or in-depth profiling, the 'sputtering' method is used in which each layer from the surface is removed after the analysis and then the next layer is taken as the surface of the material. [10] Same is the case with polymer coatings on different materials and study of their interaction with the material that each layer will be sputtered until the common layer is reached and the analysis is performed on that layer.

7. The aim of the study

The aim of this project was to prepare FR coatings for paper-based products used in packaging and construction materials. The coating was low-density polyethylene (LDPE) with FR on flame retarded paper. The major challenge is to find a processing temperature which is appropriate for both achieving sufficient adhesion of LDPE to paper process and high enough thermal stability of the FR to withstand processing. For sufficient adhesion, an extrusion temperature of at least 290 ºC is required, whereas most FRs already start to degrade above 250 ºC. [13, 19]

At the laboratory scale, the LDPE was blended with FRs in two sets of formulations and each set was tested in the pilot run by coating it on the paper substrate. The LDPE formulations and coated paper both were tested according to the DIN 4102-1 B2 standard at laboratory scale. Adhesion of the coated layer was examined by manual peeling and evaluated according to the standard set by the organization. Further, the formulations and coated paper samples were tested using DSC, Cone calorimeter and XPS in the laboratory.

Both polypropylene and polyethylene are used for coatings and are among the most used polymers around the world. However, for polypropylene (PP), only laboratory scale FR testing has been carried out at this stage and the results of the experiments are included in the appendices.

8. Description of materials

Most of the FRs used were purchased from the market and used in combinations with other FRs for the synergistic effect. Some were prepared on the laboratory scale according to the literature.

8.1 Flame retardants and other additives

The list of the FRs used in LDPE is given below. These FRs were tested according to DIN-4102 and UL94 tests in the laboratory before the extrusion coating procedure. Even if the formulations work in these tests, the results may change when they adhered to the paper substrate. The adhesion and bonding between the coating and the substrate alter the results for flame retardancy in either way. The best-known combinations are therefore tested in this work for the efficient flame retardancy of polymeric coatings on paper.

Table 2: Materials for LDPE and their source

Flame retardant	Source
FR-A	Synthesized in Laboratory
FR-B	Synthesized in Laboratory
FR-C	Synthesized in Laboratory
FR-D	Clariant oy
FR-E	Clariant oy
FR-X	Clariant oy
FR-Z	From Market

9. Batch production for Pilot Runs

9.1 Polymer extrusion

The batch mixing of LDPE with FR was performed at Turun Ammattikorkeakoulu (AMK), Turku, Finland, and VTT Technical Research Centre, Finland. A temperature of 220 ºC was used with the formulations given in Table 3. After the extrusion, the mixtures were passed through a water bath right after the extruder and cut into pellets using a cutter at the end of the water bath. A series of heaters gradually heated the polymer to the desired temperature inside the extruder till the die. Before the extrusion coating on the paper, the pellets must be dried so that the residual moisture is removed and does not cause problems in runnability during coating.
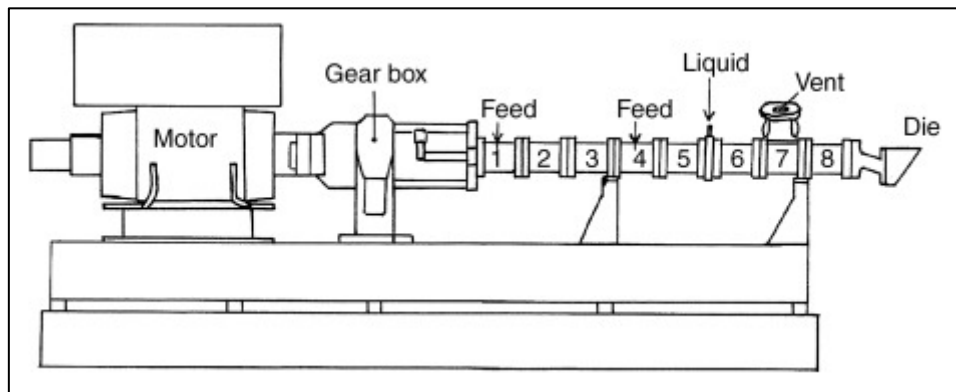
Figure 12: Schematic view of a twin-screw extruder. [14]

9.2 Formulations for 1st Pilot Run

For the first pilot run, several FRs were used in combination with FR-E in **Abo** 1 to **Abo** 3 (names for reference). FR-X used at 4 wt% and 2 wt% alone and in combination with FR-D in **Abo 4** to **Abo** 6 respectively.

Table 3: FRs with weight percentage

Polymer	FR1 (wt %)	FR2 (wt %)	Reference
LDPE PG7004	FR-E (5%)	FR-A (3%)	**Abo 1**
LDPE PG7004	FR-E (5%)	FR-B (3%)	**Abo 2**
LDPE PG7004	FR-E (5%)	FR-C (3%)	**Abo 3**
LDPE CA7230	FR-X (2%)	-	**Abo 4**
LDPE CA7230	FR-X (4%)	-	**Abo 5**
LDPE CA7230	FR-X (1%)	FR-D (5%)	**Abo 6**

The twin screw extruder had different temperature zones as shown in Figure 12 marked from 1 to 8. The starting temperature to soften the polymer was 50 $^{\circ}$C in zone 1 and it increased to 220 $^{\circ}$C till zone 6 for the total melting and efficient mixing of the polymer with the additives. After that, it is gradually decreased to 190 $^{\circ}$C till the die and then ejected to a water bath. The extrusion was performed at a speed of 40 rpm. Different feed sections were used for the polymer and the additives as it is better if the polymer is already melted before the FR additives are added.

9.3 Conditions during extrusion coating in the 1st pilot run

Extrusion coating experiments were carried out at a pilot extruder. The processing temperature was 280 $^{\circ}$C. In most cases, smoke and smell were observed from LDPE which is mainly due to the oxidation and degradation of the polymer during extrusion. [20, 21]

Table 4: Observations during extrusion coating

Reference	Adhesion (1-5)	Runnability	Comments
Abo 1	Good / 5	Good	Light smell.
Abo 2	Intermediate / 3	Poor	Smoke generation and degradation.
Abo 3	Poor / 2	Good	Some smell and gets bubbles when running slowly.
Abo 4	Poor / 2	Good	Some smell and smoke with color (Apple juice)
Abo 5	Poor / 2	Good	Some smell and smoke with color (Apple juice)
Abo 6	Poor / 2	Good	Lesser smoke and smell.

9.4 Formulations for 2nd Pilot Run

For the second pilot run, FR-X was the preferred choice as it gave encouraging results at the first pilot run. FR-X alone and in combination with FR-D was used in Åbo1 and Åbo3 (names for reference).

FR-Z is known to decompose to CaO and CO_2 at high temperatures which dilute and hinder the spread of flame. LDPE containing FR-A had the better adhesion among the formulations used previously so this FR is used with every formulation solely for the purpose of obtaining a better adhesion between the polymer and the substrate. The following formulations were prepared as shown in Table 5.

Table 5: FRs with weight percentage

Polymer	FR1 (wt %)	FR2 (wt %)	FR3 (wt %)	Reference
LDPE PG7004	FR-X (4%)	FR-A (1%)	-	**Abo 7**
LDPE PG7004	FR-D (5%)	FR-A (1%)	FR-X (4%)	**Abo 8**
LDPE PG7004	FR-Z (10%)	FR-A (1%)	-	**Abo 9**

9.5 Conditions during extrusion coating in the 2nd pilot run

Extrusion coating on the paper substrate was carried out at the pilot extruder for the evaluation of LDPE FR formulations once again. The processing temperature was 280 degrees Celsius which is the same as previously used. In most cases, smoke and smell were observed from LDPE which is mainly due to the oxidation and degradation of the polymer during extrusion in this run like the previous one. [20, 21]

Table 6: Conditions during extrusion coating

Reference	Adhesion (1-5)	Runnability	Comments
Abo 7	Poor / 2	Good	Some smoke and light smell.
Abo 8	Poor / 2	Good	More Smoke generation and smell than Abo 1.
Abo 9	Good / 4	Intermediate	Some smell and the melt breaks when the extruder speed is slowed down.

10. Results and discussions

LDPE with FRs before and after the extrusion coating on paper was tested according to DIN-4102 standard. The paper substrate also contained a certain FR. The substrate in combination with LDPE is expected to have better flame retardancy. The results from both pilot-runs along with the pre-runs with LDPE are explained in the following sections.

10.1 Laboratory-scale testing for the 1st pilot run

After the mixing of FRs in LDPE, small amounts were taken from the batches to perform the pre-run FR testing in the laboratory according to DIN-4102 B2 test standard.

Table 7: LDPE DIN-4102 results

(%) in LDPE PG7004	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-A= 3 %	1	95.0	All	Yes
FR-E =5%	2	95.3	All	Yes
(Abo 1)	3	88.1	All	Yes
FR-B = 3 %	1	117.6	All	Yes
FR-E =5%	2	108.4	All	Yes
(Abo 2)	3	54.8	All	Yes
FR-C =3%	1	66.8	All	Yes
FE-E =5%	2	36.1	All	Yes
(Abo 3)	3	98.7	All	Yes

Table 7: LDPE DIN-4102 results (continued)

(%) in LDPE CA7230	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
Reference LDPE CA7230	1	28.22	All	Yes
	2	27.19	All	Yes
	3	28.45	All	Yes
FR-X=4% **(Abo 5)**	1	50.98	All	Yes
	2	32.20	All	Yes
	3	64.33	All	Yes
FR-X=5% FR-D=1% **(Abo 6)**	1	79.60	All	Yes
	2	63.30	All	Yes
	3	99.70	All	Yes

The results from LDPE with FR show a significant increase in the time taken by the sample to completely burn. This shows that the FRs are playing a role in a longer combustion period and making LDPE more resistant to the flame. However, once these formulations will be coated on the paper, the behavior may differ from the present results. The main reasons could be that the paper also contains FR and the bonding between the two layers might alter the results due to composition.

10.2 Paper samples from the 1ˢᵗ pilot run

The LDPE coated paper was checked for the quality of adhesion by manually peeling the coating layer and then tested for flame retardancy. The paper samples were evaluated using DIN-4102 standard in the laboratory and the results are presented in Table 8.

Table 8: Paper samples DIN-4102 results

(%) in LDPE	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-A= 3 %	1	11.5	All	No
FR-E=5%	2	23.8	All	No
(Abo 1)	3	18.2	All	No
FR-B= 3 %	1	26.3	All	No
FR-E=5%	2	29.7	All	No
(Abo 2)	3	34.8	All	No
FR-C=3%	1	0	16+3	No
FR-E=5%	2	0	17+4	No
(Abo 3)	3	13.6	All	No
FR-X= 2%	1	20.8	All	No
(Abo 4)	2	0	17+3	No
	3	18.9	All	No
FR-X=4%	1	35.6	All	No
(Abo 5)	2	1.6	18+5	No
	3	1.6	17+3.5	No
FR-X=5%	1	0	18+3.5	No
FR-D=1%	2	48.8	All	No
(Abo 6)	3	24.1	All	No
LDPE PG7004	1	21.3	All	No
(Reference)	2	24.7	All	No
	3	25.4	All	No

The results show a good FR performance for Abo 3 and Abo 5 samples. However, there was an issue in the runnability of the film in the case of Abo 3 at pilot scale extruder. Abo 1 had the best adhesion among all the formulations. Abo 1 and Abo 3 due to encouraging results along with some new formulations were selected for further testing.

10.3 DSC analysis for oxidation study

The interesting observation made during the first pilot run was the excellent adhesion in case of Abo 1, i.e. the formulation containing FR-A. We speculated, that the increased oxidation of the polymer in the presence of additive FR-A could potentially be a reason for the better adhesion. In order to check this hypothesis, various tests were performed including OIT and XPS. The results from Differential Scanning Calorimeter (DSC) used for the observation of oxidation behavior are shown in Figure 13 and Figure 14.
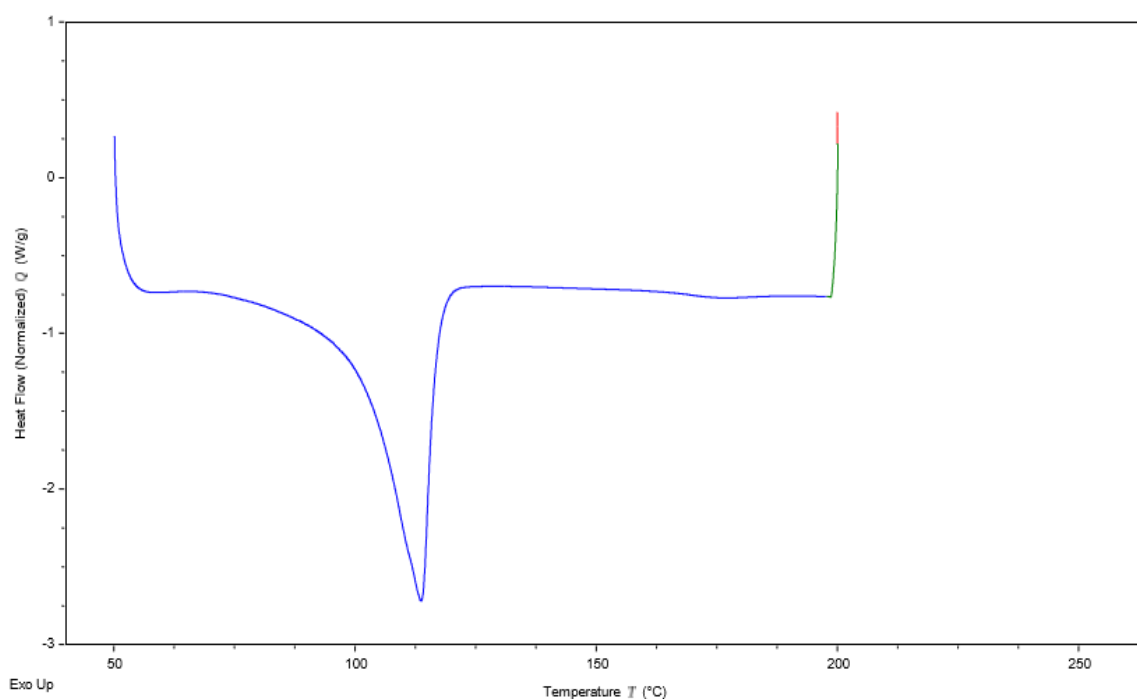
Figure 13: OIT pure polymer PG7004
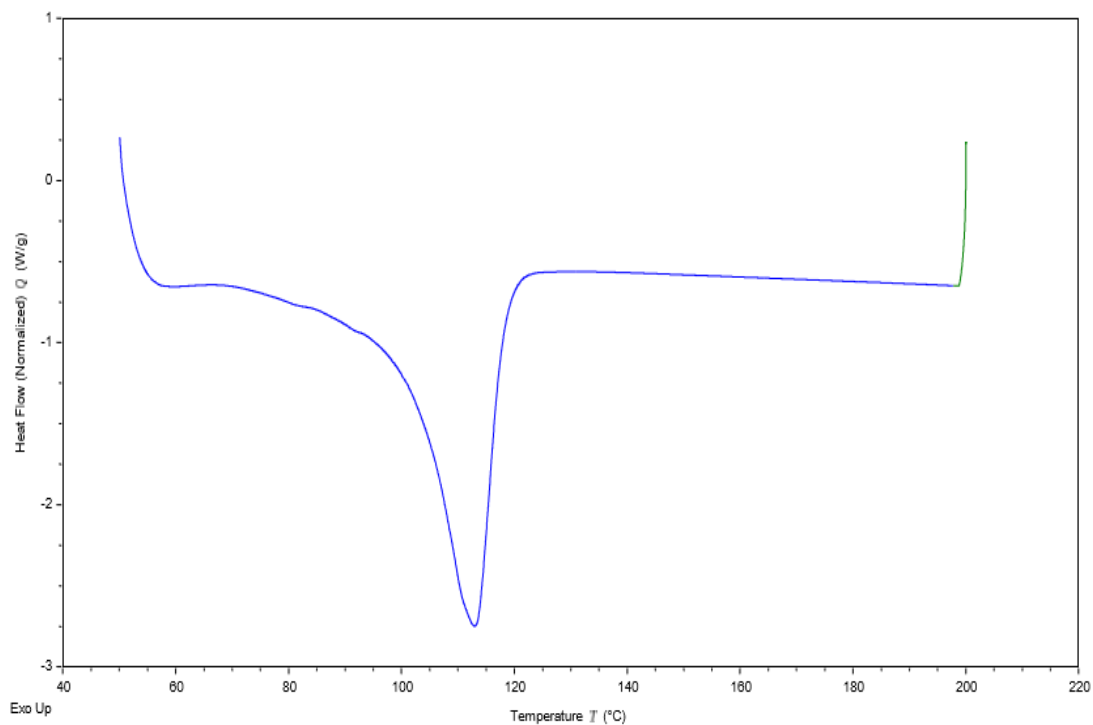
Figure 14: OIT polymer and FR (PG7004+FR-A)

There was no significant difference observed in the oxidation behavior before and after the addition of FR-A in LDPE as seen from the results. The oxidation of the sample starts around 200 °C in both cases. Further testing will be performed to investigate the possible causes of better adhesion and the combination of FR-A with P-type flame retardants.

10.4 XPS analysis for oxidation study

X-ray photon spectroscopy is a method used to analyze the surface properties of any material and it can also be used to study the layers under the surface. XPS was used in this study to evaluate the oxidation at the surface of both LDPE with and without FR-A. Three samples were tested starting with LDPE without the FRs, with FRs and then after being coated on the paper substrate. The results are shown in Table 9 and Figures 15 to 17.

Table 9: Analysis results from XPS.

Sample	C1s	N1s	O1s	P2p	S2p
LDPE + FR-A + FR-E	92.2	2.3	0.9	0.0	4.6
LDPE	100.0	0.0	0.0	0.0	0.0
LDPE coated paper	92.0	1.9	0.8	0.0	5.4

Results are given in atomic-%.

Figure 15: XPS of LDPE

Figure 16: XPS of LDPE coated paper
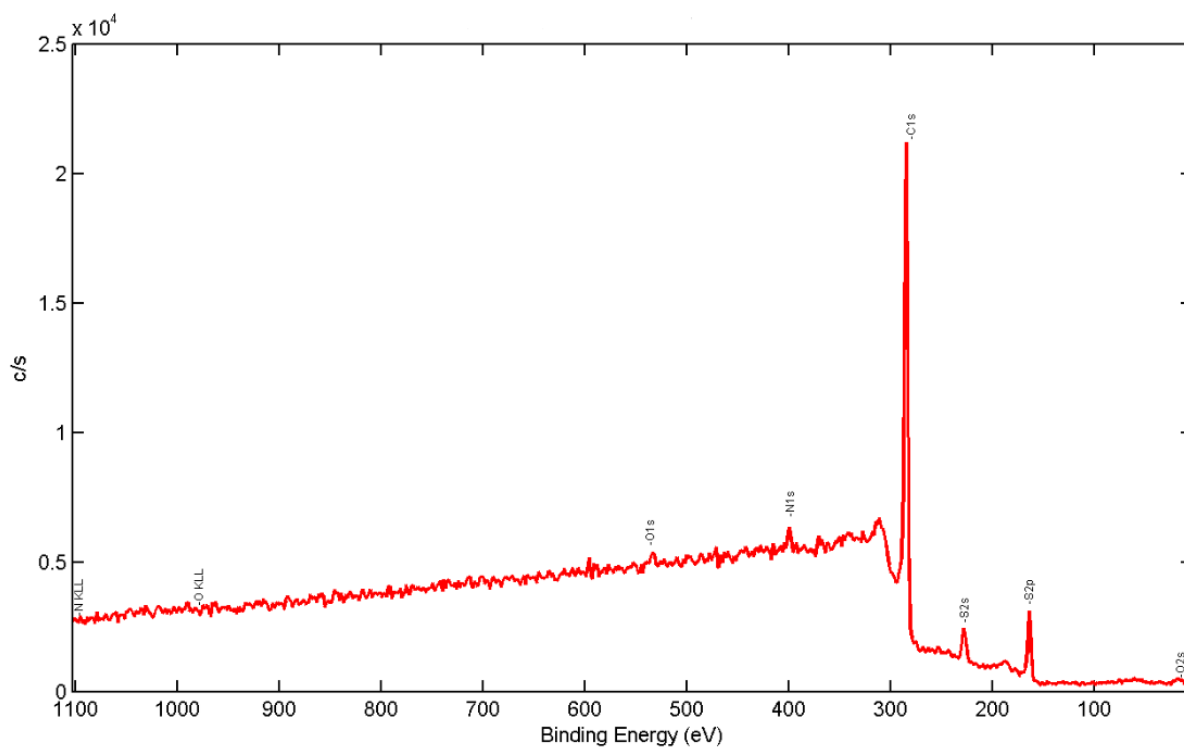
Figure 17: XPS of LDPE with FR

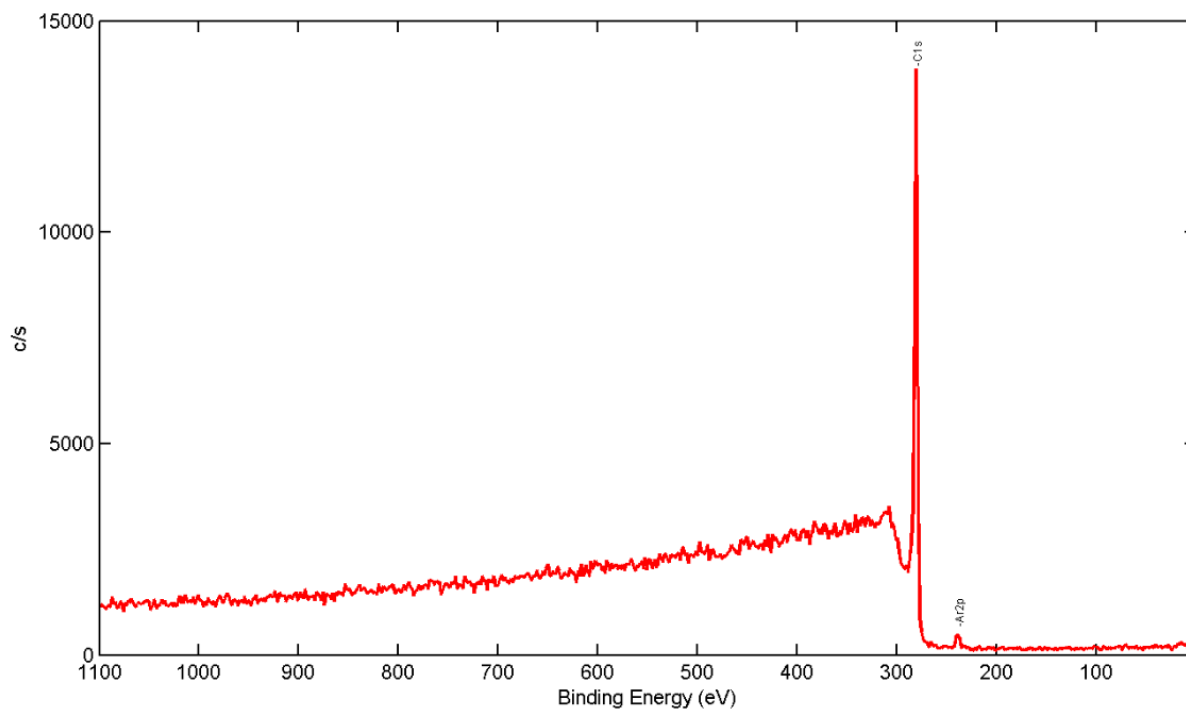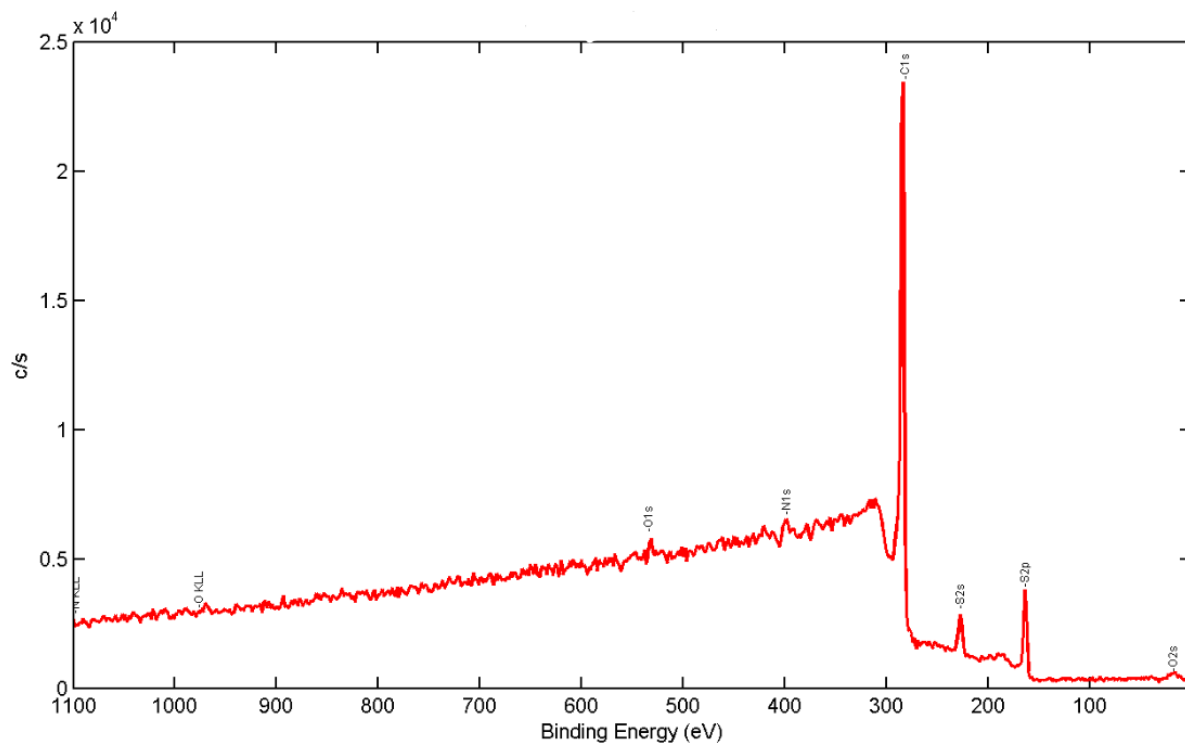No significant increase in oxidation was observed with XPS after the addition of the FRs in LDPE on the surface of the samples. The presence of carbon and sulfur atoms can be seen from the results at the surface. Hence, the reason behind better adhesion in the case of FR-A remains unclear. Further testing could be performed in the future to investigate the true cause of the phenomenon.

10.5 Din test for FR-Z (2nd Testing Series)

A very fine variant of FR-Z was evaluated in the second series of tests. FR-Z decomposes to release carbon dioxide which hinders the process of combustion. DIN-4102 test was performed with FR-Z in the laboratory and the results are presented in Table 10.

Table 10: DIN-4102 for FR-Z

Formulation (%) in LDPE	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-Z=10%	1	8.2	7.5+6.5	Yes
FR-A=1%	2	4.5	6.5+6	Yes
	3	5.7	7.5+7	Yes

The compound exhibited very good results with some dripping. FR-Z along with other FRs was then used in the second pilot run. More testing for the compound is presented in the following sections to check the stability and efficiency regarding flame retardancy.

10.6 CONE calorimeter analysis for FR-Z (2nd Testing Series)

The formulations described in Table 10 were tested on cone calorimeter to check the efficiency of FR-Z with a forced decomposition at higher temperatures. Results from the testing are presented in Figure 18 and Figure 19.
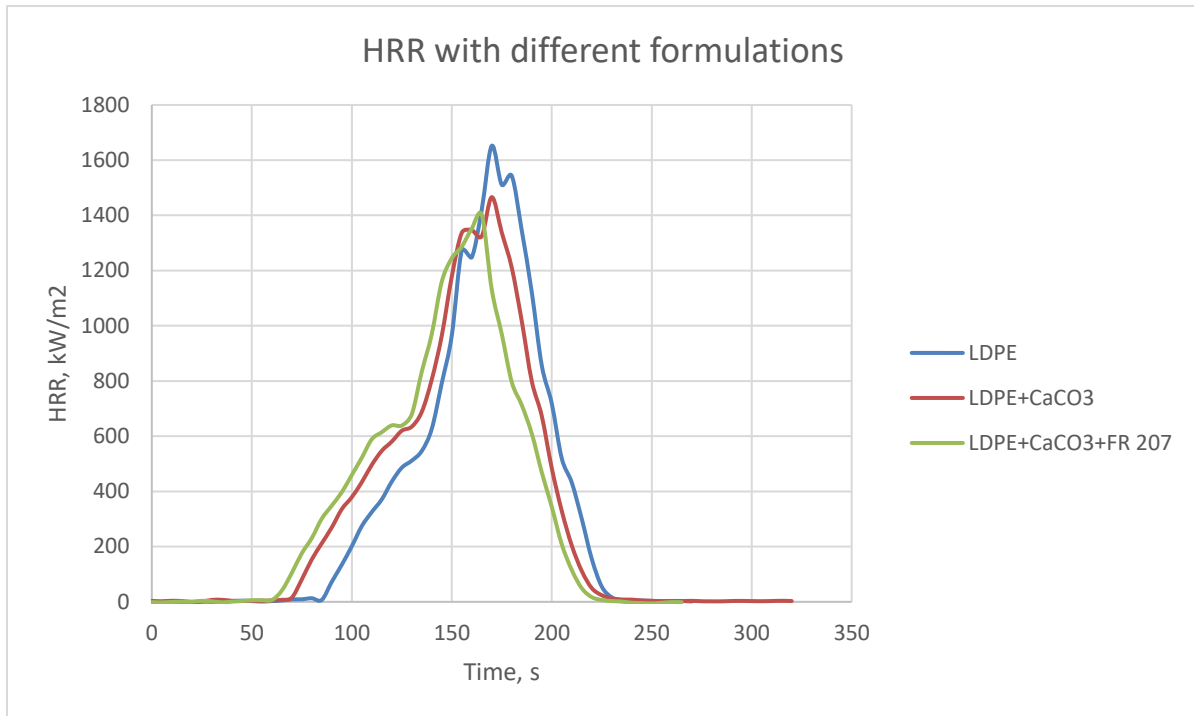
Figure 18: HRR analysis using cone calorimeter

The addition of FR-Z decreases only slightly the heat release rate (HRR) as compared to the plain LDPE as shown in Figure 18. However, the addition of FR-A does not bring much difference in the HRR. As mentioned before that FR-A had the better adhesion on the paper substrate so it will be used with every formulation just for the purpose of achieving good adhesion.
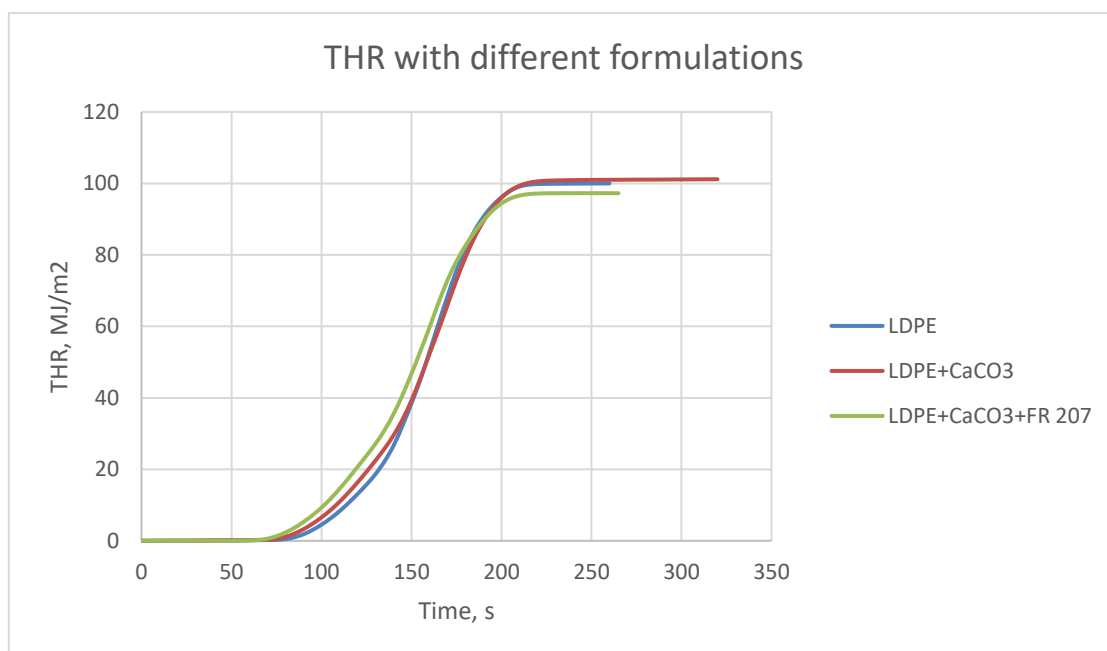
Figure 19: THR analysis using cone calorimeter

There was no significant difference observed in total heat released (THR) by the addition of the additives as shown in the figure. However, the previous DIN-4102 test for the compound presents a promising FR behavior after the extrusion coating of LDPE on the paper.

10.7 Paper samples testing (2nd pilot run)

The LDPE coated paper samples were again tested by DIN-4102 test in the laboratory. As previously described, the issue of a good adhesion remains a problem even though a good fire retardancy is achieved in some samples. The results of the paper samples are as follows:

Table 11: DIN 4102 test for paper samples

(%) in LDPE	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-A= 1 %	1	28	All	No
FR-X= 4%	2	28.3	All	No
(Abo 7)	3	1.6	16+3	No
FR-A= 1 %	1	0	12+2	No
FR-X= 4%	2	0	14+2	No
FR-D =5%	3	9.5	All	No
(Abo 8)				
FR-A= 1 %	1	18.0	All	No
FR-Z =10%	2	8.9	All	No
(Abo 9)	3	1.3	7.5+2.5	No

The DIN test proved that Abo 8 has very good flame retardancy as seen from the table. However, the adhesion was not satisfactory in the case of Abo 8. FR-Z seems not to be decomposing at the lower burning temperatures to liberate useful gases. FR-X has shown good results in both pilot scale runs in combination with FR-D and this combination is surely promising. The percentage of FR-A should be increased as it gave a good adhesion at 3% loading and that is the least amount required in the future.

11. Conclusions and Recommendations

The aim of this study was to prepare polymeric coatings for paper substrate and achieve good adhesion along with a good flame retardancy. The main challenge was to find a borderline temperature which suits both purposes. A very high temperature can give better adhesion but degrades the FR while lower temperatures cause a poor adhesion even though the FR does not decompose. All the experiments were performed at the highest possible temperature which the FRs could withstand. The two sets of pilot scale testing were performed by taking into account the best possible formulations which were selected from the laboratory scale FR testing. LDPE was used as the coating material on the paper substrate and the FRs were mixed in LDPE before coating it on paper.

The results from the study show that the temperature selected for the testing was not sufficiently high for achieving good adhesion between the polymer coating and the paper substrate. However, some formulations gave good results in DIN-4102 fire testing but they cannot directly be implemented in production due to inadequate adhesion. The bonding between the two layers is essential for viable coated products and cannot be neglected. Some FRs have shown a good adhesion even at lower temperatures and they can be used in appropriate amounts for the sole purpose of achieving good adhesion in the future. The reason behind the better adhesion was investigated but it still remains unclear even after performing DSC and XPS studies on the samples exhibiting good adhesion.

In order to achieve the goal of a better flame retardancy along with satisfactory adhesion, it is necessary to find or develop FRs which can withstand higher temperatures. Surface treatments on the paper substrate can also be performed for better adhesion but they significantly increase the cost of production. The formulations in this study which showed good adhesion can be used in combination with the ones with better flame retardancy and in this way a cost-effective solution to the problems may be found in the future.

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13. Appendices

A series of FRs have been tested in the laboratory for effective synergies and initial results of the compounds. The FRs were synthesized in the laboratory and bought from the market as well. The description is as follows.

Table 12: FRs and their source

Flame retardant	Source
FR-A	Synthesized in Laboratory
FR-I	Synthesized in Laboratory
FR-J	Synthesized in Laboratory
FR-D	Clariant oy
FR-K	Afflamit by THOR
FR-M	Afflamit by THOR
FR-Z	From Market
FR-N	From Market
FR-Y	Martinel
FR-G	Afflamit by THOR
FR-P	From Market

13.1 LDPE testing with FRs in the laboratory

LDPE was tested with different FRs, both commercial and synthesized in the laboratory. Some combinations are made to check if there is any synergistic effect between the FRs. The results of the DIN-4102 tests are shown as following.

Table 13: DIN-4102 for different FRs

Formulation (%)	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-D = 5%	1	28.6	All	Yes
	2	29.3	All	Yes
	3	29.8	All	Yes
FR-D = 3%	1	35.3	All	Yes
	2	33.0	All	Yes
	3	33.8	All	Yes
FR-I = 3%	1	7.9	15+8.5	Yes
	2	19.6	All	Yes
	3	14.0	All	Yes
FR-J = 3%	1	43.4	All	Yes
	2	25.9	All	Yes
	3	43.5	All	Yes

UL94V testing of LDPE with different FRs in the laboratory was also performed and the results are as follows. N.C stands for Non-classified in the case when burn time exceeds 30 seconds.

Table 14: UL94V test for different FRs

Formulation (%)	Sample no.	Burning time T_1+T_2 (sec)	Burn all	Cotton ignition
FR-K = 10 %	1	58.43	Yes	Yes (N.C)
	2	52.50	Yes	Yes (N.C)
	3	58.63	Yes	Yes (N.C)
	4	57.2	Yes	Yes (N.C)
	5	56.5	Yes	Yes (N.C)
FR-K = 15 %	1	49.5	Yes	Yes (N.C)
	2	51.7	Yes	Yes (N.C)
	3	55.9	Yes	Yes (N.C)
	4	54.1	Yes	Yes (N.C)
	5	53.2	Yes	Yes (N.C)
FR-M = 10 %	1	57.3	Yes	Yes (N.C)
	2	51.8	Yes	Yes (N.C)
	3	51.7	Yes	Yes (N.C)
	4	58.0	Yes	Yes (N.C)
	5	56.3	Yes	Yes (N.C)
FR-M = 15 %	1	48.0	Yes	Yes (N.C)
	2	59.1	Yes	Yes (N.C)
	3	60.6	Yes	Yes (N.C)
	4	52.1	Yes	Yes (N.C)
	5	58.6	Yes	Yes (N.C)

13.2 PP testing with FRs in the laboratory

Polypropylene (PP) was also tested with different FRs, both commercial and synthesized in the laboratory. Some combinations are made to check if there is any synergistic effect between the FRs. The results of the DIN-4102 tests are shown as following.

Table 15: DIN-4102 test for different FRs in PP

Formulation (%)	Sample no.	Burning Time (sec)	Damage L+W (cm)	Paper ignition
FR-N = 15%	1	0	6+4	No
	2	0	10+5	No
	3	0	10+4	No
FR-N = 10%	1	0	5.5+4.5	Yes
	2	0	7.5+4.5	Yes
	3	0	6+5.5	Yes
FR-J = 1%	1	3.2	6.7+8	Yes
	2	6.3	7.2+7	Yes
	3	2.5	8+8	Yes
FR-I = 1%	1	0	7+6	Yes
	2	0	10+6	No
	3	0	7.5+7	Yes

UL94V testing of PP with different FRs in the laboratory was also performed and the results are as follows. N.C stands for Non-classified in the case when burn time exceeds 30 seconds.

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Table 16: UL94 test for different FRs in PP

Formulation (%)	Sample no.	Burning time T_1+T_2 (sec)	Burn all	Cotton ignition
FR-P = 5 % FR-I = 1%	1	2.5	No	Yes (V2)
	2	0.5	No	Yes (V2)
	3	4.0	No	Yes (V2)
	4	0.7	No	Yes (V2)
	5	3.7	No	Yes (V2)
FR-G = 6 % FR-I = 2%	1	0.1	No	Yes (V2)
	2	0	No	Yes (V2)
	3	0	No	Yes (V2)
	4	0	No	Yes (V2)
	5	0	No	Yes (V2)
FR-P = 5 % FR-I = 2%	1	0.6	No	Yes (V2)
	2	0.9	No	Yes (V2)
	3	6.2	No	Yes (V2)
	4	2.3	No	Yes (V2)
	5	0.8	No	Yes (V2)
FR-G = 8 % FR-I = 2%	1	0	No	No (V0)
	2	0	No	No (V0)
	3	0	No	No (V0)
	4	0	No	No (V0)
	5	0	No	No (V0)

Table 17: UL94 test for different FRs in PP

Formulation (%)	Sample no.	Burning time T_1+T_2 (sec)	Burn all	Cotton ignition
FR-Z = 30 % FR-A = 1%	1	53.1	Yes	Yes (N.C)
	2	58.5	Yes	Yes (N.C)
	3	62.7	Yes	Yes (N.C)
	4	56.6	Yes	Yes (N.C)
	5	61.4	Yes	Yes (N.C)
FR-Z = 15 % FR-A = 1% FR-Y=15% (OL-107-LEO)	1	7.8	No	Yes (V2)
	2	25.5	No	Yes (V2)
	3	32.4	No	Yes (N.C)
	4	58.0	Yes	Yes (N.C)
	5	33.6	No	Yes (N.C)
FR-A = 1% FR-Y=30%	1	27.4	No	Yes (V2)
	2	42.8	No	Yes (N.C)
	3	68.0	No	Yes (N.C)
	4	92.7	No	Yes (N.C)
	5	35.9	No	Yes (N.C)

Table 18: UL94 test for different FRs in PP

Formulation (%)	Sample no.	Burning time T_1+T_2 (sec)	Burn all	Cotton ignition
FR-N = 15 %	1	11	No	Yes (V2)
	2	3.1	No	Yes (V2)
	3	2.8	No	Yes (V2)
	4	2.1	No	Yes (V2)
	5	6.1	No	Yes (V2)
FR-N = 10 %	1	91.8	No	Yes (V2)
	2	86.9	No	Yes (V2)
	3	16.1	No	Yes (V2)
	4	2.2	No	Yes (V2)
	5	51.8	No	Yes (V2)

Table 19: UL94 test for different FRs in PP (HP 500)

Formulation (%)	Sample no.	Burning time T_1+T_2 (sec)	Burn all	Cotton ignition
FR-G = 4.5 % FR-A = 2%	1	0.6	No	Yes (V2)
	2	3.7	No	Yes (V2)
	3	1.7	No	Yes (V2)
	4	0.4	No	Yes (V2)
	5	0.3	No	Yes (V2)
FR-G = 4.5 %	1	71.5	Yes	Yes (N.C)
	2	29.7	No	Yes (V2)
	3	61.1	Yes	Yes (N.C)
	4	36.4	No	Yes (N.C)
	5	70.9	Yes	Yes (N.C)