

INTUMESCENT FLAME RETARDANT :
SYNTHESIS, CHARACTERIZATION AND BLENDING WITH
POLYOLEFINS VIA REACTIVE EXTRUSION

by
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SYNTHESIS, CHARACTERIZATION AND BLENDING WITH
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ABSTRACT

Flame retardant polymers that may be considered for fire resistant cable jacketing polymers were developed. Synthesis of flame retardant compound in bulk amounts for extrusion process was held. Morphology, dispersion and particle size, flame retardancy, and mechanical properties of modified polymers were investigated and characterized for optimization of flame retardancy and mechanical properties.

For imparting flame retardancy to polymer matrix, intumescent type flame retardant synthesized. Improved residual char producing recipe was examined for better intumescent barrier between polymer and heat source. Stearyl alcohol, Mannitol, and Pentaerythritol were tried as carbonic sources, and Phosphorus pentoxide and Phosphoric promoter chemicals were tried for improved char residue. For better flame resistancy synergistic phenomenon was utilized by addition of nitrogen sources such as Melamine and Ethylenediamine.

Polymer and additive were processed in extruder. Due to hydrophilicity-hydrophobicity difference between flame retardant additive and polymer matrix, compatibilizers were utilized for improving interfacial adhesion. Fragile nature of flame retardant compound under high temperatures and shear forces were another concern to access improved mechanical properties in extrusion process. Processing variables were optimized by experimental trial and error methodology.

ÖZET

Bu arařtırmada kablo endustrisinde kullanılabilir yanmaya karřı dirençli polimer geliřtirildi. Adi geçen polimerlerin büyük ölçekte sentezlenmesi için ekstrüzyon makinası kullanıldı. Üretilen modifiye edilmiş polimerlerin yüzey özellikleri, dağılımı, katkı maddesinin parçacık büyüklüğü, yanmaya karřı dirençleri, ve mekanik özellikleri karakterize edildi ve bahsi geçen özelliklerin optimizasyonu için çalışmalar yapıldı.

Eklendiğı polimere yanmayı geciktirme özelliğini kazandırmak için şişerek katı bariyer oluşturarak yanmayı geciktiren özellikte geciktirici katkı sentezlendi. Bozunduğunda daha fazla kalıntı kurum bırakan katkı için değışik kimyasal tarifler denendi. Stearil alkol, Mannitol, ve Pentaeritrol denenen karbon kaynakları arasındaydı. Fosforpentaoksit ve fosforik asit denenen asit kaynakları arasındaydı. Katkının yanmayı geciktirici özelliğinin artırılması için sinerjistik özellikteki Melamin ve Etilendiamine tarife ayrı ayrı katılarak denenen nitrojen kaynaklarındandırlar.

Polimerle katkının karışırılması ekstruder'de gerçekleştirildi. Polimerle katkı arasındaki hidrofobiklik farkından dolayı katkının daha iyi karışması ve iki maddenin daha iyi yüzey yapışmasını sağlamak için iki maddeyi uyumlandırabilecek kimyasallardan yararlandı. Eklenen katkının makaslama gerilimindeki ve yüksek sıcaklıklardaki kırılğan yapısının geliştirilmesi, iyileştirilmiş mekanik özellikte kompozitleri yaratmak için dikkate alınan diğerk hususlardı. Proses değışkenleri deneysel deneme yanılma metodolojisi ile optimize edildi.

To Mother, Aysel, never exhausting and fearless warrior, third time victor...

To Father, Yasar, once upon a tough “Arap” journalist, now a cook, a bread cooker, a herbalist, a chemist, a medical doctor, a nurse, a researcher, a book writer, a defendant, a winner...

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1. INTRODUCTION

1.1 Polyolefins and Their importance in Industry

Polypropylene is one of the three general plastics [1], 19 billion tones of Pp was produced in 2003[2], and 6.3% growth is expected for each year. It is widely used for housing purposes, cables, automotives, electronic and electric industry and so on. Polyethylene is also one of the most important plastics used today. 30 billion tones was produced in 2003 as high density polyethylene, low density polyethylene and low low density polyethylene. Improvement on production and technical properties of Polypropylene together with Polyethylene creates increased market size while flame retardancy concern is an important issue to overcome in many applications for safety reasons.

1.2 Definition of Flame

A flame is the product of a highly exothermic reaction for example combustion, a self-sustaining oxidation reaction, or nuclear fusion in the sun. A flame could be said to be, for example, the visible part of a fire.

The color and temperature of the flame are dependent on the type of fuel involved in the combustion. For example: when a lighter is held to a candle. This applied heat causes the fuel molecules to evaporate, in this state they can then react with oxygen, giving off enough heat in the exothermic reaction to sustain a consistent flame. The resulting increases in temperature tear apart some of the fuel molecules, forming various incomplete combustion products and free radicals.

1.3 Combustion of Polymers and Flame retardancy Mechanisms

1.3.1 Ignition and Degradation of Polymers

Because all carbon-containing polymers are organic, they burn under one or more set of conditions. Polymers, being solid, do not burn clearly; it is the volatile products of thermal decomposition that burn.

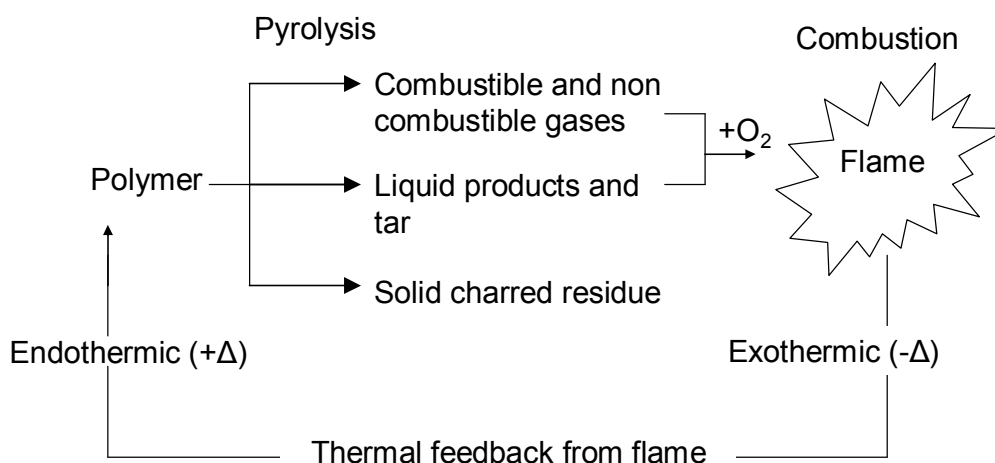


Figure 1 : Schematic diagram of polymer burning

While the overall reaction is burning, the actual reaction mechanism has two steps. When the polymer encounters a heat source, first thing that occurs is not combustion process. First of all polymer undergoes endothermic pyrolysis reaction that gives off both combustible, non combustible gases and tar as products. This first step is Endothermic, $\Delta H > 0$, thus for a polymer species to burn first it has to be activated with outside heat source. Intermediate products of the pyrolysis reaction are the things that are burning with heat supplied are low molecular weight volatile organic chemicals.

The burning of polymer is self-propagating when the heat of combustion is sufficient to maintain an adequate supply of decomposition products as fuel. Since the combustion process is spontaneous and gives off heat to the surrounding, after this point on flame becomes self-sustaining. The process of spreading a flame over the surface of a polymer material is considered a continuous diffusion ignition process for the gaseous state of the polymer's degradation products. Heat from a flame, radiating on the surface edge of a material, warms up a layer of polymer material to the temperature at which gasification starts. The gaseous fuel products then diffuse from the surface into the oxidizing atmosphere. The self-accelerating exothermal oxidation of the fuel is generated in the gaseous phase. In this way, a continuous spread of flame proceeds.

1.3.2 Thermal Degradation Pathway of Polyethylene

Since polyethylene has hydrogens on all of its carbons, random scission is expected to be dominant way of the degradation, thus monomers and oligomers are produced as result of degradation. The major products observed in the course of polyethylene degradation includes ethylene and higher oligomers which evolve from hydrogen transfer to different positions along the polymer chain, so other than ethylene one also observes propylene, butane, pentene, hexane, and so forth[5]. These formed low molecular weight volatile organic chemicals constitute main fuel source in the latter step, which are undergo in combustion reaction together with Oxygen.

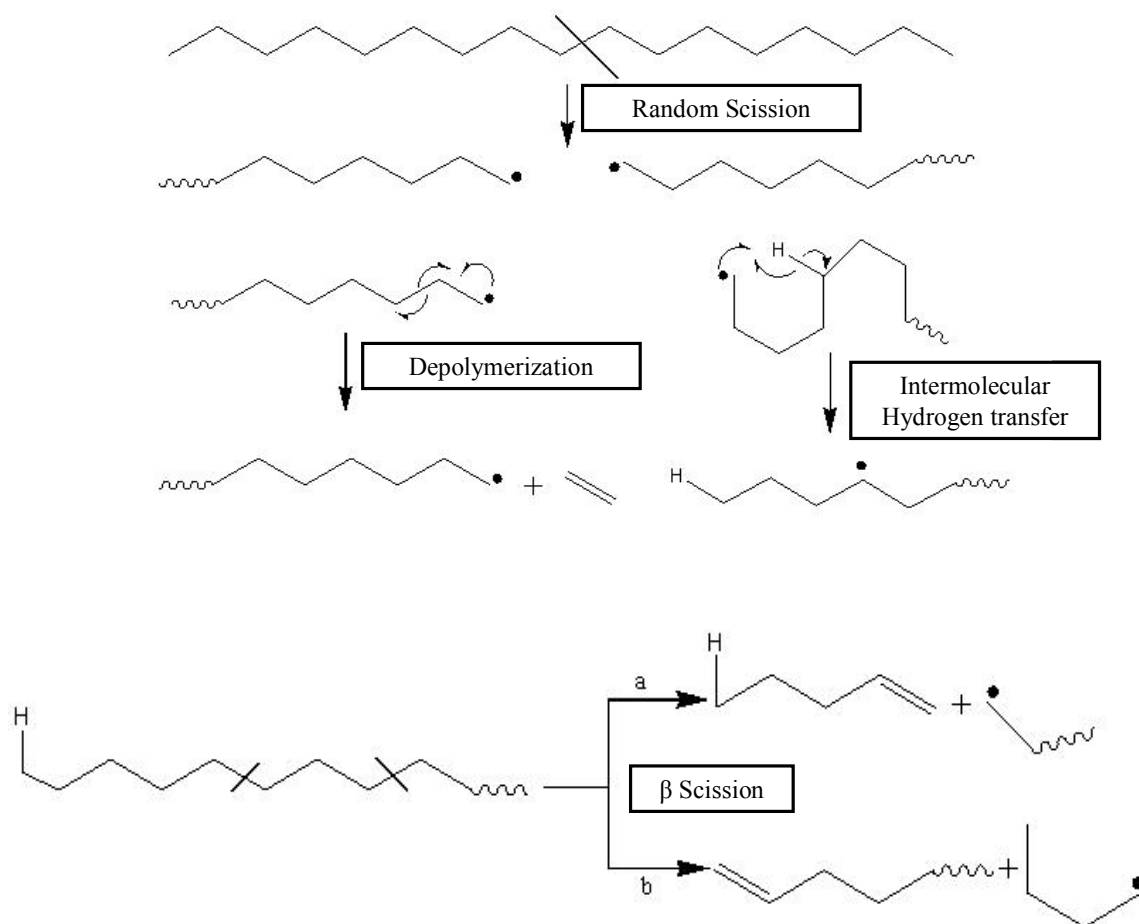


Figure 2: Degradation of Polyethylene showing initial random scission, depolymerization, intramolecular hydrogen transfer, and β -scission of the macroradical[5]

1.3.3 Retardation and Prevention of Flame in polymer burning

The objective of the additive is to prevent or retard the combustion process which occurs when polymer encounters with heat. This can be achieved following via different paths. First methodology is to suppress oxygen amount in media thus causing oxygen deficiency and due to this ending of combustion process since one of the vital chemical species is lacking. The other methodology is to usage of chemical species that lead to dilution of combustible gases, that can be achieved by producing non combustible and diluting liquids and gases. The third option is usage of some additives which in existence of heat evolve to non combustible species which acts as a heat barrier. If these mentioned non combustible heat barrier species has high heat capacity this will increase the efficiency of the additive since it behaves as a better heat sink.

One of these methodologies can be followed to produce flame retardant polymers and aim is to increase the resistance of the material to ignition and to reduce the flame spread with minimal degradation of its properties. Addition of flame-retardant material to polymer will suppress the propagation of flame due to above mentioned reasons[3]. These change the combustion characteristics of the polymeric material so that it will be more difficult to ignite. Once ignition has occurred, addition of flame retardant material will cause the flame to die out or cause the material to burn more slowly so that the flame spread, rate of heat release, or both will be substantially lowered[4].

1.4 Flame Retardation Mechanisms in Polyethylene

The different methodologies mentioned above is summed up in three different chemical systems. First one is Intumescent flame retardant systems, the second is halogenated flame retardants, and the last one is metal hydroxides.

Among many possible routes for flame retardancy that are mentioned above, recent research has shown halogen-free flame retardant intumescent-based technology that is an alternative to both halogenated and inorganic flame retardant for development of flame-retardant polymers. Intumescent char is an effective technical approach to develop the flame-retardant products with low overall fire hazards. Intumescency is preferable because it combines several advantages such as non-toxic, environment friendly nature and moderate price.

Due to the continuous trend in more strict safety regulations for plastics and paints, search for polymers with flame retardant properties is important. On this point flame retarding additives may impart their non-flammable properties to polymer matrix and can contribute to the fire propagation. In some wood and cable coating applications, significant level of fire-retardancy is required and coatings with flame retarding properties have been developed[6].

In conventional plastics, additives with chlorinated/brominated compounds had wide application to impart flame retardancy to the polymer matrix[7]. Gottlieb *et al.* utilized Pentabromobenzyl acrylate as main flame retardant and free radically polymerized the monomer via reactive extrusion in order to impart flame retardancy to Polypropylene

composites[8]. For poly(pentabromobenzyl acrylate) effective on flame retardancy loadings upto 30% is needed. In spite of achieving 25.5 Limiting oxygen index value when the halogenated compound is used together with secondary flame retardant additives, degradability problems in halogenated compounds' nature and toxic gases which are released while maintaining flame retardancy is a major drawback and their usage is decreasing for safety reasons.

On the other hand metallic hydroxides are environmentally friendly as intumescent systems but their low activity requires high loading amounts usually higher than 50% weight percent in order to impart adequate flame resistance to the polymer matrix which have negative impact on the mechanical properties of the matrix that they are applied to[1, 9, 10]. Hassan *et al.* tried to overcome this high loading amount problem by using synergistic agents, which promote metal hydroxides[11, 12]. This approach simply depends on synthesis of polymeric metal chelates, and together with Kaolin they act as promoter to metal hydroxides. However detailed mechanism for the promoter behaviour of cobalt chelate is not clear at this point. Moreover, recyclability is important aspect for plastics containing metal hydroxides other than their behavior under fire.

Flame retardants based on intumescency is preferable because of its moderate loading amount when compared with metal hydroxides, which do not have negative impact on mechanical properties of the polymer matrix[13]. Intumescent system is active in condensed phase and, do not release corrosive and toxic gases while maintaining flame retardancy[14]. Moreover, intumescent systems evolve less corrosive gases since nitrogen has higher decomposition temperature, and this is main reason for them for being used in cable jacketing industry.

For intumescent flame retardants there are several recipes, which impart desired flame retardancy. Zhang and friends use phosphorus pentoxide, as acid source, Pentaerythritol, as carbon source and Melamine, as spumific agent[15]. Since there is a compatibility problem arising from hydrophobic polypropylene and hydrophilic flame retardant, polypropylene is melted prior to mixing for improved compatibility. It is reported that 30% intumescent flame retardant has optimal flame retardancy[16].

Another method that can be utilized rather than using Pentaerythritol and reacting it to form phosphate ester, is using a polymeric carbon source[14, 17-19]. Since for a

intumescent additive reaction of hydroxyl groups with acid source is needed to form char layer, a polymer that contains poly hydroxyl groups will do the work[20]. The only problem with utilization of PVAc is its low thermal stability that cannot keep up with process temperature of polypropylene[21, 22]. However this problem can be overcome by addition of phenyl and stearyl groups to the polymeric type flame retardant. This method achieved 27% limiting oxygen index value.

Nowak *et al.* directed their research on intumescent flame retardant by reacting Melamine and phosphate and calcination of the product to get melamine polyphosphate[7]. Melamine polyphosphate together with Pentaerythritol results a decrease heat release rate of 924 kW/m² to 274 kW/m²

Another interesting study is synergism of boroxo siloxane[18, 23] elastomer with intumescent flame retardants was conducted by Bourbigot *et al.*. Since intumescency works on the principle that physical barrier prevents heat interaction with polymer, increased physical barrier results in better flame retardancy[24]. Addition of boroxo siloxane elastomer completes the cracks on intumescent flame retardant thus creating a dome like blown formation resulting in improved charred layer. Improvement is evidenced by 38% limiting oxygen index value.

Although there are many chemicals to prepare intumescent flame retardant additive, the working principle of all intumescent additives are alike. The main ingredients for intumescent additive are an acid source, a carbon source and a blowing agent[22, 25].

Phosphorus containing intumescent additive interferes with pyrolysis and combustion mechanism in way that it (fig.1);

- Promotes char formation, thus reduces the available combustible carbon containing volatiles in the gas phase[26]
- Stops the oxidation process of carbon at the carbon monoxide stage, thus decreases the exothermic heat of combustion damping the thermal-transition processes.
- Forms phosphoric and related acids, which react as a heat sink as they undergo endothermic reduction.

- Forms thin glassy or liquid protective layer in the condensed phase.
- Forms anhydrides of phosphoric and related acids, which may act as dehydrating agents and discourage hydrolytic degradation and promote char formation

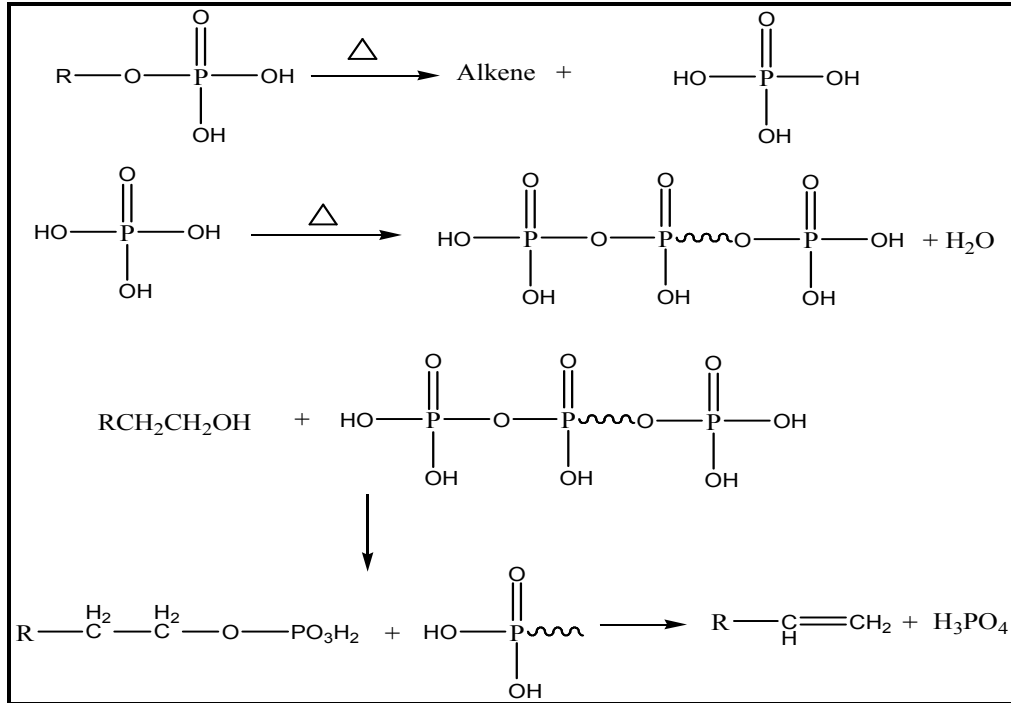


Figure 3: Activation mechanism for intumescent flame retardant[26]

2. EXPERIMENTAL PROCEDURE & MATERIALS

2.1 MATERIALS

2.1.1 Pentaerythritol:

Kindly donated by Çağ Kimya and used without further processing (fig.4).
Molecular Weight=136.2

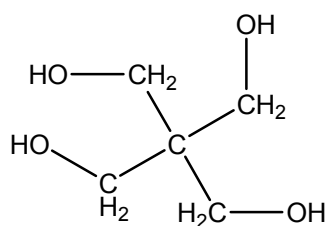


Figure 4: Pentaerythritol

2.1.2 Ortho-Phosphoric acid:

Purchased from Merck and used without further processing (fig.5).
Molecular Weight= 97.9

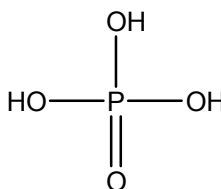


Figure 5: Phosphoric acid

2.1.3 Ethylenediamine:

Purchased from Acros Organics and used without further processing (fig.6)
Molecular Weight=60.1

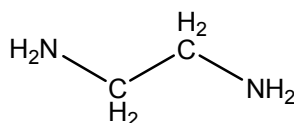


Figure 6: Ethylenediamine

2.1.4 Styrene

Technical Styrene separated from inhibitors by carrying alumina column purification

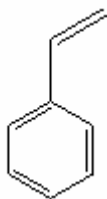


Figure 7: Styrene

2.1.5 Maleic anhydride

Maleic anhydride is purchased from Aldrich and used as received.

Molecular Weight= 98.1

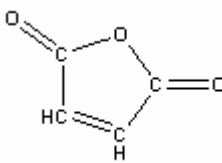


Figure 8: Maleic Anhydride

2.1.6 Benzoylperoxide

Purchased from Aldrich and used without further processing

Molecular Weight= 242.2

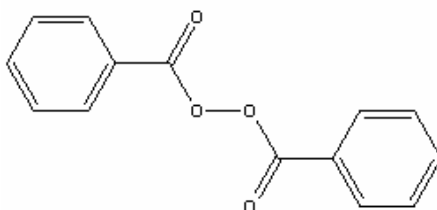


Figure 9: Benzoylperoxide

2.1.7 *α,α*-Dimethyl meta-isopropenyl Benzyl isocyanate(TMI)

Kindly donated by Cytec Industries, used without no further processing

Molecular Weight=187.3

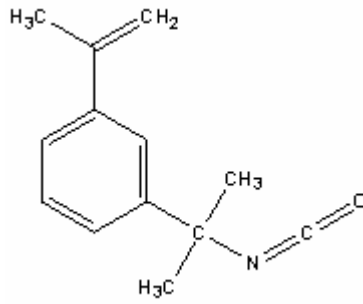


Figure 10: TMI

2.1.8 Polyethylene

Polyethylene is kindly donated by Petkim

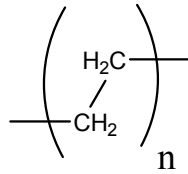


Figure 11: Polyethylene

2.1.9 Polypropylene

Polypropylene is kindly donated by Enplast

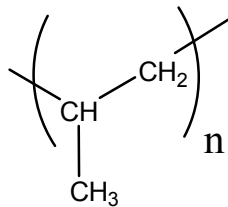


Figure 12: Polypropylene

2.1.10 Montmorillonite Clay (Mmt)

Mmt is kindly donated by Bengan Clay company. Clay is organo-modified.

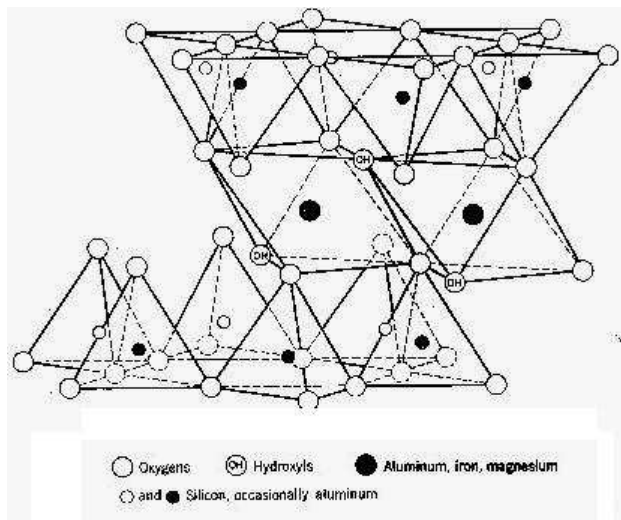


Figure 13: Bentonite clay

2.1.11 Elvaloy™

Elvaloy is kindly donated by DuPont. Elvaloy is Ethylene-Acrylate copolymer

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Synthesis of Flame Retardant Additive

Synthesis of first flame retardant additive contained two stages. In the first stage, stearyl alcohol was reacted with phosphorus pentoxide at 60 °C for 2 hours. Then melamine was reacted with the intermediary product, at 60 °C for another 2 hours. Stoichiometry and proposed mechanism for the reaction of the reactants were;

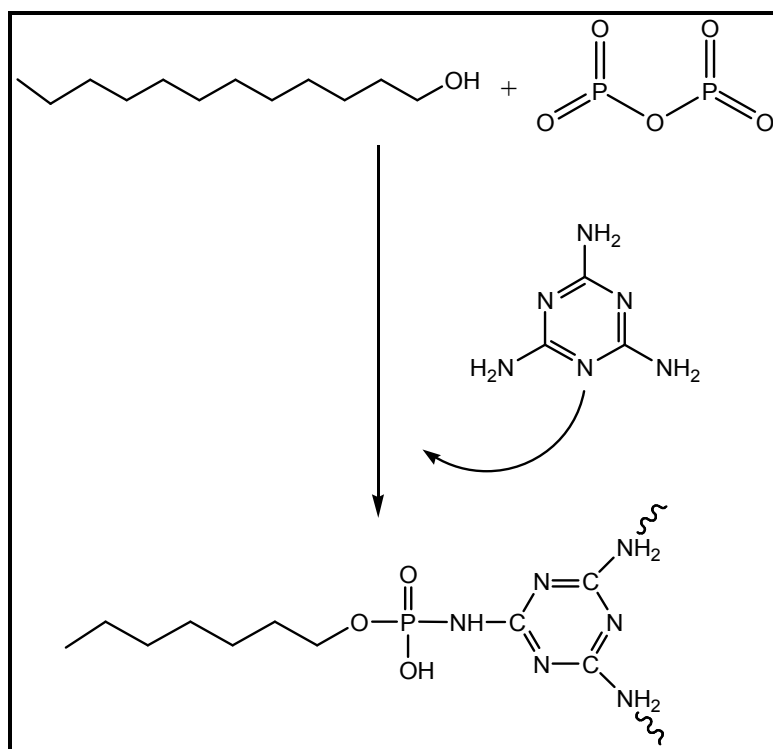


Figure 14: Synthesis of stearyl alcohol, phosphorus pentoxide, and melamine containing flame retardant

Table 1: Synthesis of stearyl alcohol, phosphorus pentoxide, and melamine containing flame retardant

Stearyl Alcohol	Phosphorus pentoxide	Melamine
1,00	1,00	2,00

Synthesis of second flame retardant additive contains two stages. In the first stage, Pentaerythritol is reacted with phosphoric acid at 130 °C for 8 hours. Then Ethylenediamine (EDA) is reacted with Phosphorus ester the intermediary product, at room temperature for several minutes. Second step of the reaction is exothermic and takes place immediately as soon as EDA is added onto the intermediary product. Special caution is needed during reaction because of EDA's extreme reaction affinity. Stoichiometry for the reaction of the reactants is follows;

Table 2: Synthesis of strearyl alcohol, phosphoruspentaoxide, and melamine containing flame retardant

Pentaerythritol(mol)	Phosphoric Acid(mol)	Ethylenediamine(mol)
1,00	2,66	1,00

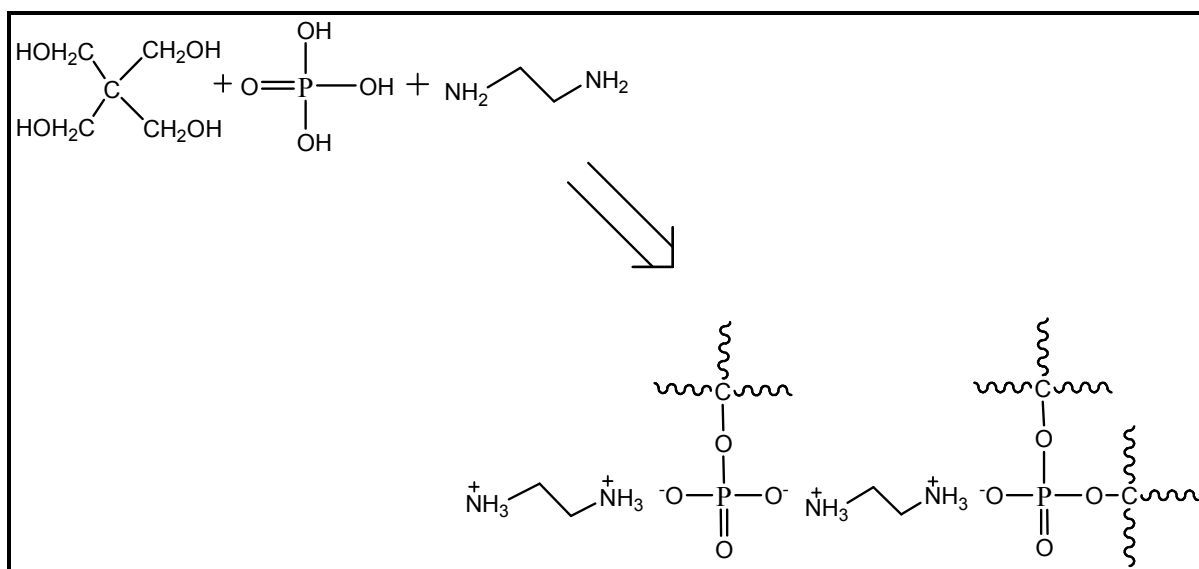


Figure 15: Synthesis of pentaerythritol, phosphoric acid, and ethylenediamine containing flame retardant

Another material used for increasing flame retardancy and mechanical properties of polymer composites was Montmorillonite (Mmt) Clay. Since there were gaps, galleries between each clay layer, synthesized flame retardant was intercalated to clay galleries. For this purpose after synthesis of flame retardant compound it is dissolved in distilled water and clay added to distilled water without any disturbance and stirring. After precipitation of Mmt clay, the flame retardant and Mmt mixture mixed for two days for intercalation of Mmt by flame retardant compound. Then mixture was precipitated in Acetone and dried in oven overnight at 70 °C.

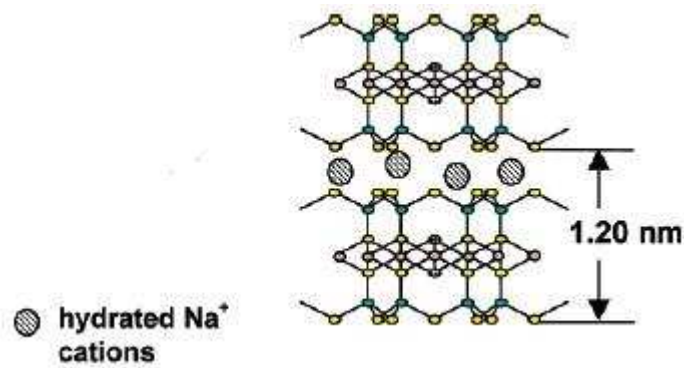


Figure 16: Mmt Clay before intercalation with flame retardant compound

2.2.1.1 Functionalization of Polyolefin via Reactive Extrusion

Either polyethylene or polypropylene does not have any functional group for flame retardant (FR) additive to bind chemically, thus prior to dispersion of FR additive, polymer gets functionalized with a bifunctional group in extruder via reactive extrusion. For functionalization of polyolefin, vinyl monomers used were 3-isopropenyl- α,α -dimethylbenzene isocyanate(TMI), and Maleic anhydride(MAH).

2.2.1.2 Dispersion of Flame Retardant Additive in Polymer Matrix via Reactive Extrusion

In the second part of the compatibilization of flame retardant additive to polymer matrix dry functionalized polyolefin, dry phosphorus and nitrogen containing flame retardant are utilized.

2.2.2 Limiting Oxygen Index (LOI) Testings

Most credited and wide-spread test for analyzing resistance of polymeric materials against fire is Limiting Oxygen Index test. In this method, sample is fixed in a vertical position in a glass chimney, providing a flux of a mixture of Nitrogen and Oxygen gases from the bottom of chimney. 4 centimeters high flame is applied to the sample from above. LOI value is the minimum amount of Oxygen volume that is efficient for spreading of flame for a given distance or for a given time. Greater LOI value for a material means greater resistance against burning (fig.8). LOI value can be calculated using below equation;

$$LOI = \left(\frac{[O_2]}{[O_2] + [N_2]} \right) \times 100$$

Using above equation minimum amount of oxygen volume is calculated, and standard resistance of material against fire is determined[27].

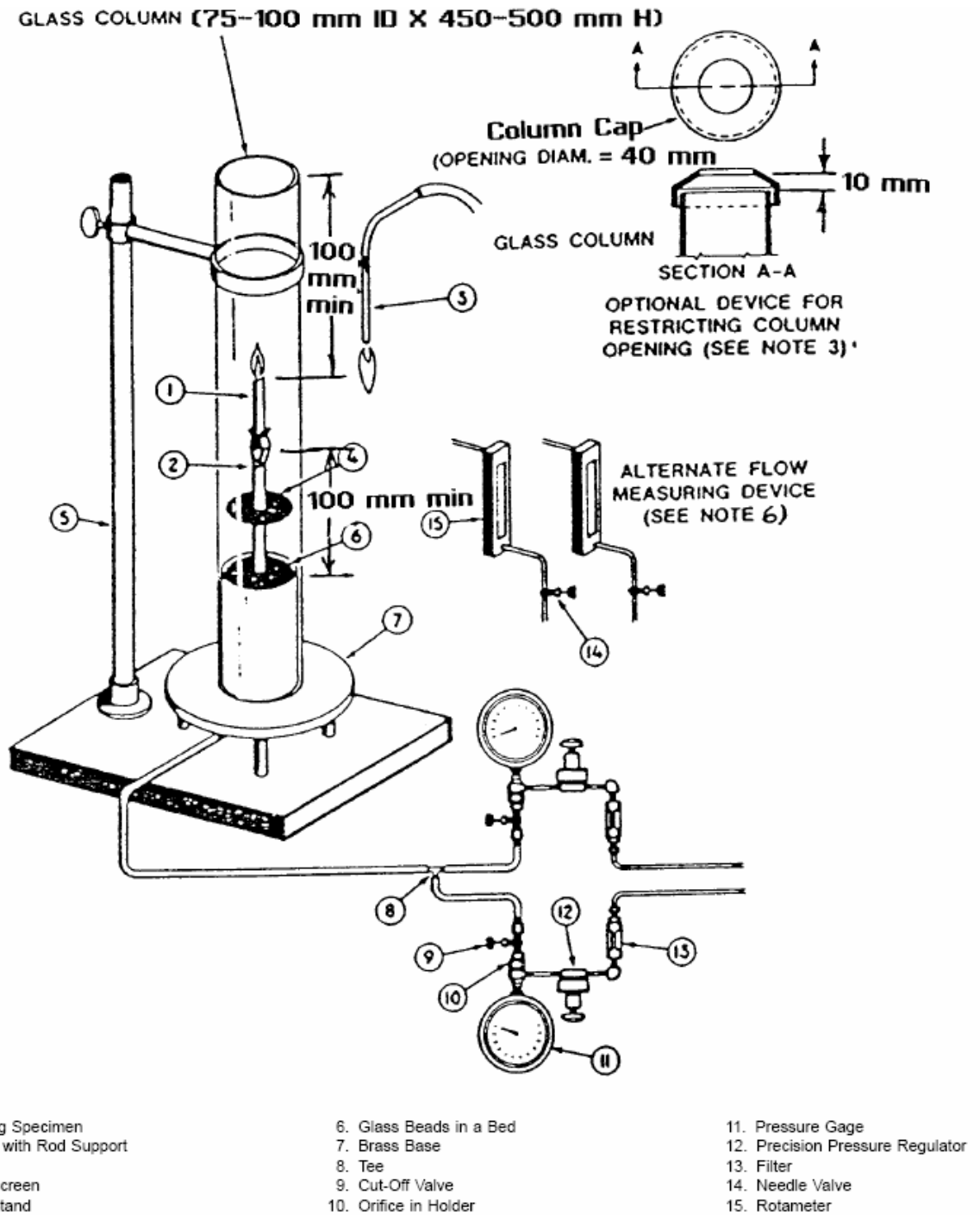


FIG. 1 Typical Equipment Layout

Figure 17: Limiting oxygen index[27]

3. RESULTS

3.1 CHARACTERIZATION OF SYNTHESIZED FLAME RETARDANT

For observing Intumescent behavior, one needs three different chemical species. First one of them is carbonic source that forms char layer, second one is char promoter, acidic source that initiates carbon source to undergo chemical reactions which is leading to carbon carbon double bond and at last charred layer acts as physical heat barrier between polymer and heat. The last species for recipe is blowing agent. Blowing agent increases the volume of the formed char by giving off gases, which create sponge like structure in charred layer during intumescent behavior is taking place. In this three component recipe for flame retardant, for each species, one is free to choose from a wide spectrum of chemicals; if the three component recipe meets the above mentioned prerequisites to cause intumescent behavior.

As a starting point due to compatibility concerns, the chemicals used were Stearyl alcohol, Phosphorus pentoxide, and Melamine. Stearyl alcohol was a long chain mono alcohol that can react with phosphorus pentoxide and the reason of its usage was, after reacting with Phosphorus pentoxide, it could act as a compatibilizer between additive and hydrophobic polymer. Melamine was used as a blowing agent and it was mixed with the product of Stearyl alcohol and Phosphorus pentoxide reaction. First step of the reaction proceeds at 60 °C and after mixing two hours Melamine was also added at 60 °C and further mixed for two hours. At the end of first 2 hours resulting product was highly viscous. Just after addition of Melamine, viscosity increased and color of mixture changed. After completion of reaction the product was grinded to the smallest particles with the help of liquid nitrogen. The smaller the particle size for additive, the better dispersion of additive in polymer matrix. This first flame retardant compound tested in melt mixer since melt mixer only needs 200 gr total amount of sample. This amount was easy to produce when compared to extruder's minimum amount of sample for operation.

Prior to addition of flame retardant compound into the melt mixer, polypropylene poured to melt mixer for melting of polymer and effective mixing. Polymer and flame retardant additive mixed for 4 minutes. Volume expansion observed at the end of mixing process due to activation of flame retardant, thus in second trial duration of mixing time while flame retardant additive is in the melt mixer decreased to 2.5 minutes for preventing the activation of flame retardant additive during processing. Then blend placed in hot plate to prepare test samples for flame retardancy and mechanical tests. UL-94 Flame retardancy tests showed the amount of flame resistance of polymer and flame retardant composite against heat source was not meeting the needs, flame extinguishing shorter than 3 minutes. Thus amount of flame retardant compound in polymer composite increased stepwise from 15 percent to 18 percent, and 21 percent. Increased additive loadings in polymer didn't result in increase the resistance of polymer against fire.

The amount of charred layer is directly proportional with the carbonic source that contains hydroxyl functional groups. When the system faces with heat source hydroxyl groups together with acidic source or with acid precursor undergoes an esterification reaction, which further reacts and leaves unstable Carbon Carbon double bond leading to char formation. Thus the amount of hydroxyl groups determines the amount of char formed. For that reason rather than mono alcohol, a polyol is favored. Due to the availability of Pentaerythritol and its wide use in paints and polymers is a key determinant in usage of Pentaerythritol as second choice for carbonic source. Another problem during synthesis of flame retardant is hygroscopic property of Phosphorus pentoxide.

Proposed mechanism for Synthesized intumescent flame retardant compound suggests that in the first step esterification reaction takes place. Outcome from reaction of polyol and phosphoric acid is phosphorus ester. Afterwards the ester that is produced is reacted with Ethylenediamine leading to final flame retardant additive. If these proposed reaction steps takes place; first the formation of phosphorus ester should be traced in FT-IR, also chemical reaction that takes place between polyol and phosphoric acid can be traceable via Nuclear Magnetic Resonance (NMR). Another evidence that grants the formation of one species from two steps reaction is differential scanning calorimetry

(DSC). Since each melting peak refers to different chemical species, DSC data also provides information about outcome of reactions.

Analysis for functional groups in synthesized flame retardant is one foot of revealing information on chemical structure of matter. Proposed mechanism for flame retardant suggests that in first step phosphorus ester should form, and in the second step reaction with Ethylenediamine should result in ammonium salt of phosphorus ester. FT-IR cannot give spatial or chemical environment information, however it reveals specific information on stretching of functional groups.

Analysis of synthesized flame retardant showed that formation of phosphorus ester in first step of reaction takes place. Peaks at around 1250 and around 1050 discloses P=O and P-O-C bonds' stretchings. Also analysis of region above 3000 points out existence of ammonium salts formation. In the existence of ammonium salt; a strong broad peak around 3300 is observed in spectrogram.

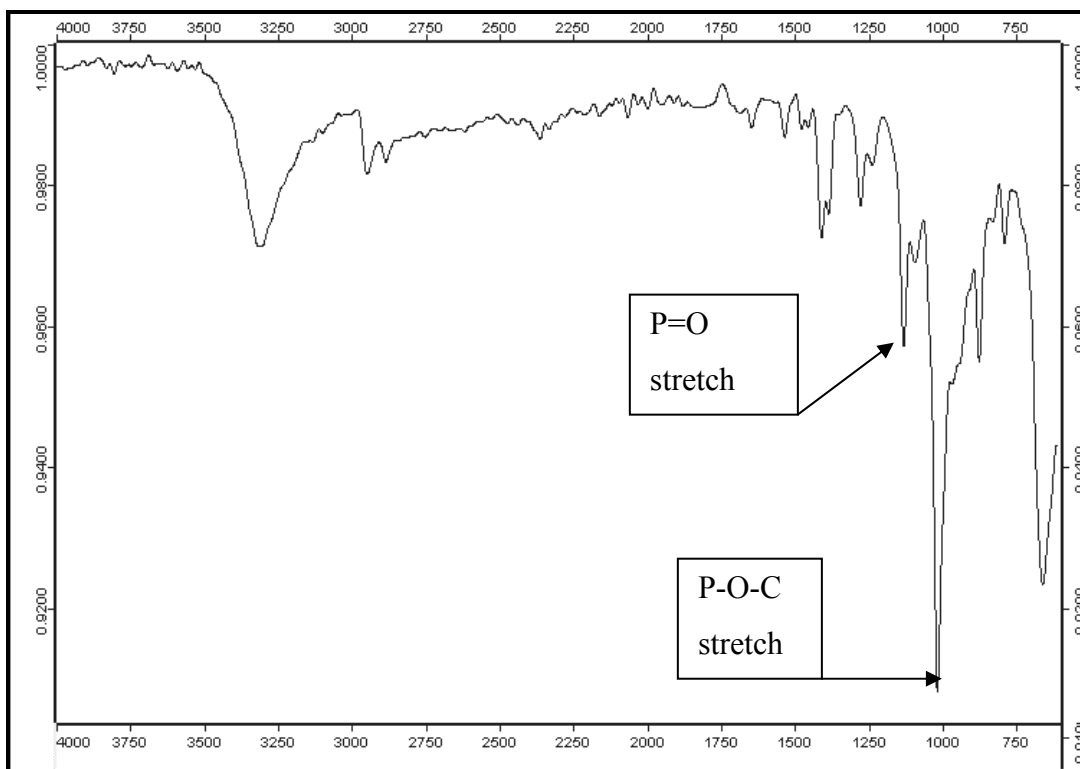


Figure 18: FT-IR of synthesized flame retardant. Peak for P=O stretch at ~1150, peak for P-O-C is at ~1030

3.1.1 Nuclear Magnetic Resonance Analysis

3.1.1.1 Proton NMR spectroscopy

In combination with FT-IR, analysis of the shifts in NMR enriches the information provided about synthesized flame retardant. Any possible reaction took place between Pentaerythritol and Phosphoric acid was investigated via comparing NMR spectrums of Pentaerythritol and synthesized flame retardant compound. If proposed reaction took place, the electronic structures of reactant and product would change. Since electron shield surrounding nucleus is the main determinant for the induced magnetic field in the negative direction to exterior magnetic field, the change in electron cloud surrounding the nucleus results in upfield or downfield shift in NMR spectrum.

Assigned proton peaks for Pentaerythritol are at 4.2 ppm and 3.35 ppm. The peak at 4.2 refers to Hydroxyl protons of Pentaerythritol and peak at 3.35 refers to $-CH_2$ protons of Pentaerythritol[28]. After reacting with Phosphoric acid and Ehtylenediamine, OH peaks broadened from NMR spectrum, and $-CH_2$ proton that is formerly at 3.35 shifts to 3.88 due to electron withdrawing effect of phosphate groups. Proton of EDA shifted to downfield due to deshielding after reaction with phosphoric acid's $-OH$ group. Peaks at 2,5 and 3,3 were assigned to protons of Dimethylsulfoxide (NMR solvent of flame retardant compound) and Water of Dimethylsulfoxide. These difference confirms the the proposed reaction mechanism of synthesis of flame retardant.

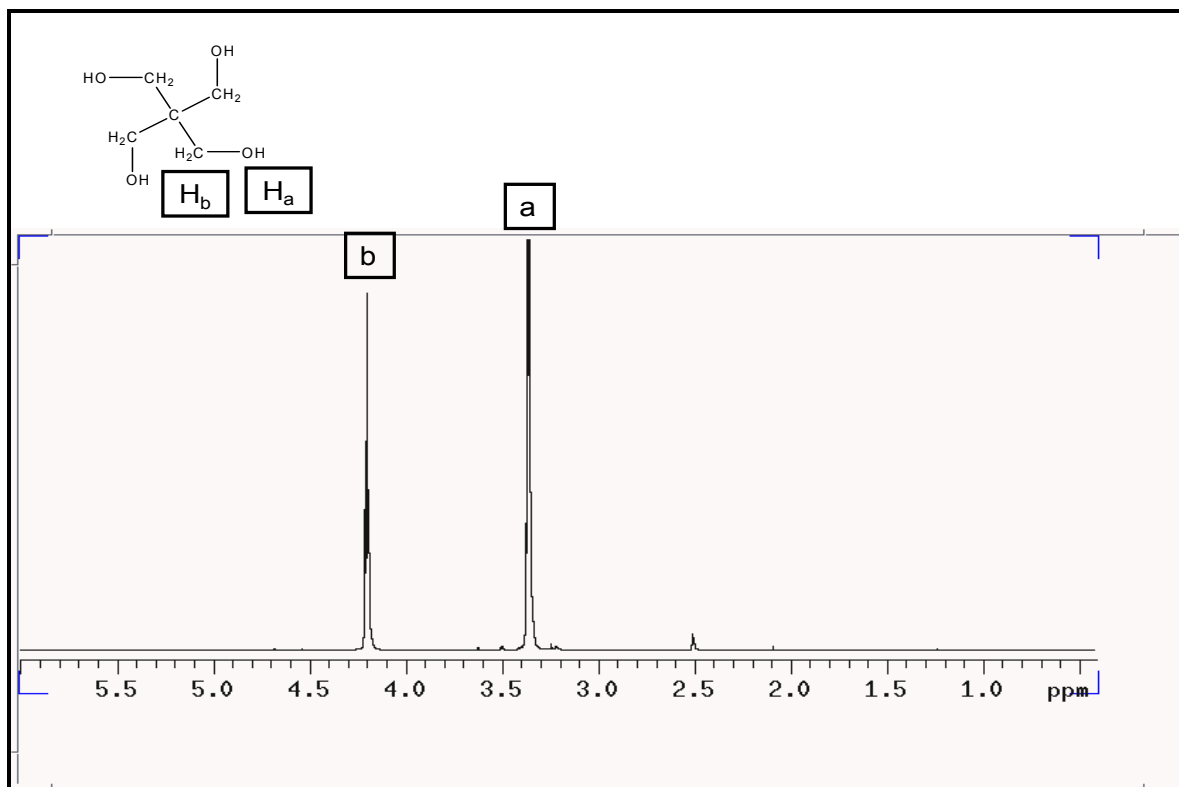


Figure 19: Proton NMR spectrum of pentaerythritol

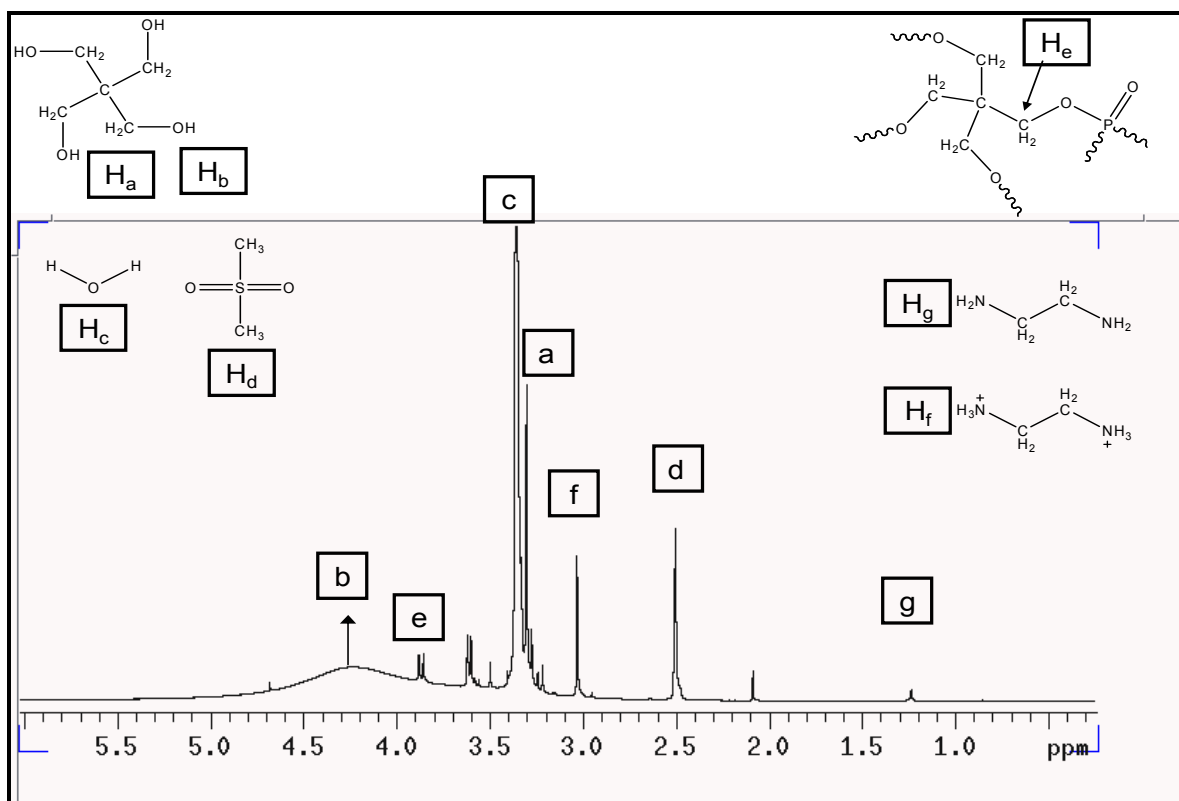


Figure 20: Proton NMR spectrum of synthesized flame retardant compound

3.1.1.2 ^{13}C NMR spectroscopy

For a better understanding of flame retardant compound, together with proton NMR spectroscopy, flame retardant compound was also investigated with ^{13}C NMR spectroscopy to observe differences occurred in electronic structure of carbons in transition from pentaerythritol to flame retardant compound. Central carbon atom of pentaerythritol gives peak at 61 ppm, while four $-\text{CH}_2\text{OH}$ carbons give peak at 45 ppm[28]. After esterification reaction with H_3PO_4 and acid base reaction with Ethylenediamine, previous peaks of Pentaerythritol carbons' peaks observed at 60, 45, and 36 ppm. It is expected for the central carbon peak not to shift since phosphate group's electronegative oxygens are farther than 3 bonds. Expected shift for $-\text{CH}_2\text{OH}$ carbons are in a upfield direction since phosphate group that is bonded to hydroxyl oxygen creates more electron rich environment. Thus shift from 45.5 to 36.0 ppm is an indicator for reaction of Pentaerythritol with of H_3PO_4 . Residual peak at 45 indicated that there was residual unreacted pentaerythritol which was in consistence with proton NMR spectrum results.

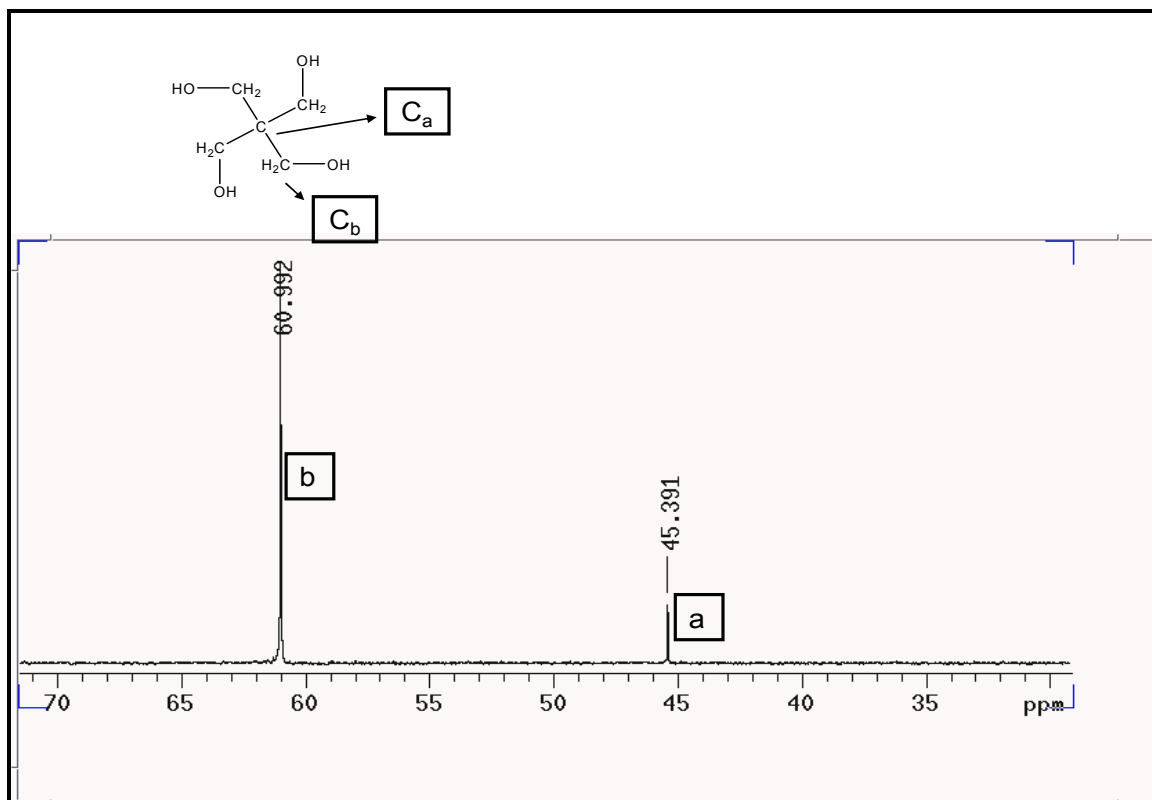


Figure 21: Carbon NMR spectroscopy of pentaerythritol

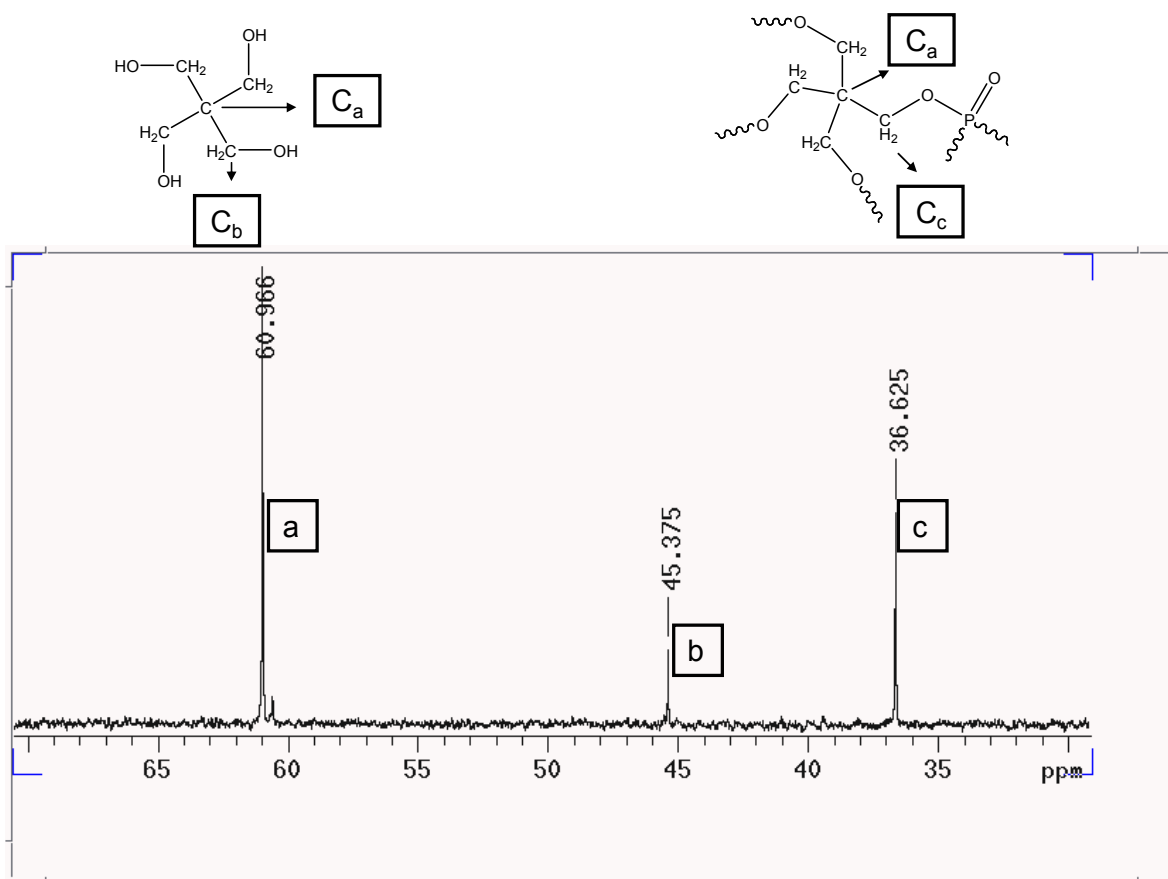


Figure 22: Carbon NMR spectroscopy of flame retardant compound

3.1.2 Flame retardant/ Clay composite

Due to intercalation results from X-ray diffraction measurements, it was certain that flame retardant could not be intercalated. The d distance of neat clay sample was 11.9, after treating clay with flame retardant compound the d distance was 14.7. Since intercalation was unsuccessful another approach applied. Clay was added to the composites as master batch. This was simply functionalization of polyethylene with maleic anhydride and then addition of clay to the polymer in 20 percent as a masterbatch. The prepared masterbatch was added to the polymer for second run in extruder in amounts so that it is diluted to 5 percent and 3% percent.

3.2 THERMAL ANALYSIS

3.2.1 DSC Result of Flame Retardant Compound

Melting and thermal decomposition temperature of flame retardant compound was obtained by DSC thermogram is illustrated. Flame retardant compound showed two melting points which is indicating there is unreacted species in flame retardant. Flame retardant compound decomposed at around 220 °C.

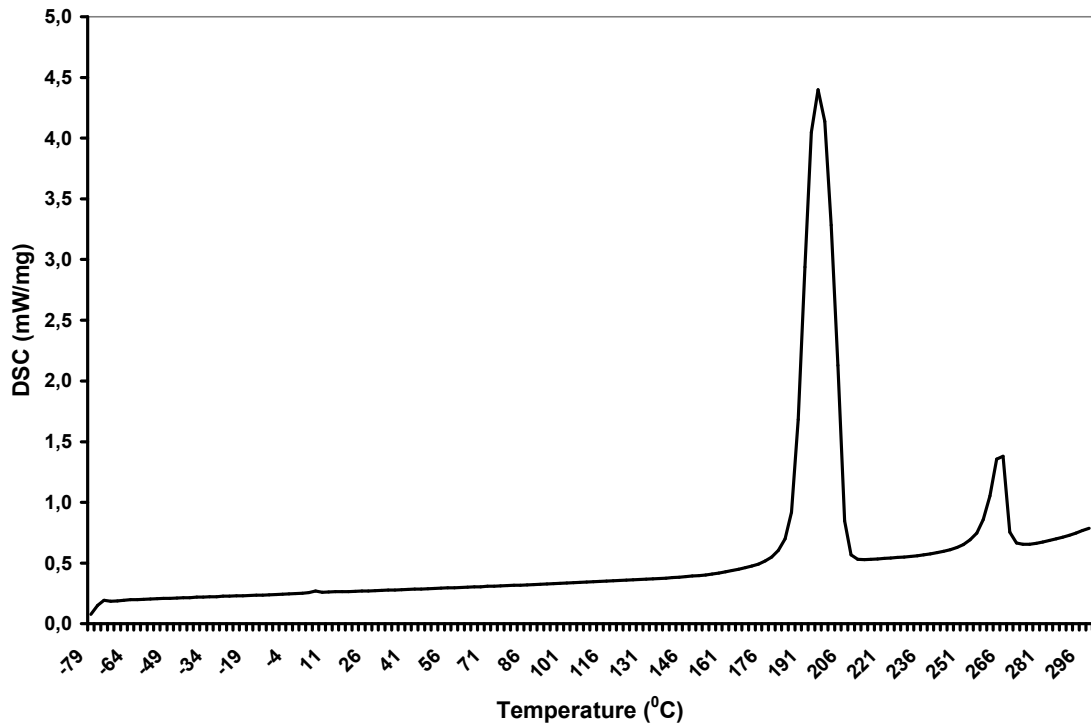


Figure 23: DSC of neat pentaerythritol

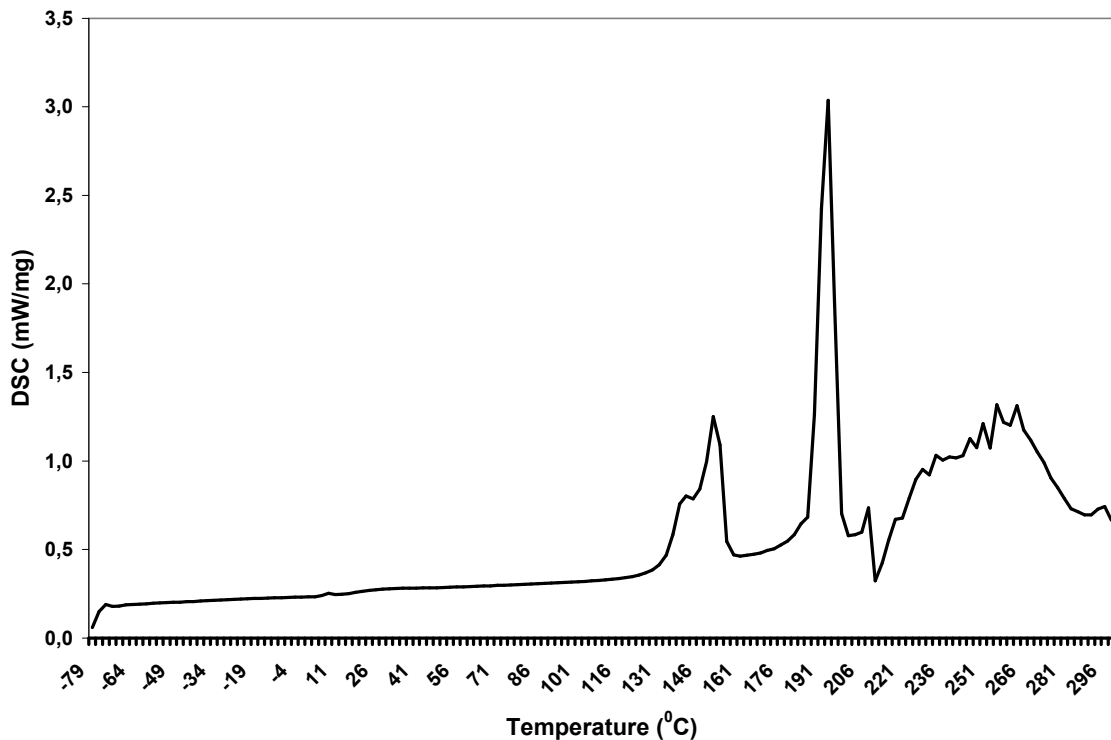


Figure 24: DSC of flame retardant compound

3.2.2 TGA analysis of Flame retardant compound and flame retardant polyethylene

Thermal stability of both flame retardant and flame retardant polyethylene were characterized using TGA as illustrated in below figures. Char yields were investigated to obtain information the fire resistance of both species.

Flame retardant compound without clay begins to decompose first at 210 °C, and second phase of weight loss was at 294 °C and 348 °C. Flame retardant compound totally charred at 726 °C. Flame retardant compound preserves 40% of its original weight upto 726 °C. When clay is added to the flame retardant compound thermal stability of compound increases as expected. From the first derivative it is observed that existence of clay decreases amount of exothermic reactions. Addition of clay pulled first decomposition of flame retardant to 201 °C, however the stability increased up to 800 °C. Flame retardant compound with clay preserves 50% of its original weight. Addition of neat flame retardant compound without clay into polyethylene matrix seemed to decrease thermal stability of polyethylene since one decomposition peak of PE was at 443 °C. Addition of flame retardant pulled first decomposition to 210 °C. then complex

decomposition behavior was observed. Blend noticed to have decomposition peaks at 210 °C, 240 °C, 270 °C, 320 °C, 469 °C, and 530 °C. These decompositions that flame retardant compound increased PE's thermal stability from 3% to 30% at around 500 °C. When there is a 5% clay together with flame retardant compound in polyethylene matrix residual weight at 500 °C decreases.10 percent. This may lead one to assume that thermal resistance of composite decreases. However closer analysis reveals that 20% residual weight is stable up to 800 °C in contrast with neat flame retardant compound was having its stable thermal heat barrier property up to 500 °C.

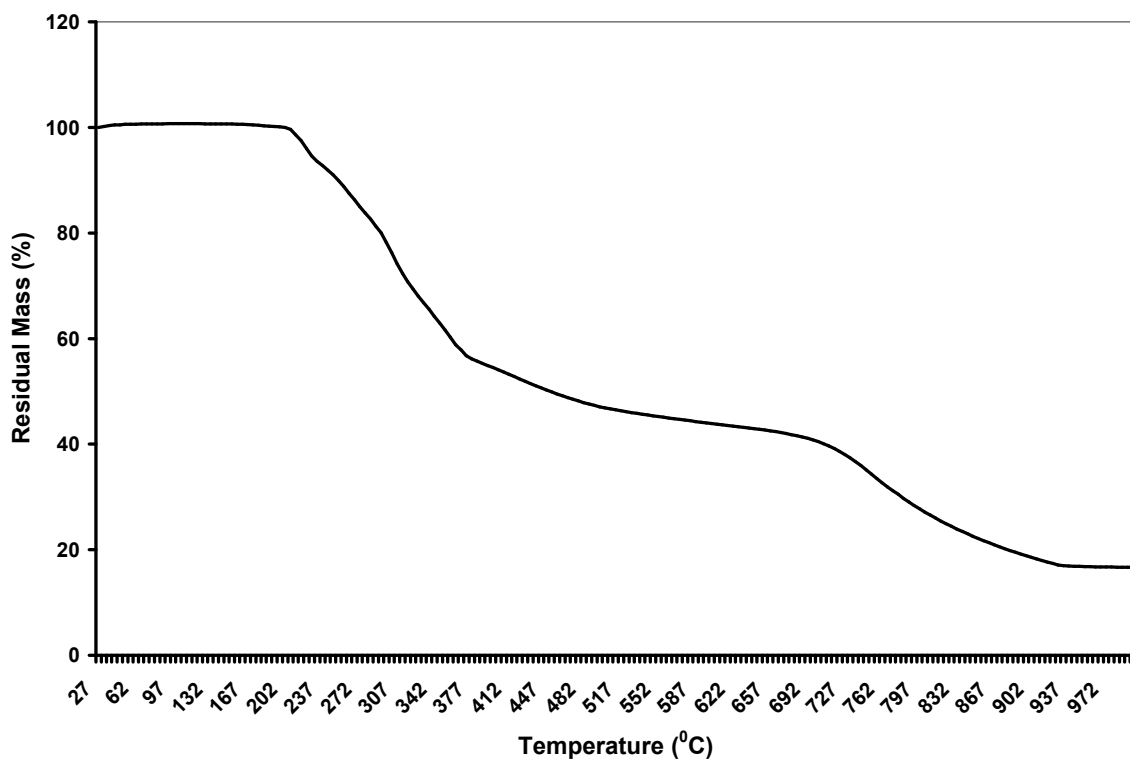


Figure 25: TGA of flame retardant compound

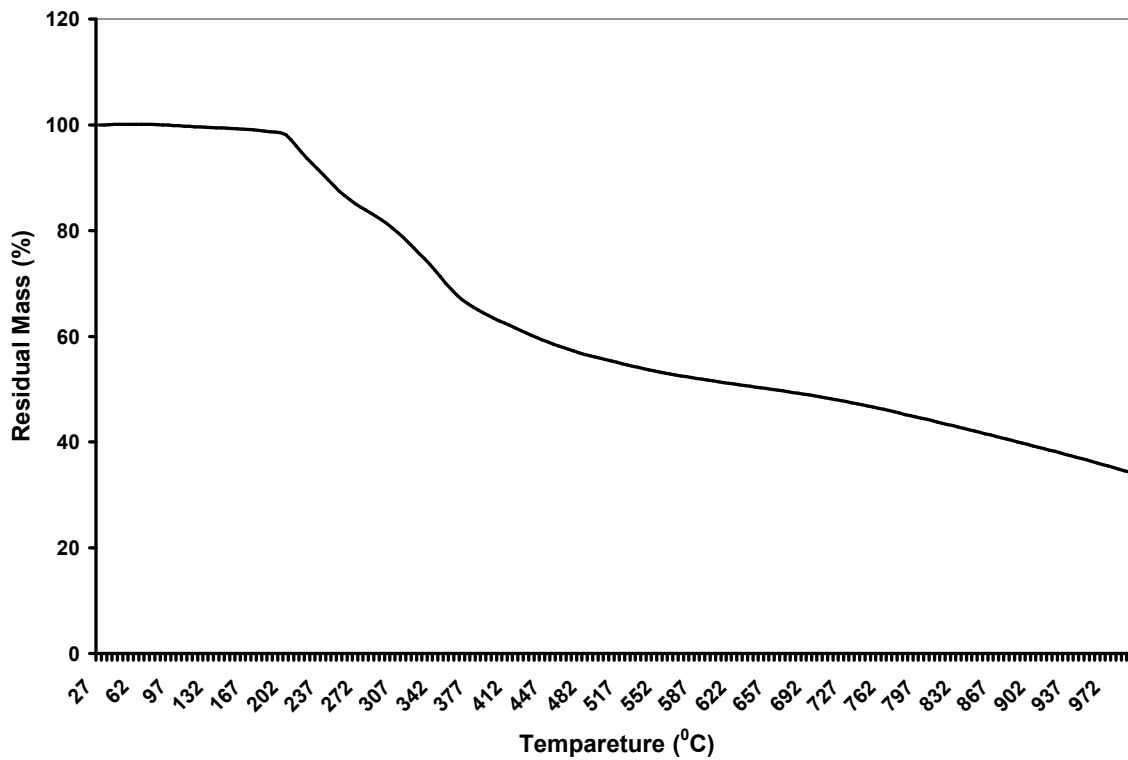


Figure 26: TGA of Flame retardant compound

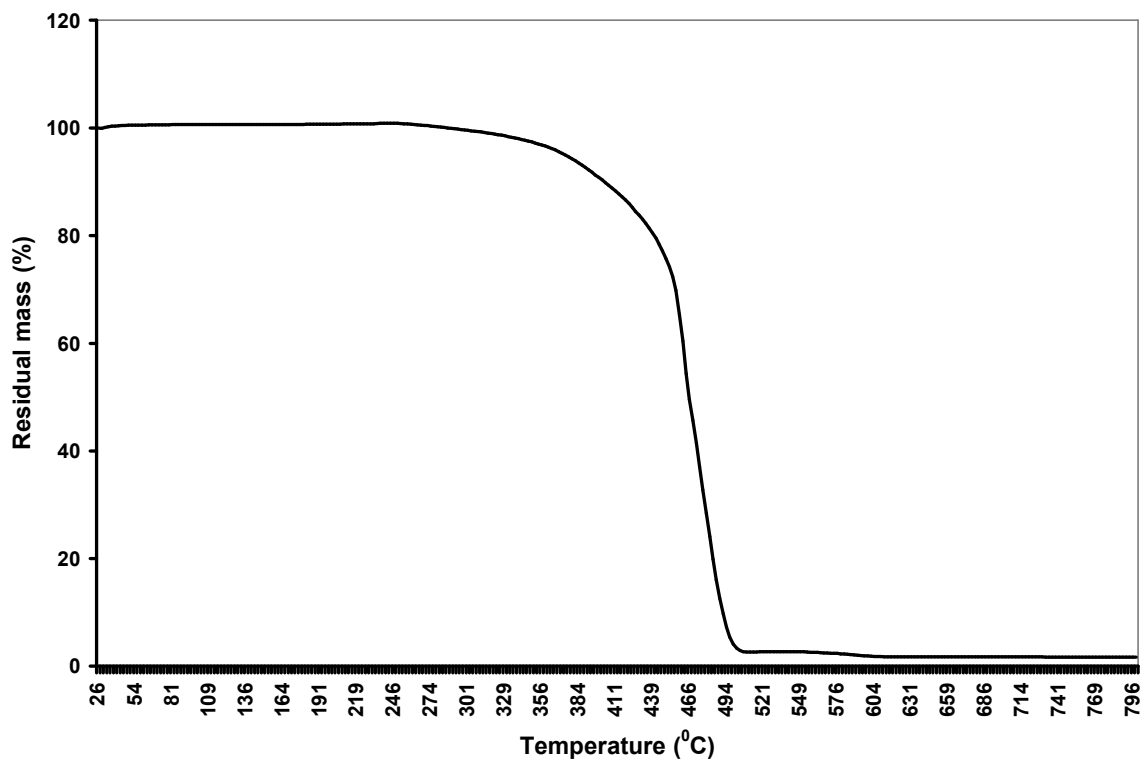


Figure 27: TGA of neat polyethylene

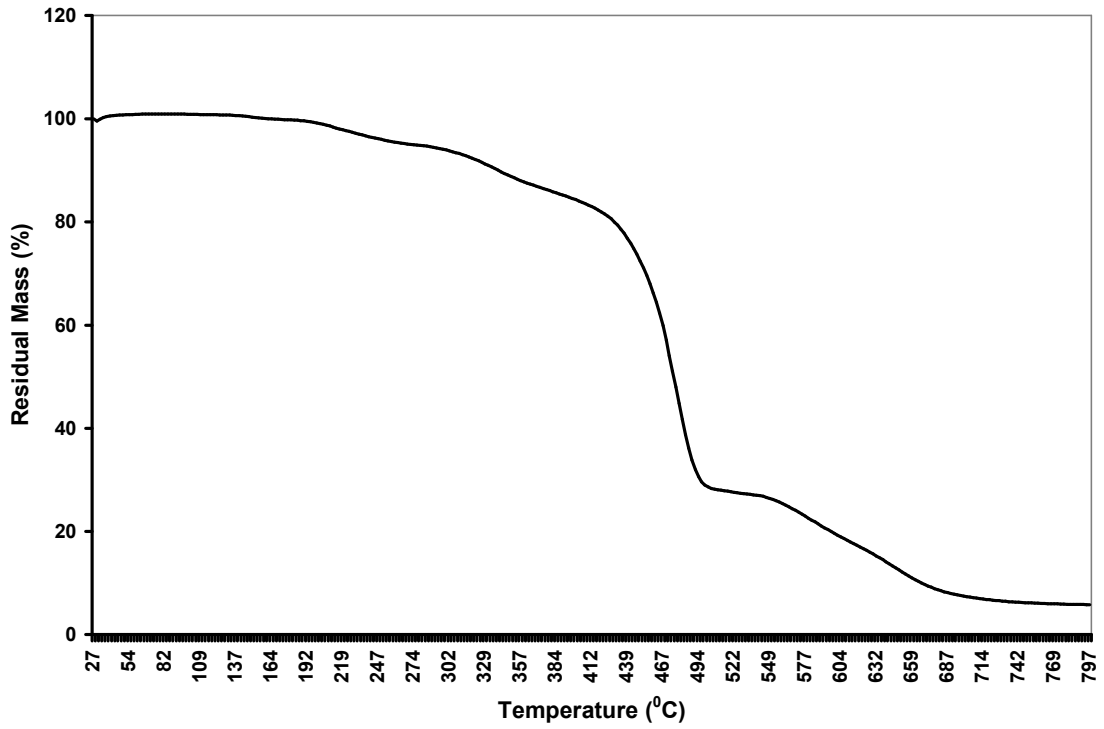


Figure 28: TGA of flame retardant polyethylene

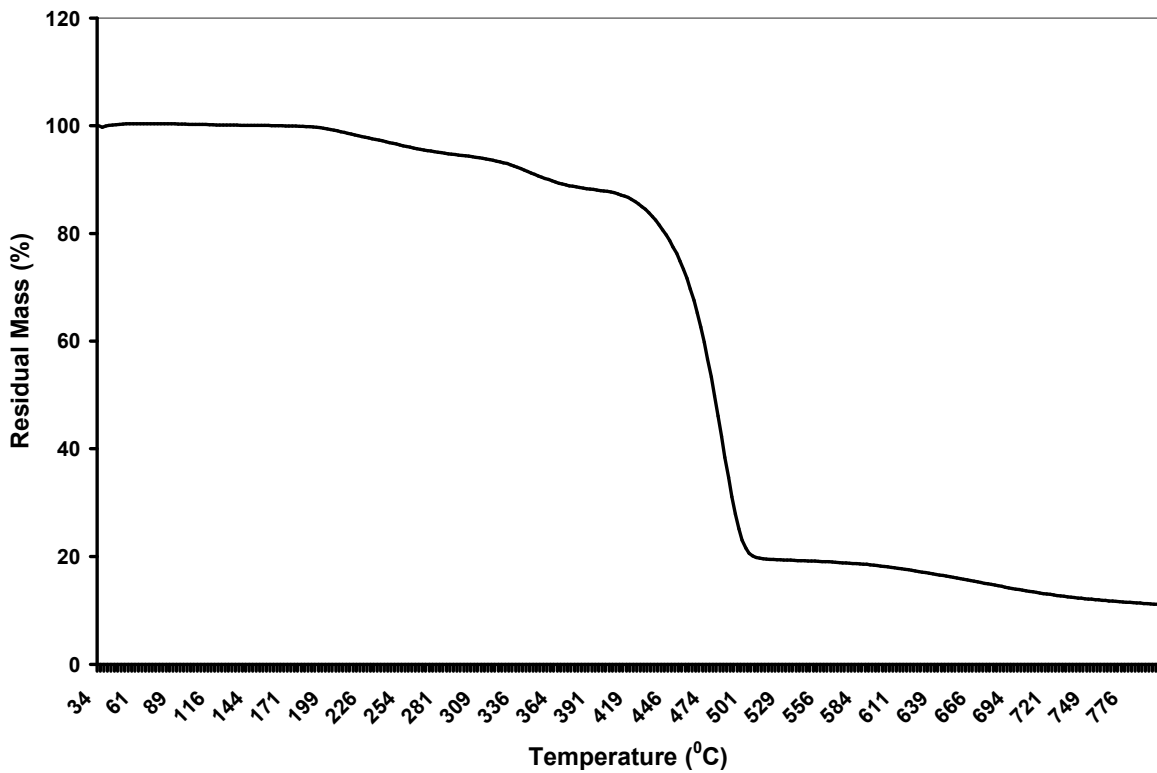


Figure 29: TGA of flame retardant clay added polyethylene

3.3 DISPERSION OF FLAME RETARDANT WITH BASE POLYMER MATRIX

3.3.1 Physical mixing of Polypropylene and flame retardant

It is important for the flame retardant additive to be dispersed in polymer matrix for improved flame retardancy properties and mechanical properties. With increasing average particle size in polymer matrix decreased quality of both mentioned properties are observed. Thus parallel with improved flame retardant synthesis, also efforts on better wetting of polymer with flame retardant additive has been spent. Physical blending between polymer matrix and flame retardant additive was tried as a control group for determination of average additive size in polymer matrix without a chemical compatibilizer. Since the polyolefin polymers do not have any polar groups they are hydrophobic unless they are modified, and intumescent flame retardants are highly hydrophilic in their nature, no well dispersion was expected. Due to compatibility problems occurring between two species, flame retardant additive did not disperse in polymer and 100 micron size agglomerates are observed.

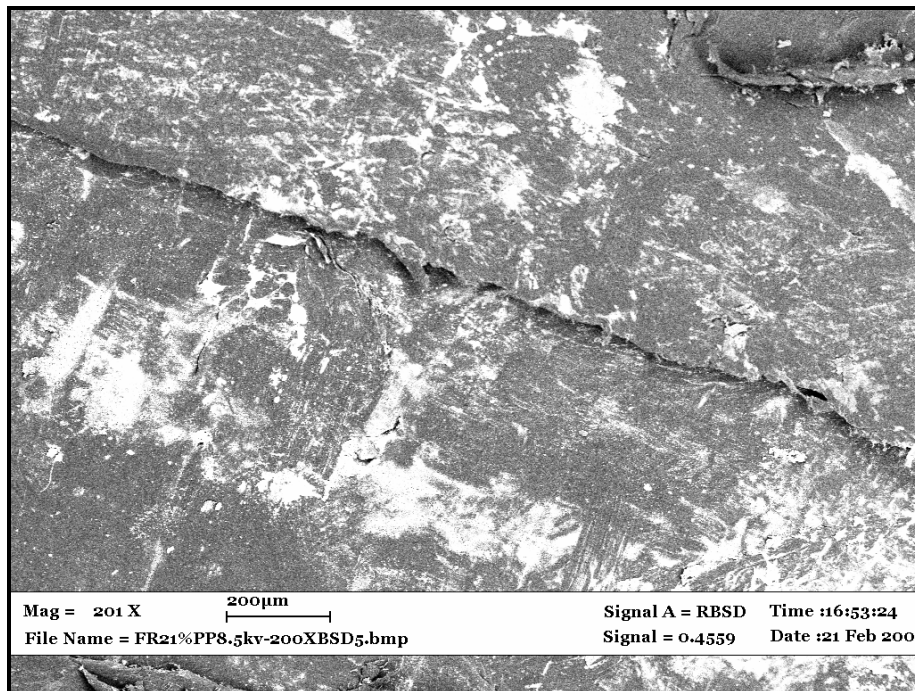


Figure 30: Physically blended Pp and flame retardant compound in melt blender

3.3.2 Chemical compatibilization of flame retardant with polymer matrix

From physical mixing trials it was obvious that intumescent flame retardant compound needed a third component for chemical compatibilization with polymer matrix. Criteria for this compatibilizer was to have two functional groups that can bind with both of the species or is capable of binding with one them and being miscible with latter. For this hydrophilicity hydrophobicity difference between additive and polymer matrix; the first chemical used was α,α -Dimethyl meta-Isopropenyl Benzyl Isocyanate(TMI).TMI had two functional group, double bond opened via radical grafting polymerization to the polymer backbone of polyethylene in extruder. Other remaining functional group designated to increase compatibility between polymer and flame retardant compound. Since reactivity of TMI wasn't high enough for effective grafting onto polymer matrix, for improved grafting yield co-monomer concept was utilized via using styrene as co-monomer[29, 30]. Since styrene has higher reactivity towards the macro-radical of the polymer, improved grafting is achieved.

Polyolefin granules (or powders) were sprayed with BPO dissolved in Acetone and sprayed with Styrene and TMI. For homogenous dispersion of chemicals sprayer is utilized, since this homogenous dispersion leads to better grafting reaction in reactive extruder. After evaporation of acetone out of polymer-initiator-graft monomer mixture, the Mixture of Polyolefin, BPO, Styrene, and TMI were poured at once from first feeder of the extruder and the mixture traveled in co-rotating screws at temperatures between 140 °C and 160 °C approximately 2-3 minutes till it flushed out from die. After palletizing functionalized polyolefin, it is dried for overnight at 60 °C prior to use for dispersion of flame retardant in polymer matrix.

To control the reaction, small amount of functionalized polymer dissolved in Xylene and precipitated Acetone for investigation of bound TMI on polyolefin backbone. FT-IR spectrum of functionalized polymer shows a peak at 2250 which is characteristic peak for isocyanate group of TMI.

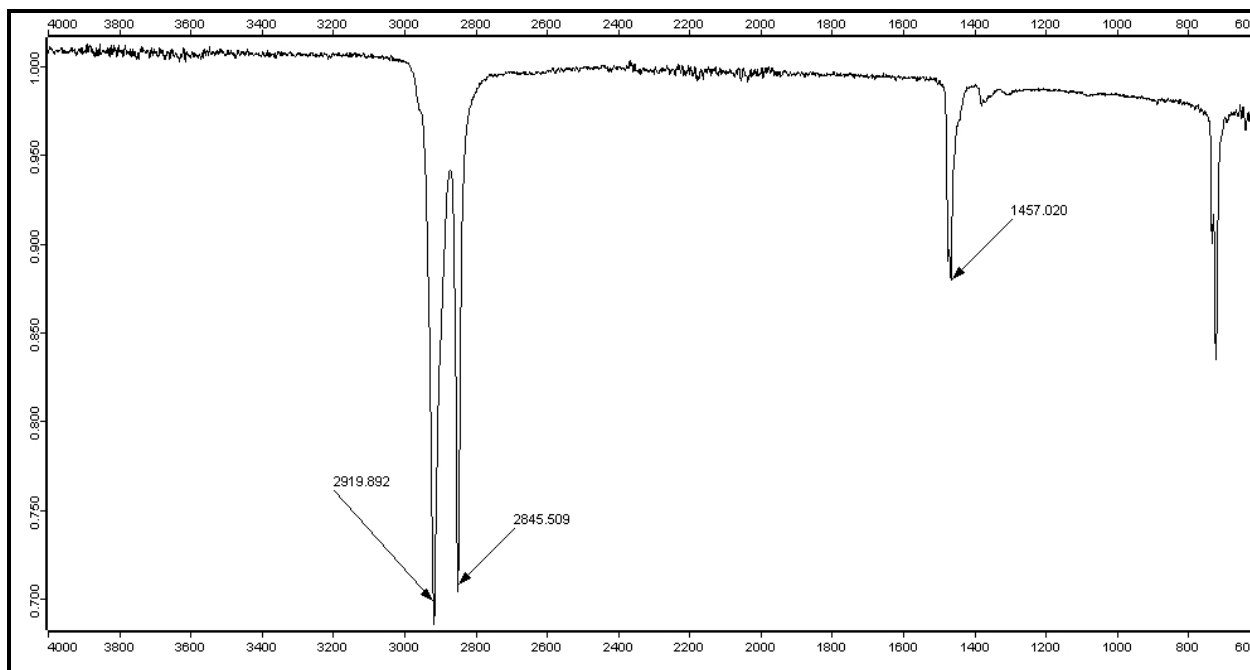


Figure 31: Neat Polyethylene

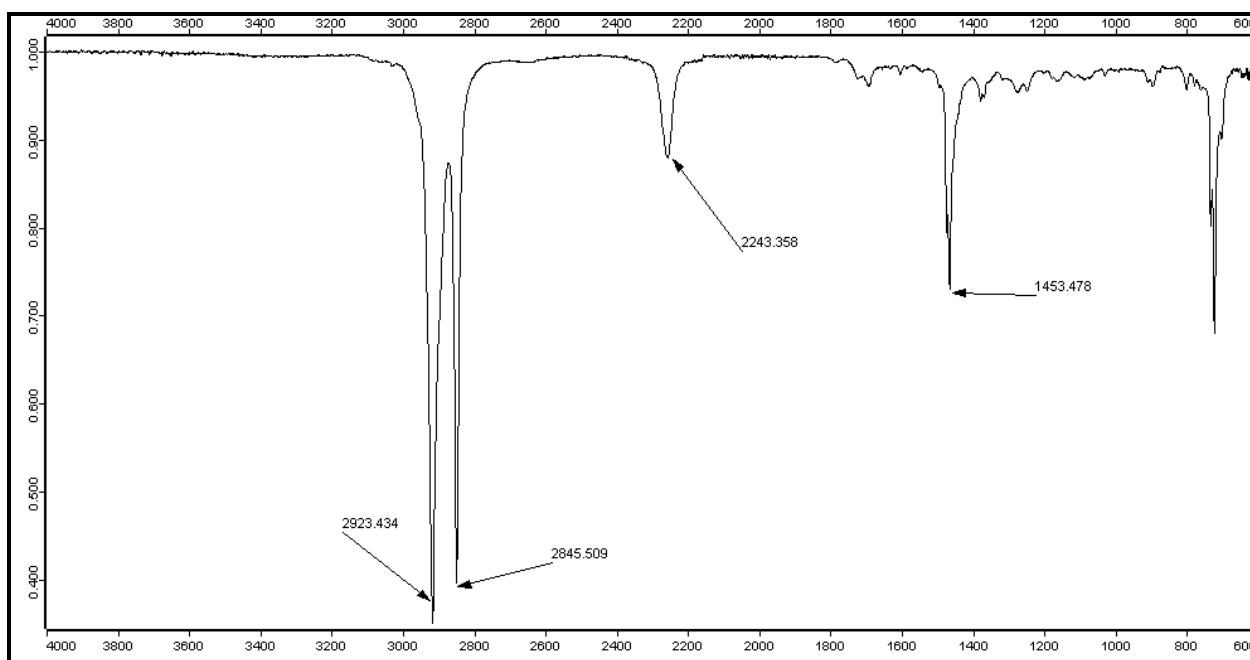


Figure 32: TMI grafted Polyethylene. Peak at 2250 refers to isocyanate group stretching

For improved dispersion of additive in polymer, polymer was fed to extruder from first feeder and was melted, from second feeder flame retardant additive mixed onto molten polymer. This strategy resulted in improved dispersion. The mixing ratio of polymer to

additive is 70/30, if possible. This is determined by making gravimetric adjustments for both feeders prior to actual run on the extruder. The temperature range is important while dispersing additive into the polymer matrix; for better dispersion polymer should be molten, and for flame retardant additive not to degrade. For processing Polyethylene lower temperature limit is 140 °C and for minimum degradation of flame retardant additive the upper limit of temperature in the 9th and 10th temperature zones were 150 °C. After extrusion of polymer, it is palletized and put into the oven for overnight drying prior to injection for mechanical testing.

3.3.2.1 PE/PE-TMI/FR1

First trials were done by melt mixer for forecasting the flame retardancy results. Although melt mixer does not give accurate samples for mechanical testing, it gives an idea about flame retardancy of the mixed polymer and additive. Also melt mixer is advantageous because of the needed amount of sample is lower when compared with sample needed for extrusion process. Polyethylene and Pe-TMI were premixed and added stepwise to melt mixer. Mixture was applied shear and heat in melt mixer four minutes until got into molten state, then prepared flame retardant compound added and mixed for two and a half minutes at 140 rpm. At the end of the duration the mixture taken out and placed to hot plate for test plate formation. Effect of compatibilization agent on wetting of polymer matrix by flame retardant additive is great. Without chemical compatibilization average agglomerate size is around 100 microns, and with chemically compatibilized sample in melt blender is down to 2-3 microns average particle size.

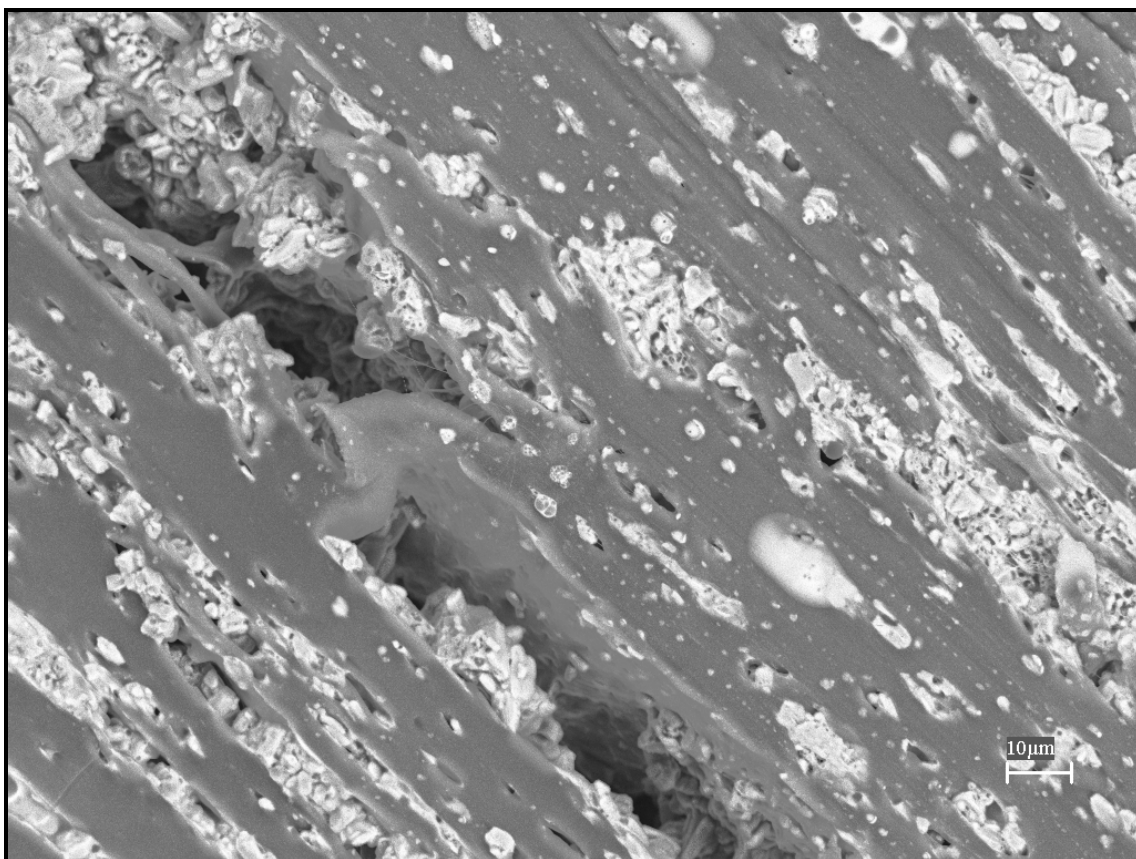


Figure 33: SEM view of PE/PE-TMI/FR1

3.3.2.2 PE/PE-TMI/FR2/CLAY

Polyethylene and PE-TMI were together added stepwise to melt mixer and mixture resided in melt mixer four minutes until its torque decreases which is a sign for melting, then prepared flame retardant compound and Montmorillonite clay were added and mixed for two and a half minutes at 140 rpm. At the end of the duration the mixture taken out and placed to hot plate for plate formation. Dispersion of flame retardant additive was good. Particle sizes was usually around 5 microns. Dispersion of clay in polymer was poor due to the difference of hydrophobicity and hydrophilicity between polymer and clay. Polymer cannot get between clay galleries resulting in poor dispersion of clay.



Figure 34: SEM view of PE/PE-TMI/FR2/Clay

3.3.2.3 PE/PE-TMI/FR2

Since Melamine Stearyl alcohol Phosphorus pentoxide containing recipe did not meet the required flame retardancy level, a recipe consisting of Ethylenediamine, Pentaerythritol, and Phosphoric acid synthesized, and tested in melt blender. Conditions for melt blender was same as previous trials, 140 rpm and four minutes for polymer to melt and two and a half minutes for additive to disperse in polymer matrix. Activation of flame retardant additive was not observed. Plate prepared by hot plate process and average particle size for flame retardant additive for this sample was around lower than 2 microns.

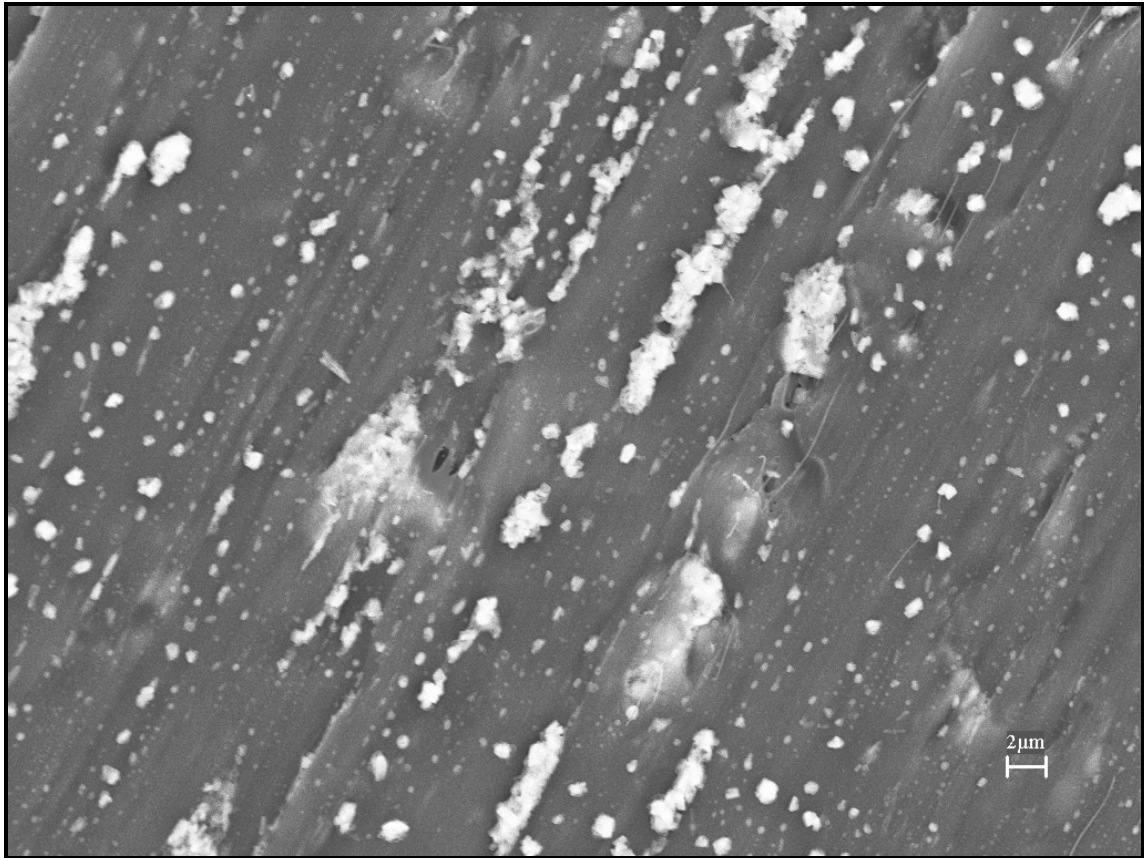


Figure 35: SEM view of PE/PE-TMI/FR2

3.3.3 Chemical Compatibilization with ELVALOY™

Another compatibilizer agent that was used along with TMI was, Elvaloy. This ethylene-acrylate copolymer also showed good compatibility between polymer matrix and flame retardant additive due to its amphiphilic behavior. Usage of Elvaloy has both advantages and disadvantages. It is effective as good as TMI in dispersing flame retardant additive in polymer matrix, however Elvaloy also decreases the resistance of polymer matrix against fire since it is also a highly flammable fuel source. Thus it is a trade-off between mechanical properties and flame resistance.

3.3.3.1 PP/ELVALOY/FR1/CLAY

Dispersion of clay in polymer matrix is poor if compatibility between polymer and clay isn't established. Thus other than using clay as a composite together with flame retardant compound, clay was incorporated to the polymer matrix as a clay master batch, resulting in better dispersion of clay in polymer matrix. Then flame retardant was added into polymer matrix at 170 °C at melt blender. Mixing conditions for this sample

was same as previous samples. Average size of flame retardant additive was around 2 microns

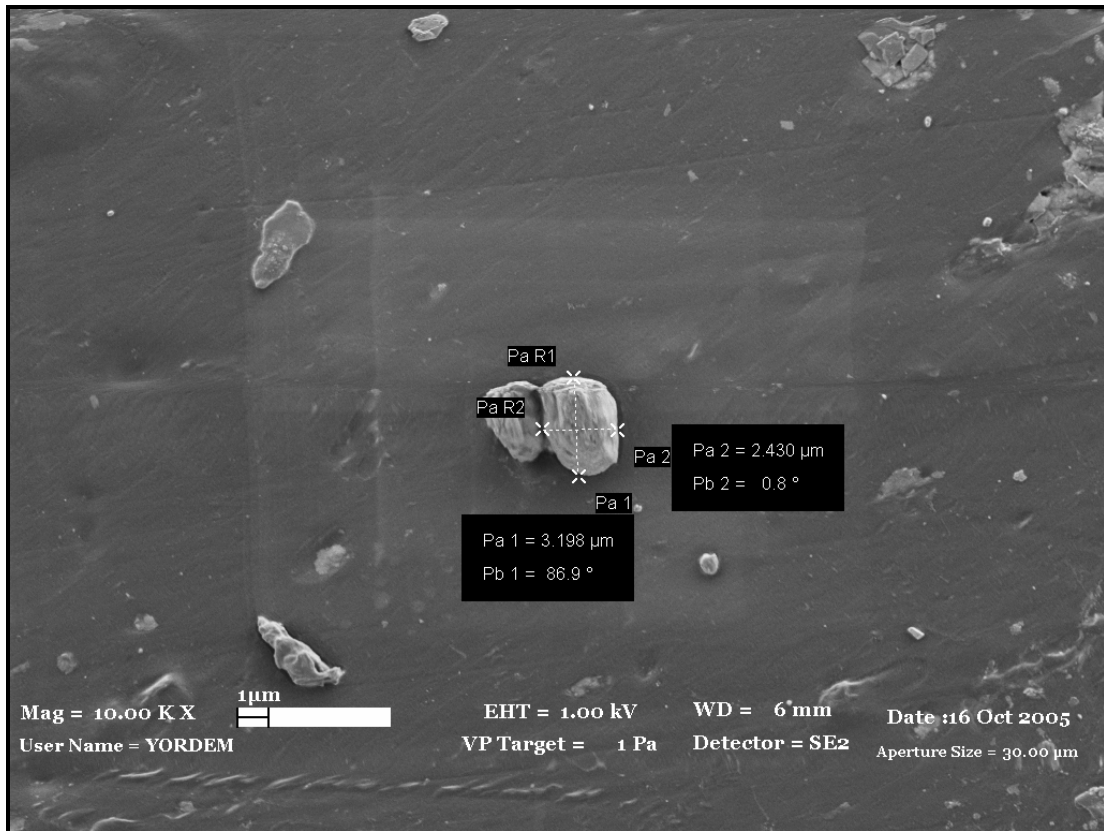


Figure 36: SEM view of PP/Elvaloy/FR1/Clay

3.3.3.2 PE/ELVALOY/FR2

Increased flame retardancy for polymer has two components one of them was good dispersion of additive in polymer matrix, the other one was effective flame retardant compound. Due to low amount of char formation with the Stearyl alcohol containing recipe, new flame retardant recipe was prepared and it was dispersed with polymer with Elvaloy. For preparation of flame retarded sample melt blender was utilized. And the procedure was same as previous PE containing samples. Reaction conditions were 140 °C and four minutes for polymer melting and two and a half minutes for flame retardant compound to disperse. Size of flame retardant additive was 3-4 microns, however the real size was smaller but electron beams which is used for focusing and image taking activates the flame retardant compound. The actual size was 2 microns.

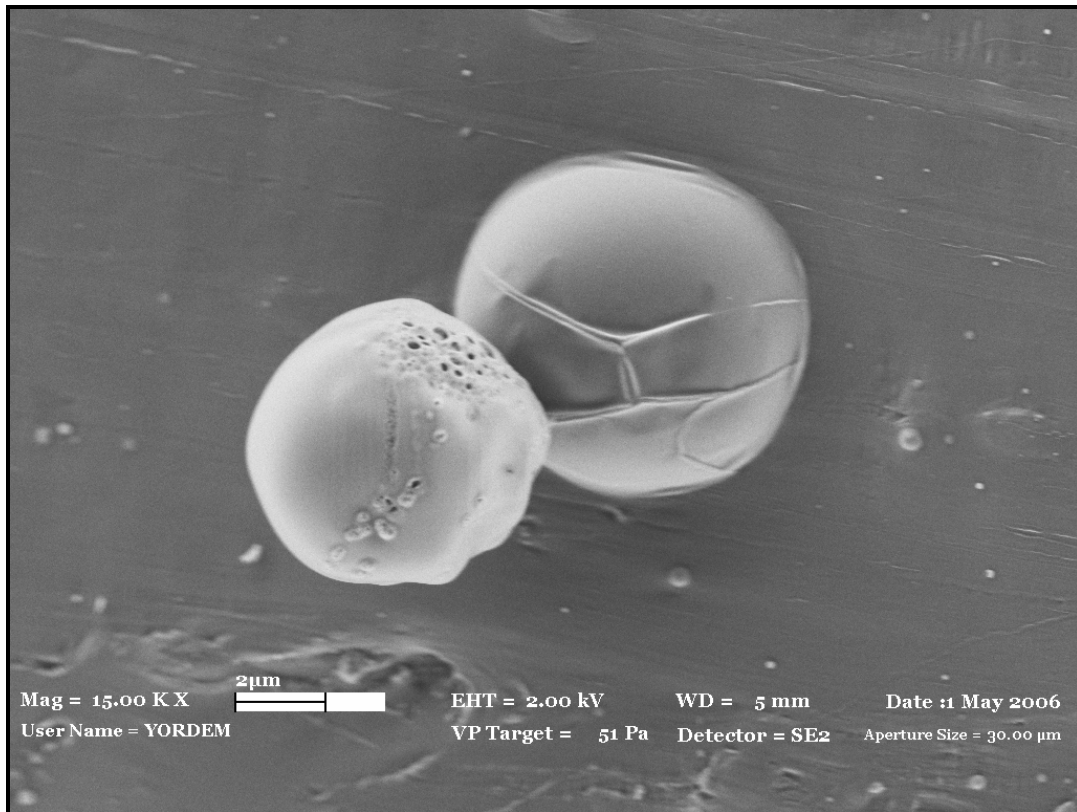


Figure 37: SEM view of PE/ELVALOY/FR2

3.3.3.3 PE/SIL-PE/FR

Another compatibilizer chemical used was Sil-PE. This compatibilizer has free hydroxyl ends that can increase the compatibilization of flame retardant in polymer. However, this compatibilizer resulted in very poor compatibilization and dispersion of flame retardant and mechanical properties was very poor. The same mixing procedure is assigned for this trial in melt blender, but sample produced is so brittle and weak that it is fractured even with a very small touch.

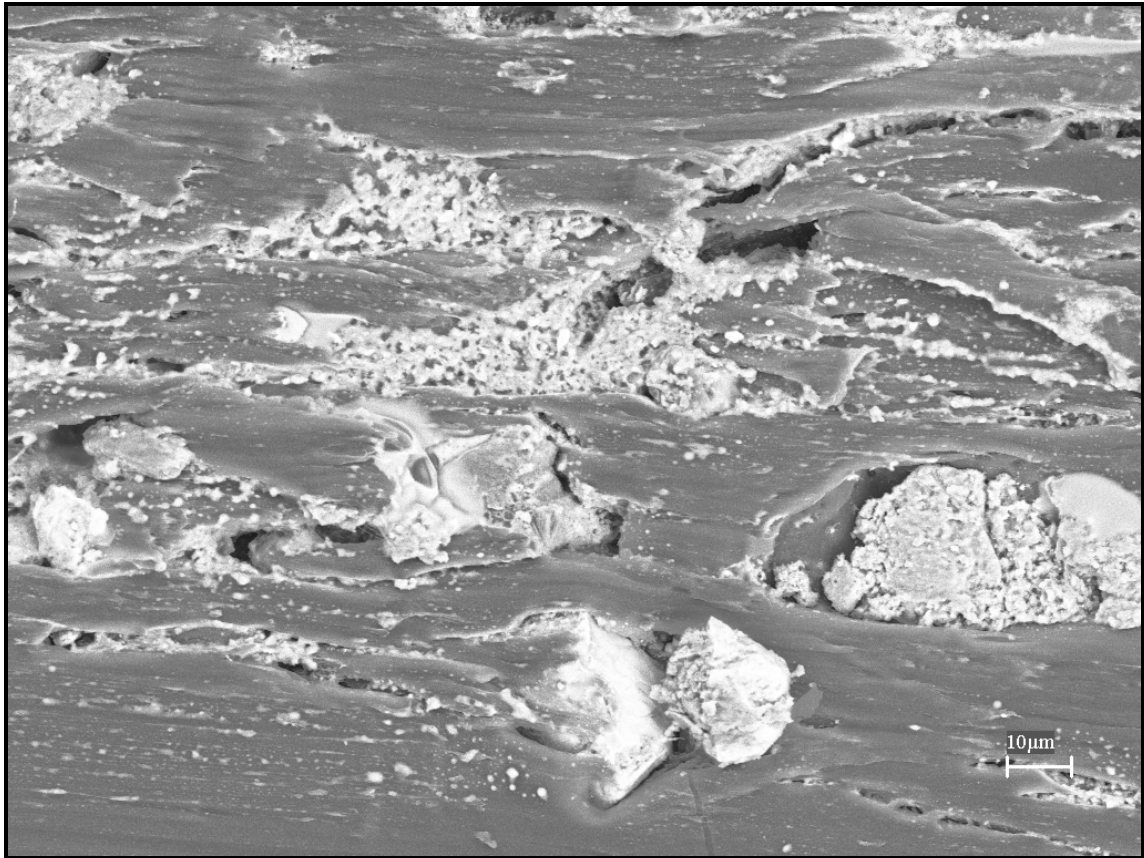


Figure 38: SEM view of PE/SilPE/FR2

3.3.3.4 PE/PEGLUE/FR2

Another compatibilizer used was product named Peglue. It was a product used for compatibilizing polyethylene and metal surfaces. It contains hydroxyl groups that compatibilizes hydrophilic flame retardant compound to the polymer matrix. After few trials it is seen that using powder polyethylene results improved results. The reason for using powder polyethylene was lowering degradation of flame retardant compound in extruder. Since the shear forces applied onto polymer was lower in melt blender when compared to extruder, the same temperature profile in extruder may result in degradation of flame retardant compound if it was not stable enough. For that reason powder polyethylene was used in extruder trials for preventing the increase in torque and high shear forces. The powder polyethylene proved the proposed outcome and flame retardant compound containing polymer showed increased properties as extrudate. Also Peglue showed good dispersion properties as compatibilizer for flame retardant compound in polymer matrix. Together with extruder's shear force Peglue results in

flame retardant compound particles lower than 1 micron size in sample without clay, 3% clay containing, and 5% clay containing samples.

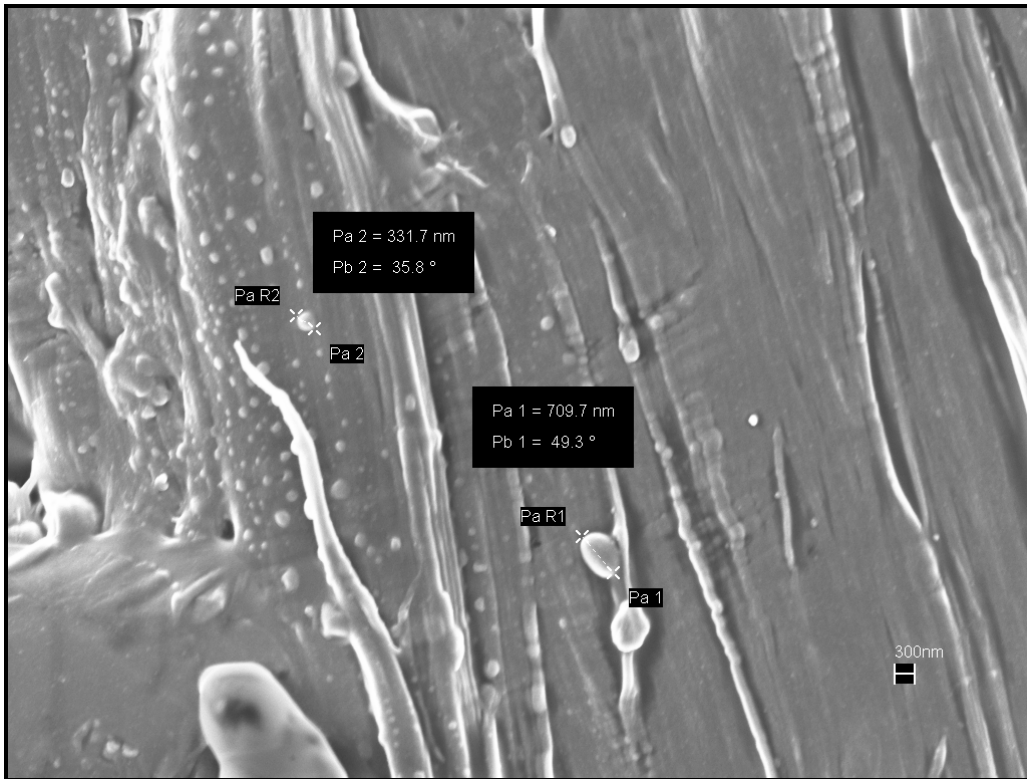


Figure 39: PE/PEglue/FR2

3.3.3.5 PE/PEGLUE/CLAY-PE/FR2 (3% CLAY containing)

For this sample Clay was added as Clay containing master batch to the mixture. Original master batch contains 20 percent clay in it, thus Clay-PE was diluted six times for reaching 3 percent clay in sample. Flame retardant compound used is 30 percent as previous sample without clay. Reaction procedure was same as previous sample, temperature profile is between 110 °C and 155 °C and both four component flame retardant compound, Peglue, Polyethylene, clay containing master batch were mixed in a plastic bag prior to one feeder addition. One feeder addition prevented errors occurring in gravimetric adjustments and ratios of different components. By one pot feeding amount of flame retardant was stabilized in polymer matrix. The average size for flame retardant is also good and around 800 nanometers which is in accordance with improved flame retardancy results for this serie.

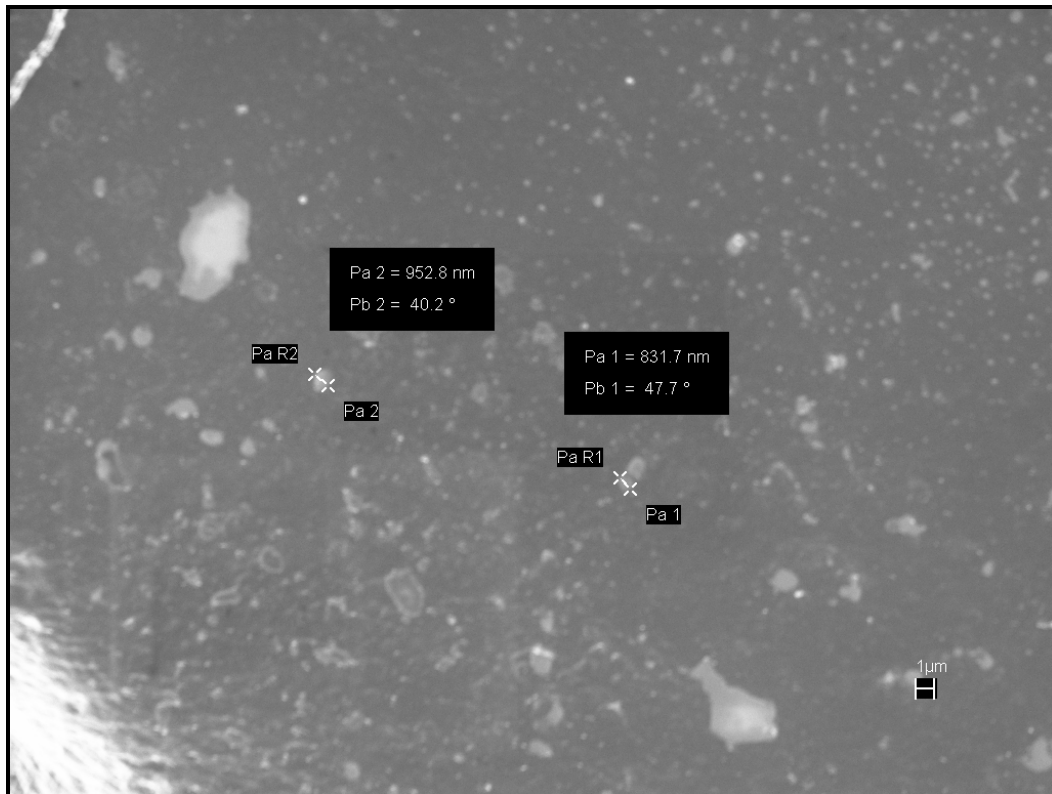


Figure 40: PE/PEglue/FR2/ 3% Clay

3.3.3.6 PE/PEGLUE/CLAY-PE/FR2 (5% clay containing)

The clay component in this sample was also coming from clay master batch. Original master batch contains 20 percent clay, thus it was diluted five four times for 5 percent clay containing sample. The amount of flame retardant in this sample was 30 percent as previous samples in this serie. Like previous samples in this serie Peglue was used for compatibility and good dispersion was observed for this sample. The temperature profile as between 110 °C and 155 °C and both four component flame retardant compound, Peglue, Polyethylene, clay containing master batch were mixed in a plactic bag prior to one feeder addition. One feeder addition prevented errors occurring in gravimetric adjustments and ratios of different components. By one pot feeding amount of flame retardant was stabilized in polymer matrix. The average size for flame retardant was also good and around 600 nanometers which is in accordance with improved flame retardancy results for this serie.

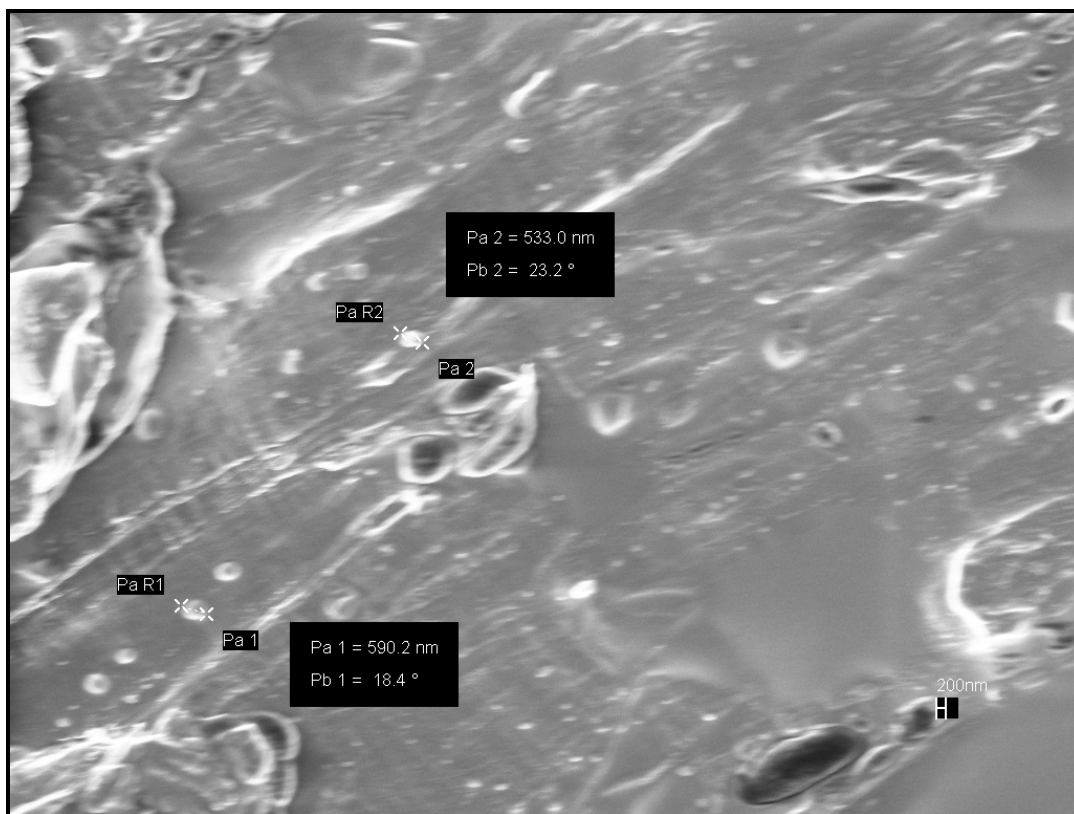


Figure 41: PE/PEglue/FR2/5% Clay

3.4 FLAMMABILITY TEST

3.4.1 Limiting Oxygen Index Test

The aim of this research was to synthesize and incorporate novel flame retardant additive into polymer matrix in order to reduce the combustion of polyethylene polypropylene resin. Effect of synthesized phosphorus and nitrogen containing flame retardant on flammability of polyolefins was investigated using Limiting oxygen index (LOI) test method. The test samples with dimensions of 120x4x10 mm were prepared by either injection molding of reactively extruded polymer granules or test samples with dimensions of 120x2,7x10 mm for the ones couldn't be processed in injection molding machine due to various problems.

It was found out that increasing the amount of phosphorus-nitrogen in polyolefin increases the flame retardancy of polymer, whilst decreasing the mechanical properties. Also for flame intumescent flame retardancy mechanism the needed carbon source is rather a polyol instead of mono alcohol. During combustion, degradation products of

polyolefin lead to intumescent char that serves as a physical heat barrier which is reducing heat transfer to the unburned polyolefin.

Another proposition that is evidenced by various melt blending and extrusion trials is, the better dispersion of flame retardant additive in polymer matrix is the more increased flame retardancy of polymer matrix. Since the flame retardant additive is intumescent type, when the particles are wet by polymer in a more effective manner, this results more effective intumescent coating of polymer surface. Better the heat barrier between polymer and heat source better the resistance of polymer that is encountering fire.

In the below there are some abbreviations for the sake of simplicity of both tables and graphs;

FR1= P₂O₅/Stearyl alcohol/Melamin

FR2= Pentaerythritol/Phosphoric acid/ Ethylenediamine

TMI= α,α -Dimethyl meta-Isopropenyl Benzyl Isocyanate

SilPE= functional group containing silicon grafted polyethylene

Table 3: LOI values of composites

Sample	LOI	Compatibilizer
Neat PP	18	xx
Neat PE	18	xx
PP+ 30% FR1	18	physical compatibilization
PE+30% FR2	18	SilPE
PE+ 30% FR1	21	TMI
PE+ 30% FR2	21	TMI
PE+30% FR2+ 3% Clay	22	TMI
PE(F2-12)+30% FR2	23	Peglue
PE(F2-12)+30% FR2+ 3% Clay	24	Peglue
PE(F2-12)+30% FR2+ 5% Clay	24	Peglue

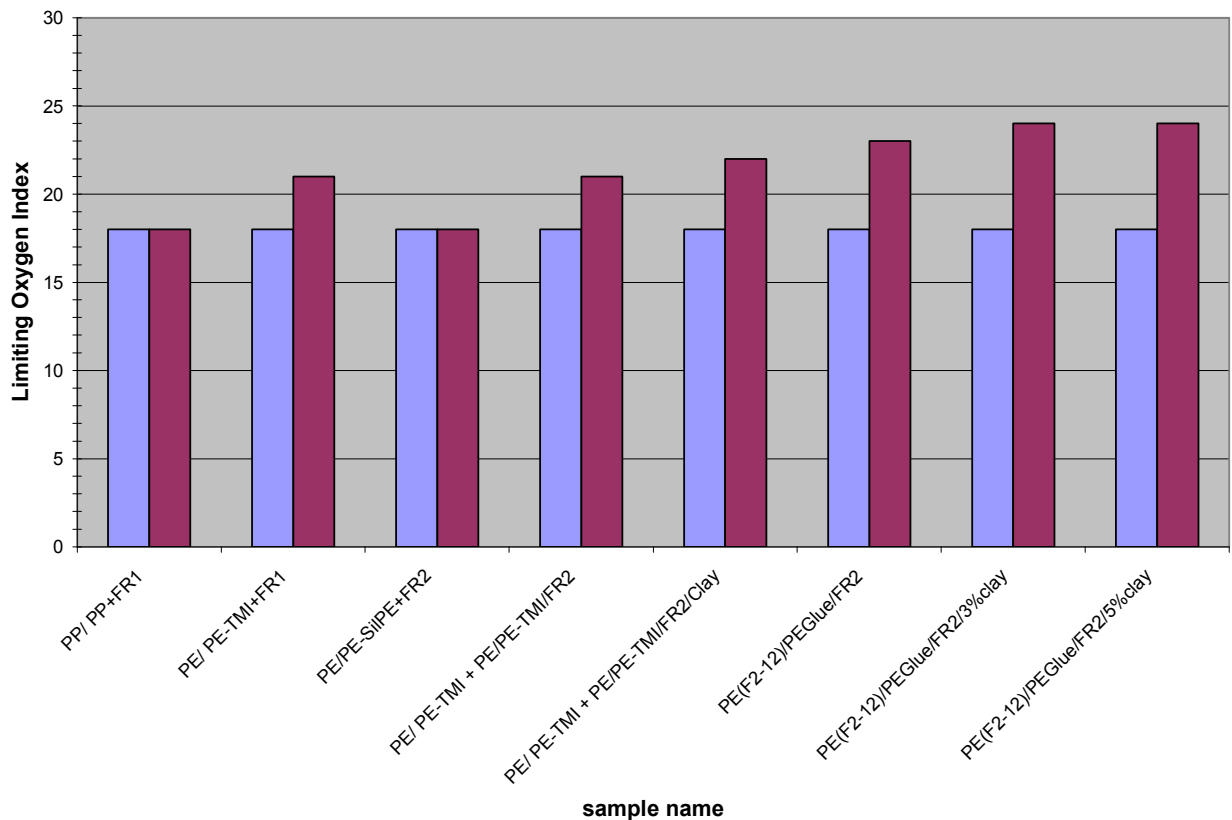


Figure 42: LOI values of various FR/ Polymer composites

3.5 MECHANICAL TESTS

Polymers are structural materials, while imparting them any property such as flame retardancy, one must also deviate as minimum as possible from mechanical properties. If an elastic polymer becomes brittle, then the polymer can not be used for the designed purpose. For that reason; while main objective was imparting flame retardancy to polymer, mechanical properties of polymers were also investigated by using tensile testing methods.

Mechanical tests were done in Universal Testing Machine, Zwick. Speed of tensile pull was 50 mm/min for all samples, and grip to grip separation was 65 mm for all samples. Each sample were applied preload of 1 N prior to actual test. All tests were done in

room temperature. Because of production difficulties most of the samples were produced in small quantities. Thus there wasn't enough statistical sample space for deviation calculations.

Comparing mechanical properties of neat PE with composites containing the flame retardant compound of 30 percent by weight, confirms the fall in tensile strength, elongation at maximum force applied, and elongation at break due to presence of filler. The reduction in strength properties with composites was caused both by the effective cross section reduction and stress concentration increase. In both sets without clay, one with compatibilized with TMI and one with compatibilized with PEglue, decrease from 11,9 Mpa to 6,6 Mpa was observed in tensile strength. Decrease in elongation at maximum force applied differed in two sets, TMI containing set showed decrease from 72,4 percent to 20,8 percent, while PEglue containing set showed decrease from 72,4 percent to 34,6 percent. Same trend in elongation at break was observed for the two sets. TMI containing set showed a decrease from 83,9 percent to 28,5 percent; while PEglue containing sample showed a decrease to 44,7. This decrease in strength is due to great hydrophobicity difference between flame retardant additive and polymer matrix which creates a decrease in interfacial adhesion. Since mechanical properties of polymer containing rigid particles are determined by the size, shape, concentration, properties of filler, better the dispersion smaller the deviations from original polymer's mechanical properties were expected. The results together with electron microscope images showed consistency with this expectation. TMI containing samples were bigger in size in comparison with samples compatibilized with PEglue, which is an explanation to difference of elongation behavior of the two sample sets. Also PEglue containing samples' increased elongation behavior is an evidence to increased dispersion with respect to TMI containing samples. Another thing to be compared between two sets of samples was their toughness. The area under the curve of stress strain graph gave the amount of energy needed for polymer to break. PEglue containing set showed improved toughness, less deviation from original polymer in other words, since tensile stresses were similar in two sets and PEglue containing set had better elongation

For both of the clay containing sets of samples the correlation of mechanical properties showed similar trend. The set compatibilized with PE-TMI had a major decrease of both tensile stress and elongation at break value. Tensile stress decreased 11,9 MPa to 5,4

MPa, while elongation at break value decreased from 83,9 percent to 6,6 percent. On the other hand, the set compatibilized with PEglue and containing 3 percent clay, had a decrease in tensile strength from 11,9 MPa to 6,5 MPa and a decrease in elongation at break from 83,9 to 37,6. The set containing 5 percent clay in composite showed further decrease in mechanical properties. Tensile stress decreased to 6 MPa and elongation at break decreased to 13,6.

Table 4: Tested mechanical properties of flame retarded polyethylene

	$\delta_0(\text{N/mm}^2)$	Agt(%)	At(%)
LDPE	11.9	72.4	83.9
PE/PE-TMI/FR2	6.9	20.8	28.5
PE/PE-TMI/FR2/Clay	5.4	5.7	6.6
PE/PEglue/FR2	6.6	34.6	44.7
PE/PEglue/FR2/ 3%Clay	6.5	20.4	37.6
PE/PEglue/FR2/5%Clay	6.0	12.9	13.6

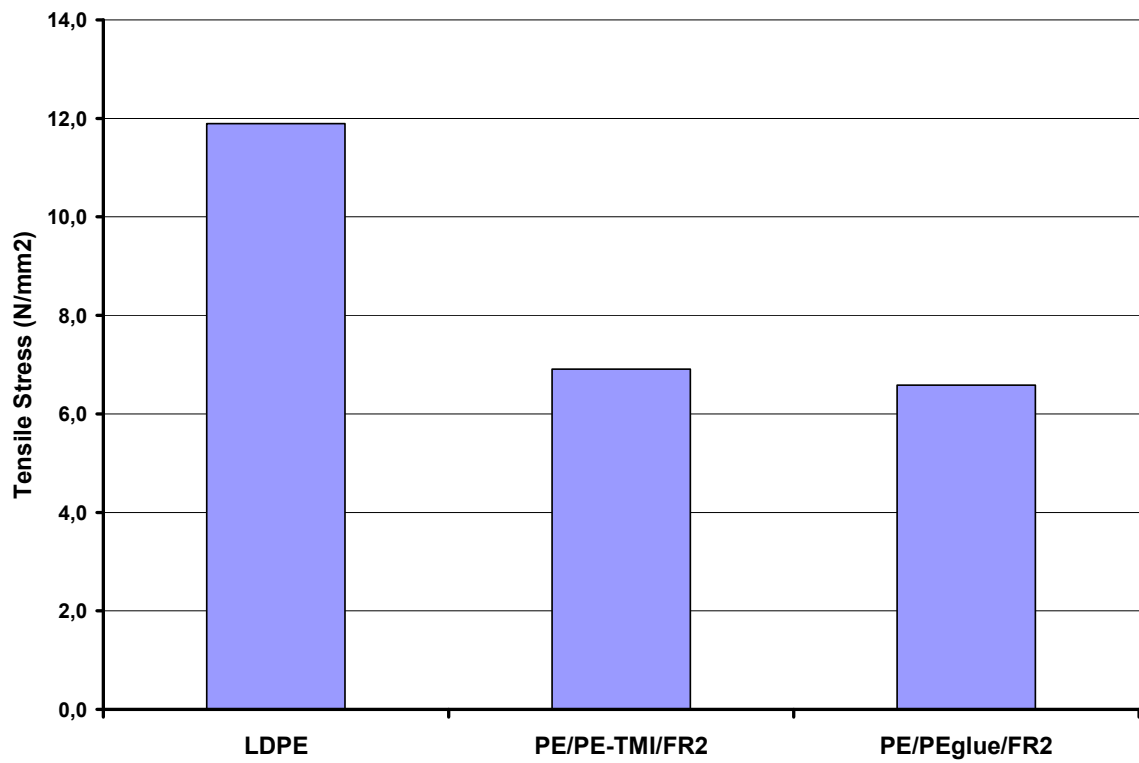


Figure 43: Tensile strength of tested flame retarded Polyethylene samples without clay

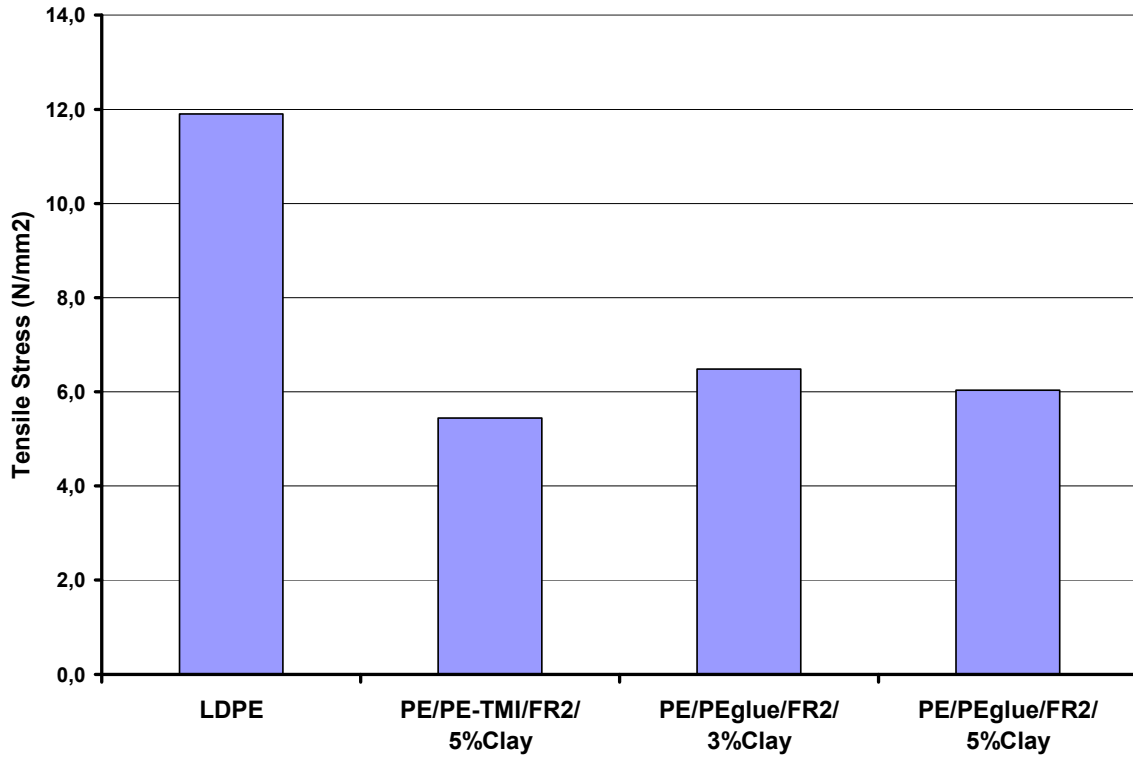


Figure 44: Tensile strength of tested flame retarded Polyethylene samples with clay

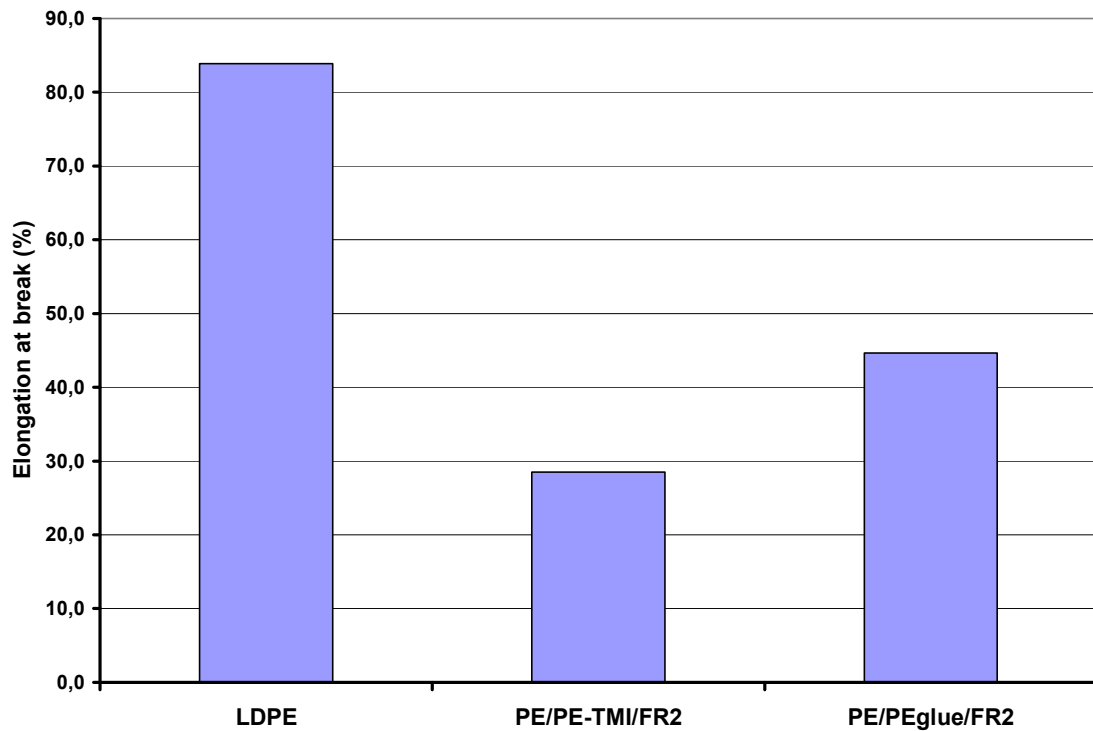


Figure 45: Elongation at break of tested flame retarded Polyethylene samples without clay

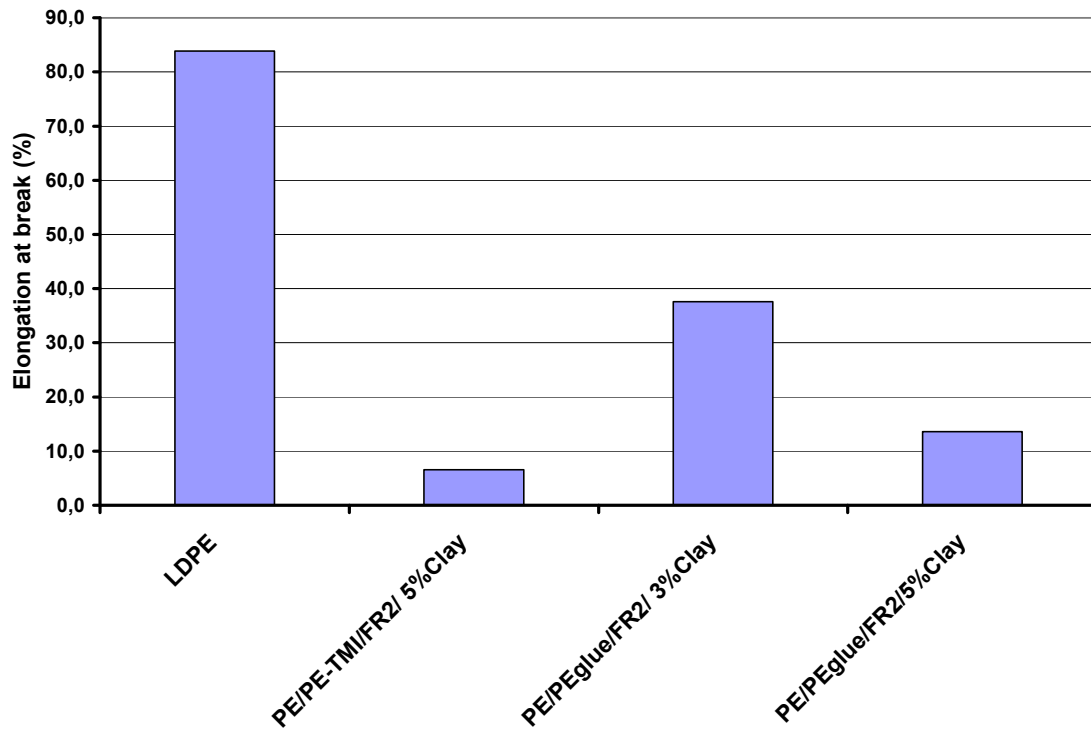


Figure 46: Elongation at break of tested flame retarded Polyethylene samples with clay

Tensile stress and percent elongation at break results, in comparison to metal hydroxide containing polymer composites is worthwhile to take a look at. Metal hydroxides are not fully effective flame retardants not until 60 percent of the composite is composed of metal hydroxide. Tensile stress in metal hydroxide composites decreases 30 percent[10], in comparison to 50 percent decrease in intumescent flame retardant composites. However decrease in elongation property of intumescent flame retardant composites has improved results. Metal hydroxide composites' elongation at break decreases from 250 percent to 1.31 percent[10], whereas intumescent flame retardant containing composites showed decrease from 83,9 to 44,7.

4. DISCUSSION

4.1 Flame Retardant

Generally increasing the amount of the low molecular carbon species lowers the resistance of the material in which they are added. This idea follows most people and they conclude that while preparing the flame retardant additive, they should lower the amount of carbon source. Conducted research showed the opposite of this idea. Since the carbon source is the main ingredient for the formation of heat absorbing charred species, it is critical to have enough charred residue during combustion. However, also functionality of the used carbon source important. At the beginning of the research the carbon source used had monohydroxyl functional group containing stearyl alcohol, and the efficiency of produced flame retardant was low. As proceeded with the conducted experiments, it is understood that since hydroxyl groups react with acid source and produce meta stable phosphorus ester, the increased amount of this meta stable phosphorus ester favors the crosslinked charred residue. Comparison of efficiency of pentaerithrytol to stearyl alcohol clearly shows that amount of hydroxyl functional groups important. Differential scanning calorimeter experiments provides evidence for this proposed importance of hydroxyl groups' on char formation mechanism with having increased char formation with the increased volume of the char produced after treating the crucibles to same elevated temperatures.

4.2 Compatibility of Flame Retardant with Polymer Matrix

4.2.1 Examination of Compatibility of Flame Retardant Additive in Polymer Matrix

After synthesis and compatibilization of additive to polymer in extruder, we examined the compatibility and average particle sizes of the additive in polymer matrix with varied compatibilizers used.

4.2.1.1 Physical Mixing of Additive to Polymer Matrix

First trial was physical mixing of hydrophilic flame retardant and hydrophobic polymer matrix. Since there is polarity difference between materials, the additive added showed

poor wetting on the polymer matrix. The particles of 100 micron observed. The results are clearly showing that, since the particle sizes are bigger than critical particle size for crack propagation, fracture stress observed was much more lower than neat sample. Existence of that big particles increases the stress felt on polymer sample just around the additive surface three times more in theory. On the other hand, existence of such big particles means that most of the additive was sitting together as a chunk of agglomerate; thus most of the surface is prone to attack of heat. The additive responsible for heat insulation is centered on some point not in whole surface leading to penetration of heat and oxygen easily to the system. This decreased the efficiency of the flame retardant to a very low effectivity.

4.2.1.2 Compatibility with TMI

With its bifunctional structure, TMI binded to the polyolefin backbone with its vinyl group in existence of peroxide initiator and binded to polar filler with its isocyanate group. This increased the dispersion of polar additive and decreased the average particle size from hundred microns to 3-4 microns. This resulted in decreased brittleness when compared with physically mixed system and increased toughness. Also better dispersion of additive resulted in higher surface area of flame retardant additive and increased intumescent shield for polymer matrix. Limiting oxygen index data was consistent with increased intumescent shield power of lower particle size containing polymer composite. From 18 percent to 21 percent increase was obtained by only changing the compatibilizer system, which stated that the effect of flame retardant system is not only a result of effectiveness of flame retardant but also its dispersion.

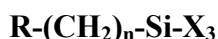
4.2.1.3 Compatibility with Elvaloy

This ethylene-acrylate copolymer increased compatibility between polymer matrix and flame retardant additive due to its amphiphilic behavior. Polymer chain was miscible with both hydrophilic and hydrophobic phases due to its bicharacteristic chain behavior, ethylene part dissolved in polyethylene and acrylate part dissolved in hydrophilic flame retardant additive. This copolymer showed increased dispersion of additive to the base matrix when compared with TMI, since copolymer has longer compatible chain parts with both of the phases. This amphiphilic behavior had a positive effect on mechanical properties of the composite, however usage of Elvaloy had negative effect on flame

resistance of the composite. Elvaloy consisted of low molecular weight copolymer which increased the amount of volatile organic chemicals in composite. Addition of ten percent Elvaloy to the polymer led to decreased thermal stability and lowered decomposition and increased fuel formation which in turn decreased resistance of whole composite against fire condition. This clearly reflected the decrease from 21 percent to 18 percent LOI value for FR2 consisting composite.

4.2.1.4 Compatibility with Sil-PE

Silane coupling agents are another class of compatibilizers that can be used for overcoming the dispersion problem of hydrophilic additive and hydrophobic polymer base. Silane coupling agents have bifunctional character which enable them to form a durable covalent linkage between organic and inorganic materials. Inorganic materials that silane coupling agents can react with are, silicates, aluminates, borates, clays, Tin, Talc, etc.



The general formula of Silane coupling agent consists of hydrolyzable X groups, which can be alkoxy ,acryloxy, halogen or amine. After completion of hydrolysis step reactive silanol group is formed which can further react with silicate surface to form siloxane linkages. The R functional group is organofunctional group that does not take part in hydrolysis reactions but posses vinyl functionality which can be used for attaching desired chains to the polymer backbones via grafting reactions.

The usage of silane coupling agent did not increased the compatibility and dispersion, in contrast it suffered from very poor wetting of additive to the polymer base matrix. The result was the composite was so brittle that it had fracture even with the very minimal force exerted by bare hands. There may have been possible reasons for that, but the most possible reason was, the silane coupling agent had three reactive alkoxy functional groups, and after hydrolysis of these groups and formation of hydroxyl groups, these groups did not react with the additive to increase their dispersion. Reactive groups were very close vicinity of each other, this lowered the favorability of reacting with hydroxyl

groups of flame retardant additive and as a result silane hydroxyl functional groups reacted with each other.

4.2.1.5 Compatibility with Peglue

This product is used as it is purchased. It had hydroxyl groups attached to the polyethylene backbone. There was no chemical reaction between neat polyethylene and this additive, but since this additive had polyethylene backbone it could mix with neat polymer, and since it had reactive hydroxyl groups available for flame retardant additive.

Most successful compatibilizer was this product since it didn't have degradation problems which is caused by low molecular weight such as elvaloy, or it didn't have problems such as the reaction of hydroxyl groups with each other rather than reacting with hydroxyl group of flame retardant since the hydroxyl groups farther away which was major problem in case of SilPE compatibilizer.

4.2.2 Optimization of Extruder Trials

Preparation of flame retardant is one important issue, the other important issue is functionalization of polyethylene prior to mixing with flame retardant additive. And last but not least important step is mixing of flame retardant additive with polymer matrix in extruder.

Last two steps involved usage of extruder due to the amounts produced. Since production of flame resistant polymer is industrial scale, usage of extruder is most convenient way. However usage of extruder defined new limits such as melting point of polymer, degradation of additive, and efficient mixing of flame retardant additive and polymer matrix.

Melting of polymer was a must for the proper usage of extruder. Otherwise the engine of extruder couldn't operate. This put the temperature of 140-150 °C for effective melting of polymer. The flame retardant additive began to degrade at 210 °C, however, in extruder there was also shear stress which created the elevated temperature effect. Because of that effect, the speed of the engine should be lower than 70 rpm. Many trials

was spent solving that dispersion optimization trials. Either the materials used did not disperse in that temperature and speed range or they degraded and blocked the extruder. For this purpose methodically we tried to increase the degradation of flame retardant additive. And we also tried different polyethylene polymer base matrixes, such as polymer chips or polymer powder.

Since the temperature range due to melting of polymer and degradation of additive was not possible to change, the usage of powder polymer helped us to improve processability of flame retardant polymer. As a result, with effective compatibilizer, dry flame retardant additive, and powder polyethylene base matrix we were able to successfully produce flame retardant polyethylene that had 24 percent LOI value.

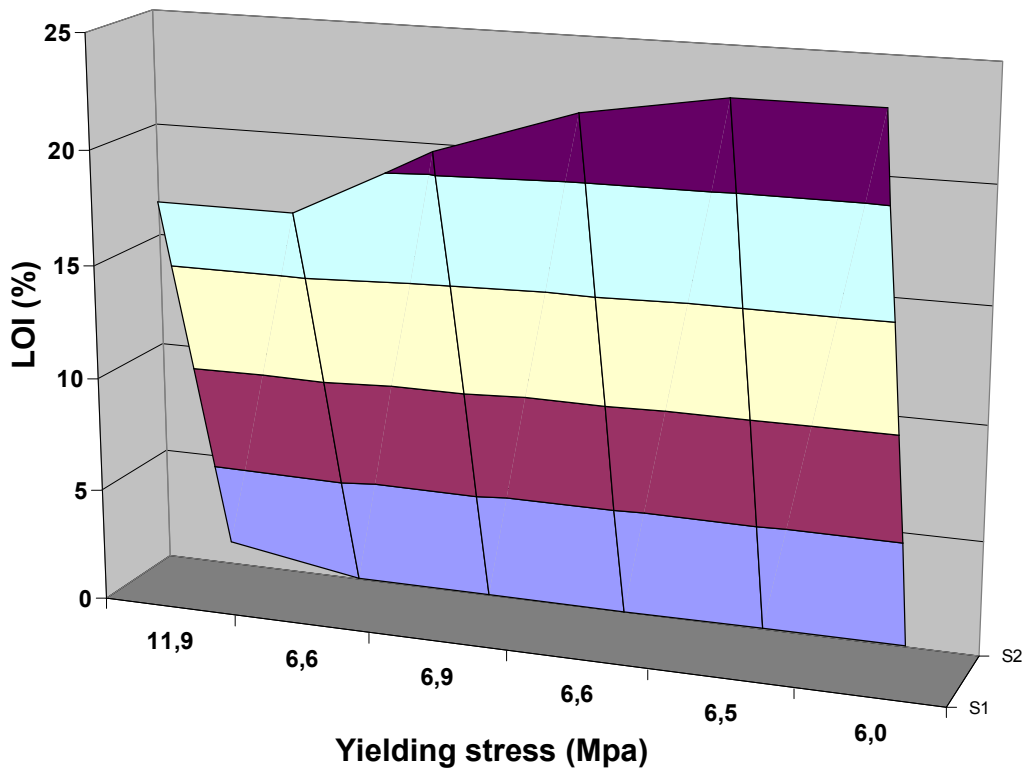
4.3 LOI in Comparison with Yielding Stress

When the obtained results for flame retardancy and results for yielding point of produced flame retardant additive polymer composites, it was seen that addition of additive to the polymer matrix decreased the yielding stress of polymer as nearly to the half of the original value. On the other hand it was clear that with that given decrease in polymer yielding stress we were able to increase the flame resistance of the polymer composite with playing the variables such as efficiency of flame retardant and its improved dispersion in polymer matrix.

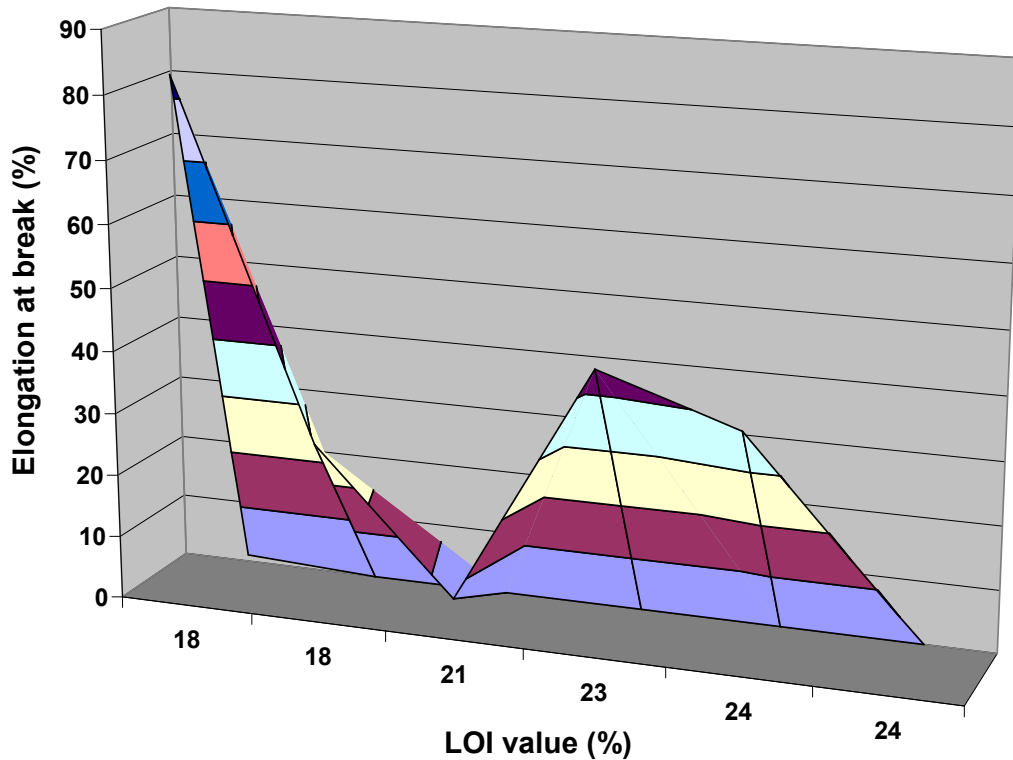
When we took a look to the response surface of flame retardancy and polymer composite elongation, it was clear that the improvements that we have done on samples without clay. In the beginning the elongation of composite fell from 90 percent to 28 percent. The optimization that we have done on processing of composite resulted in an increase from 28 percent to 44 percent elongation at break value samples without clay. When we consider the samples with clay we saw that we optimized the processing variables and we saw an increase from 7 percent to 38 percent with samples containing clay. Improvements on elongation at break values were showing that we increased the toughness of composite.

	δ_0 (N/mm ²)	Agt(%)	At(%)
LDPE	11.9	72.4	83.9
PE/PE-TMI/FR2	6.9	20.8	28.5
PE/PE-TMI/FR2/Clay	5.4	5.7	6.6
PE/PEglue/FR2	6.6	34.6	44.7
PE/PEglue/FR2/ 3%Clay	6.5	20.4	37.6
PE/PEglue/FR2/5%Clay	6.0	12.9	13.6

Table 5: Tested mechanical properties of flame retarded polyethylene



Graph 1 : LOI versus yielding stress



Graph 2: LOI versus Elongation at break

5. Conclusion remarks and future work

Intumescent flame retardancy is potential for environmental friendly flame retarding systems. Its main advantage against environment friendly metal hydroxide flame retarding systems is, lower loading amounts in comparison to. Since amount of filler is also a variable on virgin polymer's decreasing mechanical properties, lower the filler loading, lower the deviating from original properties.

Intumescent flame retardant provides passive flame retardancy, since it does not scavenge radicals needed for combustion process. Rather it creates a physical barrier

that pacifies heat transfer and radical penetration. Thus thicker the formed char residue when polymer encounters a heat source, the better intumescence. Modification that can increase elasticity of residual char residue increase barrier's capacity to pacify heat and radical transfer, and will result in increased effectiveness of polymer even in under fire conditions.

Intumescent flame retardant synthesized was hydrophilic and thus hygroscopic. Contact of flame retardant compound with air resulted in moisturizing of the product. Any moisture in extrusion process resulted in decreased compatibility between polymer matrix and flame retardant additive. This in turn resulted in lowered mechanical properties of composite. Flame retardant compound kept under vacuum conditions for improving of dispersion of flame retardant in polymer matrix with minimum deviation from virgin polyethylene. Another process variable that adjusted was, temperature and mixing speed of extruder for optimization of mechanical properties. Since flame retardant compound was fragile and sensitive to temperature and shear forces, degradation resulted in drastic decrease of polymer properties. Thus optimum extruder reaction variables were obtained by trial error methodology in real time trials. Process temperatures between up to 150 °C were tested to be safe for flame retardant compound. After that activation of flame retardant compound during processing was observed.

Flame retardancy of polymer was linear combination of effective flame retardant additive and effective dispersion of synthesized flame retardant additive in polymer matrix. During the research both aspects were improved causing 6-7 percent increase in fire resistance of polymer with respect to Limiting Oxygen Index testing standards. For effective flame retardant additive, recipe caused increased amount of charred layer was investigated. Together with this, different compatibilizer and mixing profiles were tried as long as flame retardant additive's thermal stability let.

As future work, it will be better to have thermally more stable flame retardant additive. This can be achieved by using cyclic structures for carbon source, for phosphorus containing acid precursor, for nitrogen containing blowing agent. Or another synergistic additive may be added during extrusion process that has high heat capacity and let temperature profile higher by absorbing heat given to the system. So that flame retardant compound may be protected from effects of heat for a short period of time.

Also produced polymers succeeded 24 % LOI value, these prepared polymer may act as masterbatch and can be diluted to a amount that can have 21% LOI value with virgin polymer so that lowered filler amount will increase mechanical properties of polymer more.

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APPENDIX A

Intumescent Flame Retardant Synthesis For Coating Applications

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ABSTRACT:

In the present research, aim is to impart flame retardancy to the alkyd resin. Styrene modified alkyd resin is obtained from Polisan and intumescent additive is compatibilized to the base resin for investigation of flame retardancy of modified alkyd resin. Resistance of Neat and Flame retarded Alkyd resins against fire are tested in Limiting Oxygen Index (LOI) instrument and values of 16% and 22% found respectively. Also Flame retarded Alkyd resin is V0 according to UL-94 test standard.

INTRODUCTION:

Base Resin:

Alkyd resins are the reaction product of an oil or fatty acid, polyol(s) and polyacids. These polymers are supplied in solvents and can cure by reaction with oxygen or amino based crosslinking resins to form tough, durable films. The choice and amount of oil in the polymer determines the dry rate and solubility of the polymer in aliphatic solvents. Long (over 60 %) and medium (40-60%) oil alkyds are supplied in low odor aliphatic solvents and are suitable for architectural and maintenance finishes. Short (under 40%) oil alkyds are supplied in aromatic solvents and are used in fast air dry and bake finishes. Alkyds can also be modified or co-reacted with many other material types (rosin, phenolic, urethane, vinyl monomers etc.). The precise combination of the many possible ingredients, together with careful control of the reaction, influences the final properties of the alkyd produced. For this reason there are a large number of alkyds available for the coatings formulator.

Flame retardant additive:

Flame retardant coatings are widely used in the field of protective coatings for paints. Among many possible routes for flame retardancy, intumescency is preferable because it combines several advantages such as non-toxic, environment friendly nature and moderate price.

Due to the continuous trend in more strict safety regulations for plastics and paints [1- 3], search for polymers with flame retardant properties is important. On this point coatings may impart their non-flammable properties to polymer matrix and can contribute to the fire propagation. In some wood and

cable coating applications, significant level of fire-retardancy is required and coatings with FR properties have been developed.

In conventional plastics, additives with chlorinated/brominated compounds had wide application to impart flame retardancy to the polymer matrix but degradability problems [4] in their nature and toxic gases which are released while maintaining flame retardancy is their major drawback and their usage is decreasing for safety reasons. On the other hand metallic hydroxides are environmentally friendly as intumescent systems but their low activity requires high concentrations which have negative impact on the mechanical properties of the matrix that they are applied to. Moreover, recyclability is important aspect for plastics other than their behavior under fire.

Flame retardants based on intumescency is preferable because of its moderate loading amount when compared with metal hydroxides which do not have negative impact on mechanical properties of the polymer matrix [5]. Intumescent system is active in condensed phase and, do not release corrosive and toxic gases while maintaining flame retardancy. Moreover, intumescent systems evolve less corrosive gases since nitrogen has higher decomposition temperature, and this is main reason for them for being used in cable jacketing industry. The main ingredients for intumescent additive are an acid source, a carbon source and a blowing agent [6].

Phosphorus containing intumescent additive interferes with pyrolysis and combustion mechanism in way that it (fig.1);

- Promotes char formation, thus reduces the available combustible carbon containing volatiles in the gas phase
- Stops the oxidation process of carbon at the carbon monoxide stage, thus decreases the exothermic heat of combustion damping the thermal-transition processes.
- Forms phosphoric and related acids which react as a heat sink as they undergo endothermic reduction.
- Forms thin glassy or liquid protective layer in the condensed phase.
- Forms anhydrides of phosphoric and related acids, which may act as dehydrating agents and discourage hydrolytic degradation and promote char formation

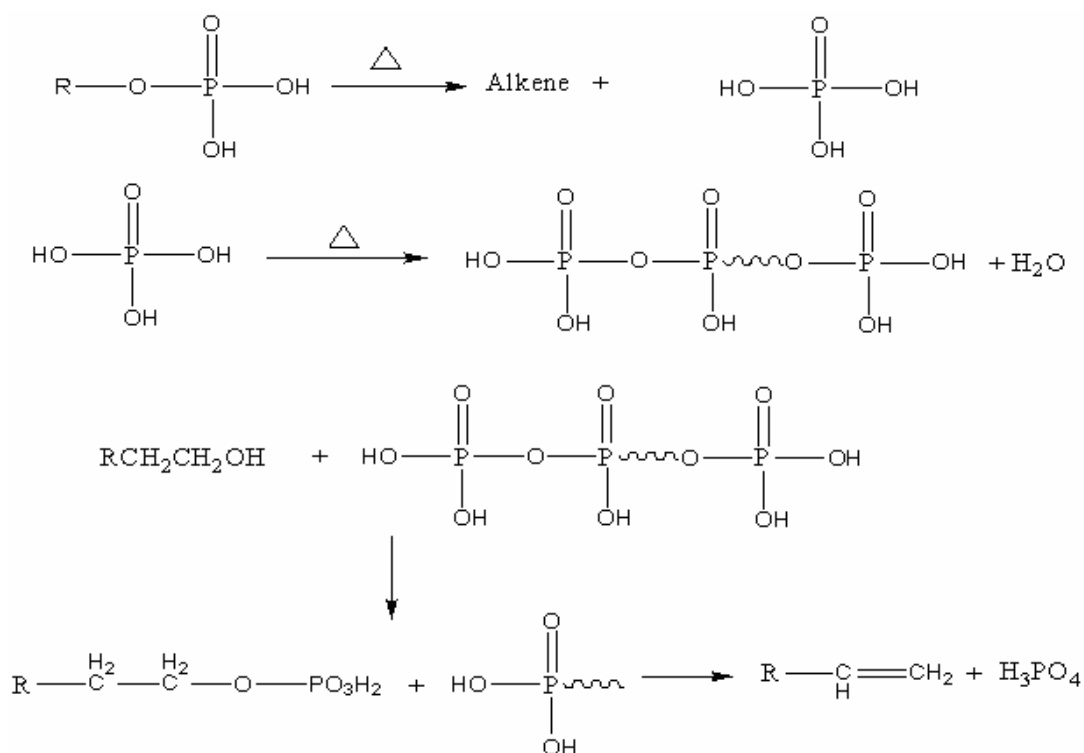


Fig.1: Pyrolysis and combustion mechanism of intumescent additive

EXPERIMENTAL PROCEDURE & MATERIALS:

Materials:

Modified Alkyd Resin:

Kindly donated by Polisan and used without further processing.

Trimethylpropane Triacrylate (TMPTA):

Purchased from UCB and used without further processing.

IRGA CURE 1700:

Purchased from CIBA and used without further processing.

Pentaerithrytol:

Kindly donated by Çağ Kimya and used without further processing.

Ortho-Phosphoric acid:

Purchased from Merck and used without further processing.

Ethylenediamine:

Purchased from Acros Organics and used without further processing.

Sebacoyl Chloride:

Purchased from Aldrich and used without further processing.

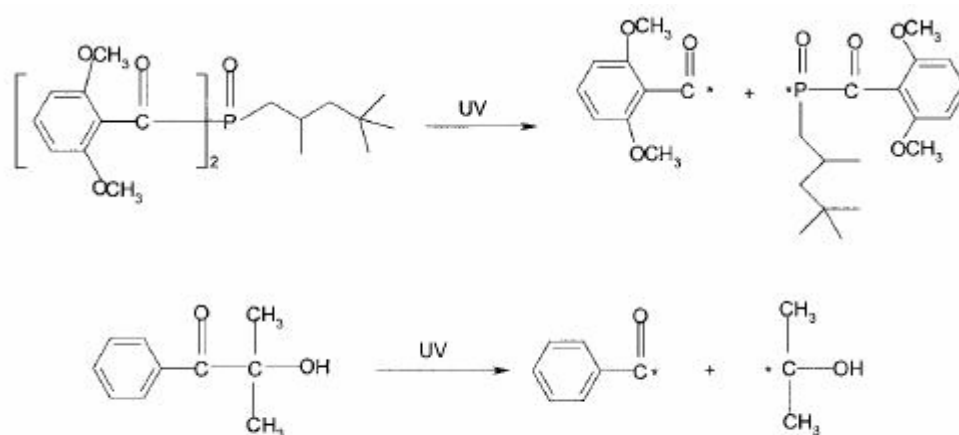
Procedure:

A) Crosslinking of Alkyd Resin [7]:

Since measuring standards for Limiting Oxygen tests uses 4mm x 15 cm x 1cm specimens flame retardant efficiency of the additive can be measured by preparing alkyd resin samples having these dimensions. Crosslinked alkyd resin contains;

- 1 gr TMPTA as crosslinking agent
- 0.5 gr IRGACURE 1700 as photoinitiator
- 8.5 gr Alkyd Resin for neat alkyd resin
- 7 gr Alkyd resin + 1.5 gr Flame Retardant for Flame retarded alkyd recipe

When UV-initiator is activated radicals formed (fig.2) and these radicals propagate the crosslinking reaction via TMPTA and unsaturations existing within Alkyd resin.



Processes of fragmentation of Irgacure 1700.

Fig.2: process of fragmentation of Irgacure 1700

After preparing crosslinked neat and flame retarded samples they were placed in soxhlet extractor for determination of crosslinking density. The samples stayed in extractor for two days for dissolving out uncrosslinked portions.

B) Limiting Oxygen Index (LOI) Trials:

Most credited and wide-spread test for analyzing resistance of polymeric materials against fire is Limiting Oxygen Index test. In this method, sample is fixed in a vertical position in a glass chimney, providing a flux of a mixture of Nitrogen and Oxygen gases from the bottom of chimney. 4

centimeters high flame is applied to the sample from above. LOI value is the minimum amount of Oxygen volume that is efficient for spreading of flame for a given distance or for a given time. Greater LOI value for a material means greater resistance against burning (fig.3). LOI value can be calculated using below equation;

$$LOI = \frac{[O_2]}{[O_2]+[N_2]} \times 100$$

Using above equation minimum amount of oxygen volume is calculated, and standard resistance of material against fire is determined.

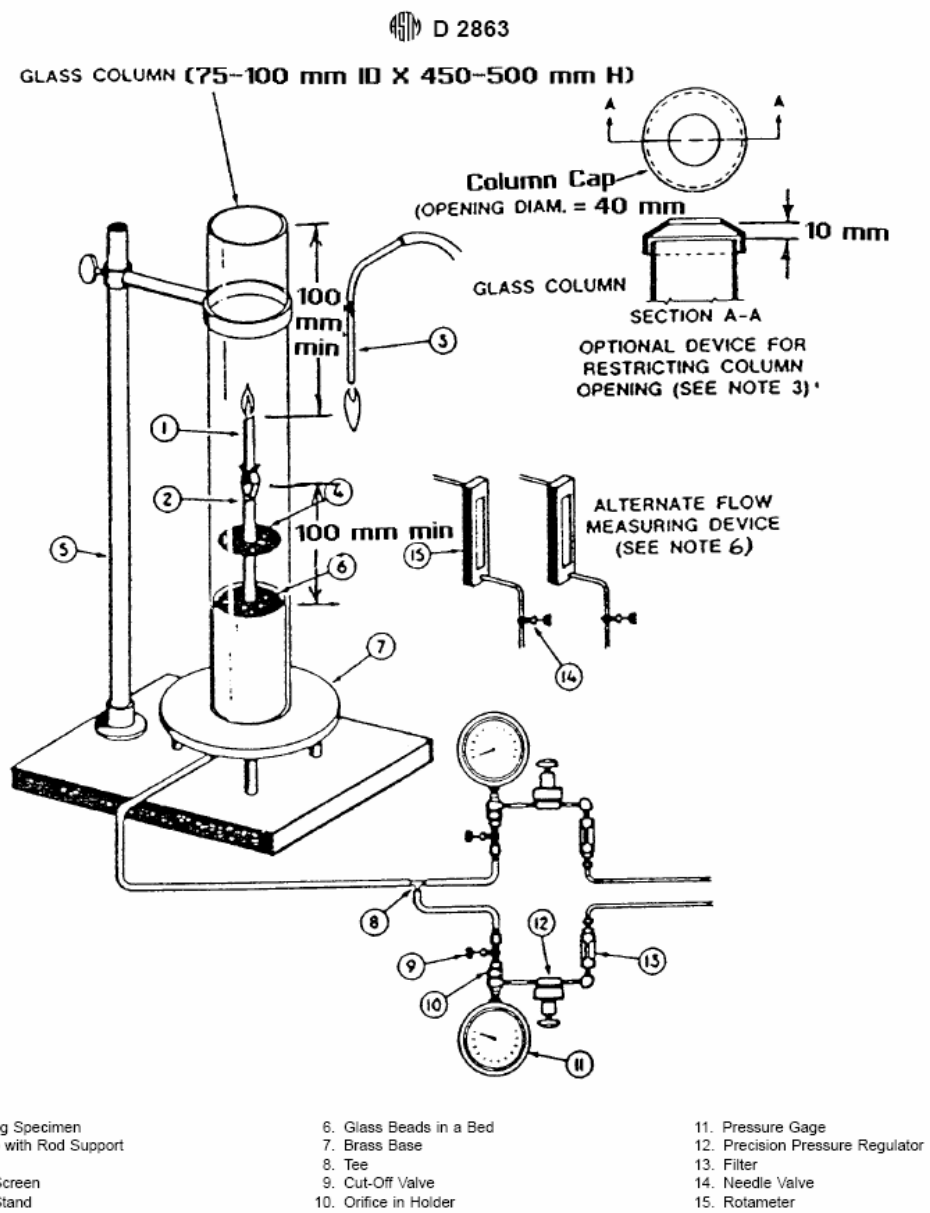


FIG. 1 Typical Equipment Layout

Fig.3: LOI instrument

RESULTS & DISCUSSION:

A) Compatibility Problems:

Synthesized flame retardant first added into the alkyd resin without modification. However, due to the polarity difference between polymer matrix and flame retardant additive, no effective miscibility occurred. This resulted in decrease in mechanical properties and transparencies of the samples. Cracks observed after UV-crosslinking of alkyd resin.

For improving efficiency of wetting of alkyd resin with flame retardant additive, we modified polarity of additive via adding hydrophobic alkyl chains with reacting Sebacoyl Chloride. This step resulted in improved wetting of alkyd resin with flame retardant; also crack formation isn't observed after modification. Mechanical properties of the improved flame retardant recipe consisting alkyd resin will be discussed in mechanical properties section.

B) Crosslinking density:

The occurrence of crosslinking reaction monitored with FT-IR. Before and after the crosslinking reaction, taken spectrums clearly pointed out the reaction, peak at ~1600 indicates carbon carbon double bond stretching, thus decrease in this peak implies crosslinking (fig.4);

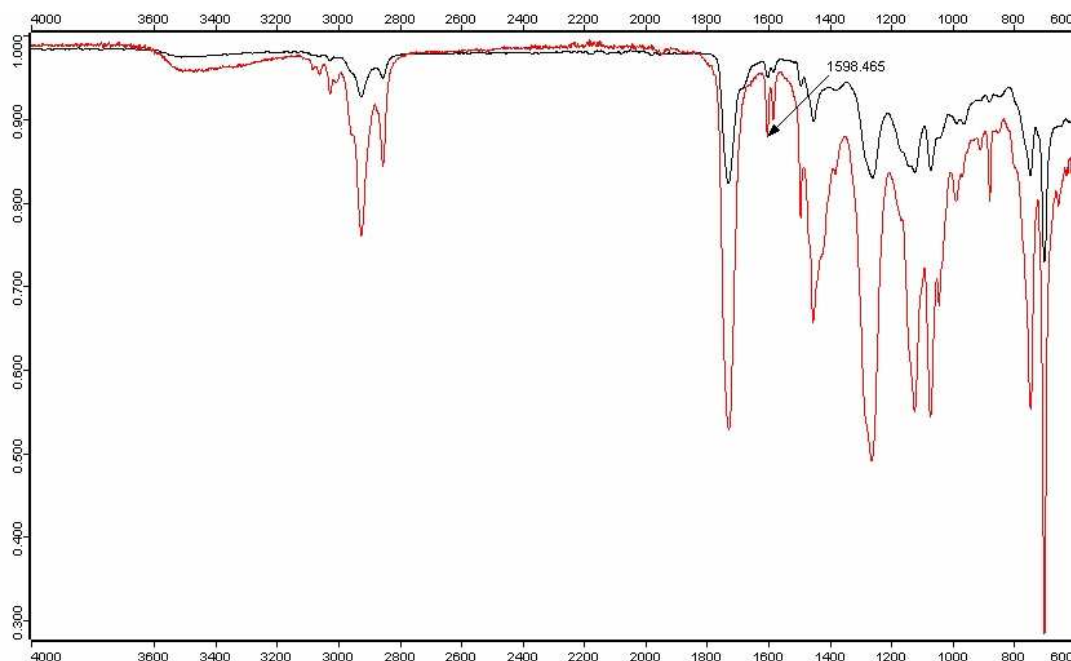


Fig.4

Also, the crosslinking density determined. For that purpose, prepared neat and flame retarded samples were put in soxhlet extractor and extracted for two days and their crosslinking density (C.D) was found with the equation;

$$C.D = \frac{\text{Weight of material after Soxhlet extraction}}{\text{Weight of material before Soxhlet extraction}} \times 100$$

Neat Alkyd Resin(%)	Flame retarded Alkyd resin(%)
60,11	56,81

C) Thermal behaviour of material:

After preparing standard specimens with desired dimensions with UV-crosslinking for LOI test, each sample tested three times to obtain an idea about resistance of samples against combustion process. Results are as listed below;

	Alkyd resin	Flame retardant/Alkyd resin	Modified Flame retardant/Alkyd resin
LOI Values	16%	22%	22%

Also, flame retarded samples were tested with UL-94 test standard which investigates flame retardancy and dripping behavior of to be tested material in open atmosphere. Flame retarded alkyd resin samples extinguished themselves and no dripping occurred, materials counted as V-0.

Thermal resistance of both samples was also monitored via thermo gravimetric analysis method. Results clearly show that added flame retardant increases residual mass of alkyd resin from 9% to 22% in temperatures up to 620 °C (fig.5). This result is expected while using intumescent additive. While the surface is degrading, it forms stable charred layer behaving as a thermal insulator.

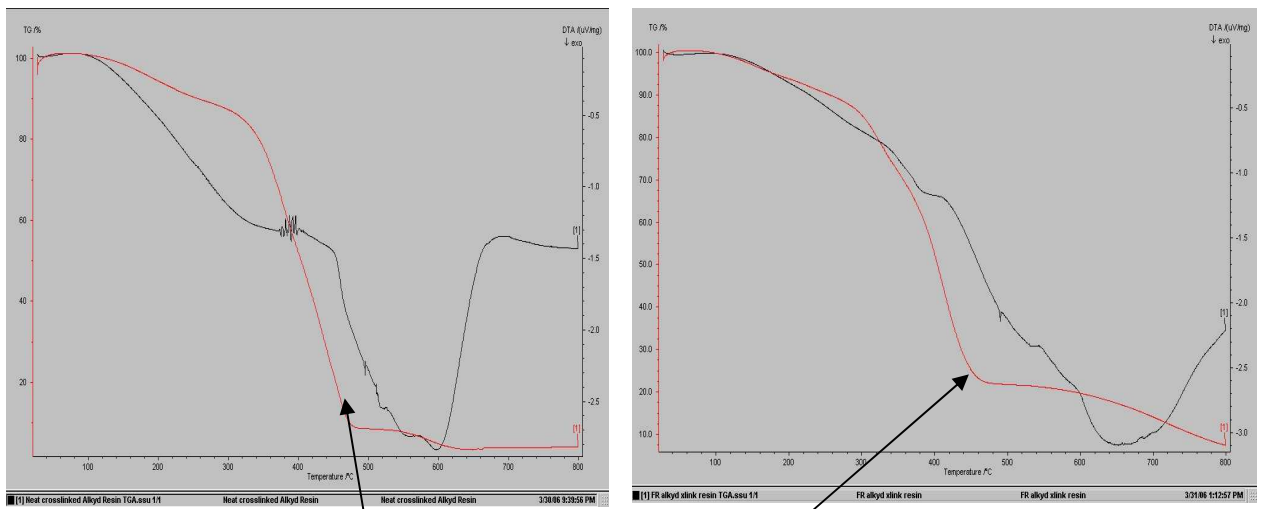


Fig.5 : Residual mass increases from 9% to 22% upto 620 °C

CONCLUSION:

After various tests with prepared samples it is obvious that flame retardant imparted its resistance to alkyd resin successfully. LOI value increased from 16% to 22%, indicating that alkyd resin is capable of extinguishing fire itself. On the other hand due to the compatibility problems occurring between additive and base matrix, visibility decrease observed. Further modification of flame retardant for alkyd resin improved compatibility and mechanical properties but still visibility loss is a factor to be corrected.

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