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APPLIED AND NATURAL SCIENCES**

(MASTER OF SCIENCE THESIS)

**PRODUCTION OF POLYMERIC COMPOSITE
CABLE SHEAT MATERIALS FILLED WITH
HALOGEN-FREE FLAME RETARDANT**

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Melih Can YILMAZ tarafından Yüksek Lisans Tezi olarak sunulan **Production of Polymeric Composite Cable Sheat Materials Filled With Halogen-Free Flame Rsetardant / Halojen İçermeyen Alev Geciktirici Katkılı Polimerik Kompozit Kablo Kılıfı Malzemesi Üretimi**” başlıklı bu çalışma E.Ü. Lisansüstü Eğitim ve Öğretim Yönetmeliği ile E.Ü. Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi'nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve **21 Nisan 2011** tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET**HALOJEN İÇERMEYEN ALEV GECİKTİRİCİ KATKILI POLİMERİK
KOMPOZİT KABLO KILIFI MALZEMESİ ÜRETİMİ**

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Bu projede, ülkemiz sınırları içerisinde üretilen alçak yoğunluk polietilen (AYPE), diğer kaynaklardan temin edilen etilen-vinil asetat (EVA) kopolimeri, mineral alev geciktiriciler sınıfından Alüminyum trihidrat (ATH) ve yardımcı malzemeleri kullanarak, kablo sanayinin kullanımına uygun, halojensiz alev geciktirici katkı polimerik malzeme geliştirilmiştir.

Polimerik kompozit bileşimleri, kesikli iç karıştırıcı kullanılarak hazırlanmıştır. Hazırlanan kompozit örneklerinde, ısıl davranışların incelenmesinde diferansiyel taramalı kalorimetri (DSC) ve ısıl gravimetrik analiz (TGA) yöntemlerinden yararlanılmıştır. örneklerin mekanik özellikleri çekme testi ile, reolojik özellikleri ise reometre ile belirlenmiş, örneklerin yanıcılıkları ASTM D2863 standardı uygulanarak sınır oksijen indisi ile saptanmıştır. Buna ek olarak, kompozitlerin hazırlanmasında kullanılan polimerler, AYPE ve EVA, ve alev geciktirici katkı, ATH, çeşitli yöntemler ile karakterize edilmiştir.

Kompozitlerin ısıl analizleri sonucunda, ATH' nin bozunmasına ait olduğu düşünülen pik sıcaklığının, saf ATH ile kıyaslandığı zaman 219 °C'den 225 °C'ye yükseldiği görülmüştür. Buna ek olarak, EVA miktarının artması ile, kompozitlerin viskozitelerinin arttığı ve kopmada uzama değerlerinin geliştiği görülmüştür. Benzer şekilde EVA oranının 26%' dan 65%' e çıkarılması LOI değerini 30' dan 34' e çıkarmış ve böylece yanma özelliklerini geliştirmiştir.

Anahtar Sözcükler: AYPE, EVA, ATH, HFFR, alev geciktirici, LOI

ABSTRACT**PRODUCTION OF POLYMERIC COMPOSITE CABLE SHEAT
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The objective of this study presented herein is to develop a polymeric composite material by using low density polyethylene (LDPE) produced within the country, ethylene-vinyl acetate (EVA) polymer which was provided from other sources, aluminum trihydrate as a member of mineral flame retardants family and auxiliary materials for cable applications.

Polymeric composite formulations were prepared by using internal mixer. Thermal behavior of samples was examined by DSC (Differential Scanning Calorimetry) and TGA (Thermo-Gravimetric Analysis) methods. Mechanical and rheological properties of composites were investigated by tensile tests and rheometer, respectively. The flame retardancy of samples was determined by applying ASTM D2863 standard (Limiting Oxygen Index). In addition, neat polymers, LDPE and EVA, and flame retardant filler, ATH, characterized by various methods.

The TGA results exhibit that the onset of decomposition of ATH in the composite increases from 219 to 225 °C. In addition, an increase in the viscosities and an enhancement in elongation at break of composites were observed with increasing EVA content. Furthermore, fire properties improved with the addition of EVA at high loading levels. The LOI value increased from 30 to 34 when 65 mass% of EVA was used in the composite.

Keywords : LDPE, EVA, ATH, HFFR, flame retardancy, LOI

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SYMBOLS and ABBREVIATIONS

ASTM	American Society for Testing and Materials
ATH	Aluminum tri-hydroxide
BFR	Brominated flame-retardants
CPE	Chlorinated polyethylene
DMA	Dynamic mechanical analysis
DSC	Differential Scanning Calorimeter
DTA	Differential thermal analysis
<i>E</i>	Young's Modulus
ϵ_B	Elongation at break
EVA	Ethylene-vinyl acetate
EVA-18	Ethylene-vinyl acetate copolymer containing 18 wt % vinyl acetate units
FR	Flame retardant
HCFR	Halogen containing flame retardants
HDPE	High-density polyethylene
HFFR	Halogen-free flame retardant
HRR	Heat release rate
IR	Infrared analysis

SYMBOLS and ABBREVIATIONS (Continued)

LDPE	Low-density polyethylene
LOI	Limiting oxygen index
MFI	Melt Flow Index
MH	Magnesium hydroxide
PB	Polymer blend
PE	Polyethylene
PEgMA	Polyethylene grafted with maleic anhydride
PP	Polypropylene
PUF	Polyurethane foam
R.H.	Relative humidity
RMS	Rheometric mechanical spectrometer
SEM	Scanning electron microscope
SEM	Scanning electron microscopy
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
T_m	Melting temperature
VA	Vinyl acetate

SYMBOLS and ABBREVIATIONS (Continued)

XRD	X-ray diffraction
XRD	X-ray diffraction
ZnB	Zinc Borate
σ_B	Tensile strength at break

1.0 INTRODUCTION

Now, in the last century, both natural and synthetic polymer materials are used in many areas under numerous environmental conditions due to their easily processed and low weighted nature. However, they pose hazard under fire conditions since they are mainly composed of carbon and oxygen atoms. Halogenated polymers release toxic and corrosive emissions such as chlorinated and brominated aliphatics and aromatics which evolve hydrogen halides, when they are exposed to fire. Furthermore, when halogenated aromatics pyrolyse, halogenated dioxins and dibenzofurans which are known as toxic, liberate (Lomakin *et al.*, 1999). Consequently, improving the flame retardant (FR) behavior of polymers is the primary issue for most applications.

1.1 Demand on Halogen-Free Flame Retardants and Polymers

The use of flame retardant additives is forecast to rise 6.1 percent in 2014 (**Figure 1.1**) (<http://www.bccresearch.com>). The leader in the flame retardant market was alumina trihydrate (ATH) in 2009. In addition, it is expected to maintain its leadership in demand through 2014, driven by trends toward non-halogenated chemicals. The use of other environmentally favorable flame retardants such as phosphorus-based compounds and magnesium hydroxide (MH) are forecast to rise, however the exact opposite situation is in question for chlorinated and brominated flame ones (<http://www.reportlinker.com>).

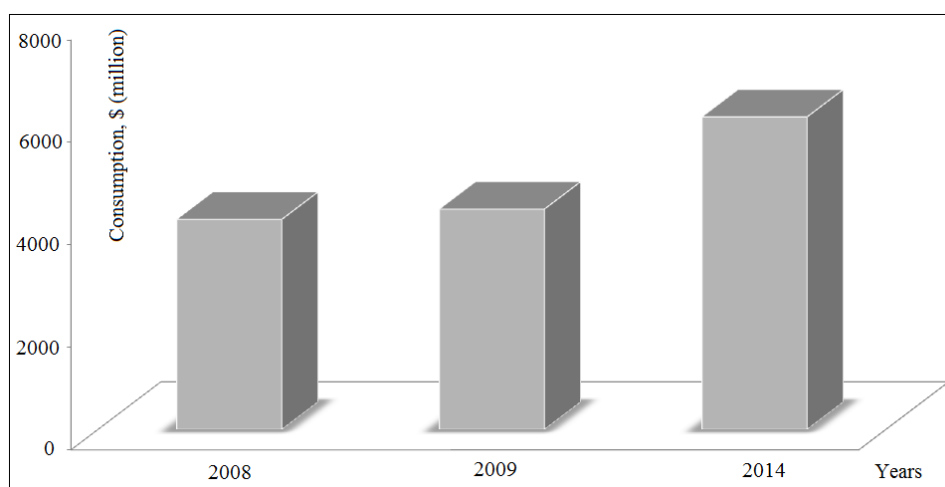


Figure 1.1 Global forecast of flame retardant chemicals consumption, 2008–2014
(<http://www.bccresearch.com>)

The types of flame retardants dominating the market in Europe are presented in **Figure 1.2** (Döring and Diederichs, 2009). The great majority of flame retardants already present in the market are halogen-free ones. Furthermore, there are so many flame retardant technology options necessary due to the wide variety in polymers used. The polymer types used in electrical and electronic applications are illustrated in **Figure 1.3** (Döring and Diederichs, 2009).

Environmental factors and government regulations force manufacturers to use flame retardant chemicals in a wide range of products. As an irony, some of these flame retardant products playing life-saving role in the case of a real fire by retarding it, can be toxic.

Most of the halogenated chemicals have been banned in all over the world for the last decade. In Japan, US and Europe, these materials are restricted to use in electric and electronics applications by directives such as Restriction of Hazardous Substances (RoHS) and Waste Electrical and Electronic Equipment. The major reason of this movement is to define the environmentally harmful materials, to forbid or restrict use of them and hereby prevent their entrance to solid waste landfills and waste incineration plants.

The Dutch State Council, the highest administrative court in the Netherlands, has denied a permit for the production of the brominated flame retardant, bis(2,3-dibromopropyl) tetrabromobisphenol-A (BDBPT) on March, 2003. The council classified the flame retardant as potentially hazardous. Additionally, Japan government announced that they limit more than 100 components used in products or in their packages. Sony, Matsushita and NTT are some of the companies implementing the policies called green procurement.

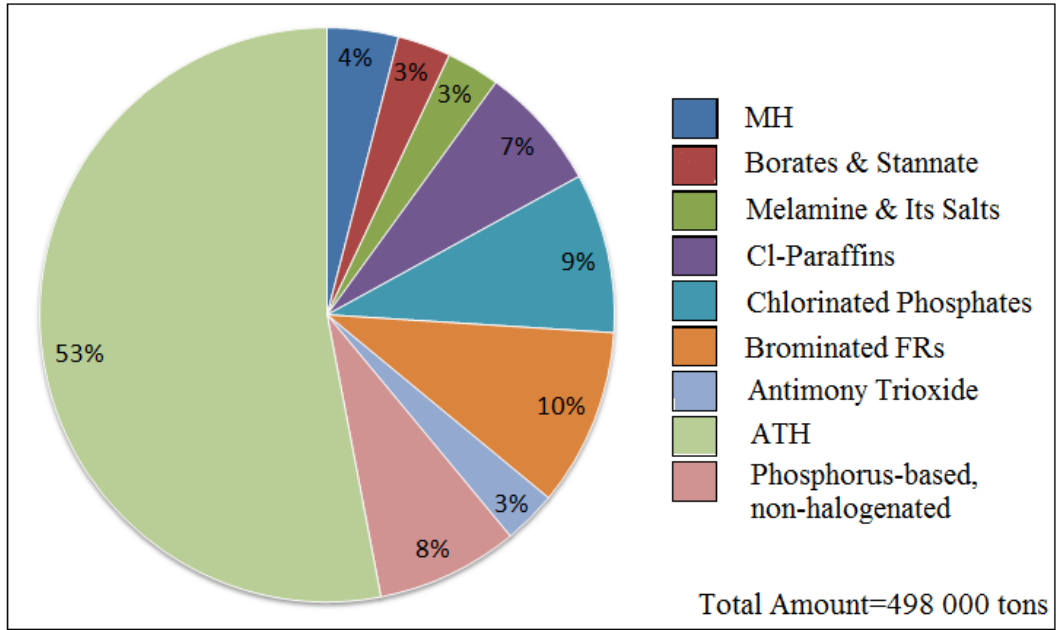


Figure 1.2 The current consumption of flame retardants in Europe (Döring and Diederichs, 2009)

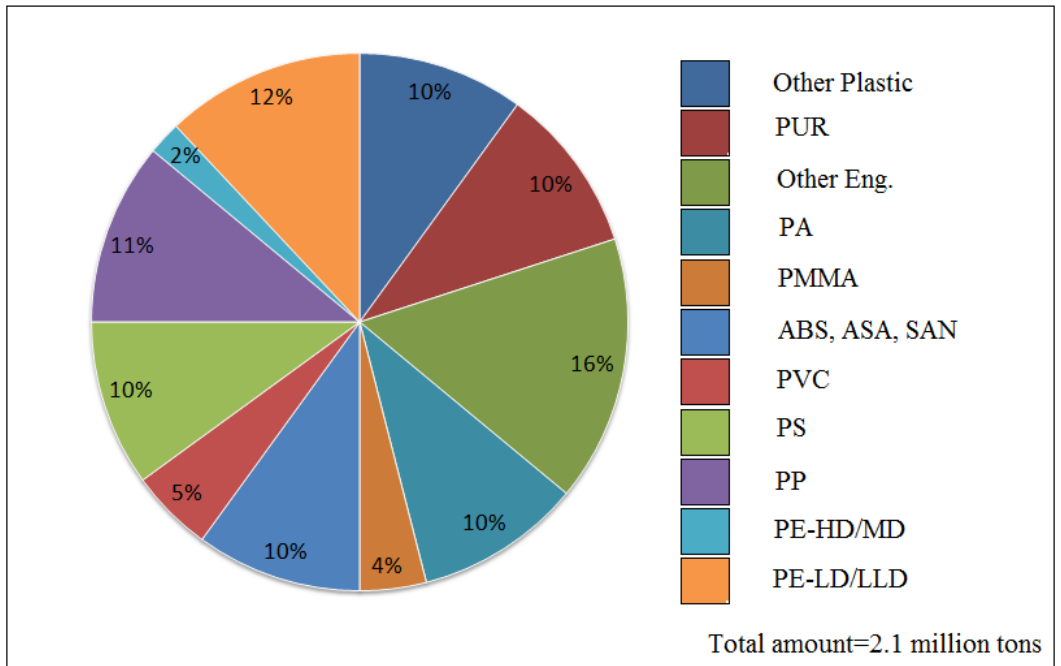


Figure 1.3 Plastics demand for electrical and electronics industry in Western Europe (Döring and Diederichs, 2009)

In Europe, halogen-free flame retardants (HFFR) are the market leader with 71% utilization rates when consumption in Europe is examined (Döring and Diederichs, 2009). If restrictions continue on halogen-containing materials and products, a significant increase in the use of these products is expected in the long term. Building and construction, electrical and electronics and transportation are the major three markets where flame retardants are frequently used since regulations are strict when human health is the major concern.

1.2 Polymers Used in Cable Formulations

Polyethylene, PE, has been used as an insulating material in cable industry due to its excellent properties such as good chemical resistance, excellent mechanical and electrical properties and ease of processing. Additionally, it makes low-density polyethylene (LDPE) one of the most preferable polymer used in the electrics and electronics industry that it does not contain elements which are members of halogen family. Despite its low melting point (105 – 110 °C) seems a drawback, cross-linking process is used to overcome this problem.

The largest amount of LDPE is used for film applications as a packaging material, due to its low-cost and low toxicity level (Takidis *et al.*, 2003).

High-density polyethylene (HDPE) is one of the most widely used polyolefin due to its balanced mechanical properties, chemical resistance and ease processing advantages; however, its inherent flammability has limited its applications in some fields where good flame retardancy is required (Liu *et al.*, 2009).

Ethylene vinyl acetate copolymer, mostly referred EVA, is a worldwide used thermoplastic material in wire and cable insulation. Since pristine EVA is easily flammable, it is not suitable for many applications and in most cases halogen-containing flame retardants or the minerals alumina trihydrate and magnesium hydroxide are used as flame retardants for this copolymer (Nyambo and Wilkie, 2009).

Ethylene copolymers such as poly(ethylene-co-vinyl acetate) are produced by free-radical polymerization in a bulk process, like that used for low-density polyethylene production, involving high pressures and temperatures. Because the vinyl acetate monomer has the same reactivity with the ethylene monomer, a variety of copolymers, containing different vinyl acetate contents, can be produced.

The vinyl acetate content affects straightforwardly the degree of crystallinity and generally all the properties of the copolymers. The copolymers are more flexible and have higher transparency, lower modulus of elasticity, and improved barrier properties to oxygen and water vapor than LDPE. However, the major drawback of EVA is its low melting temperature and melt strength, which restrict its applications at high temperatures.

Mohsen *et al.* (2007), studied the thermal properties of FR poly vinyl chloride (FRPVC), that has been used in cable insulation and jacketing construction for multi-purpose reactor at Atomic Energy Authority of Egypt, as well as carbon-black FRPVC materials, produced by Egyptian Electrical Cable Company, and compared with those of non-flame retardant materials, poly vinyl chloride and carbon-black poly vinyl chloride. The corresponding temperature variations of nano-size free volume parameters are determined using positron annihilation lifetime technique and correlated with thermal conductivity coefficients.

Rigid polyurethane foams (PUFs) are widely used as thermal insulators and mechanical shock absorbers in transport over packs and in air conditioning. They are also used as structural materials because of their light weight, greater strength to weight ratio, and energy absorbing capabilities. PUF, like other organic polymeric materials, tends to be flammable. To improve the flame retardancy properties, different FRs are added to PUF. However, some of the FR additives used in PUF adversely affect its physical properties and pollute the environment by the evolution of undesirable gases on burning.

In recent years, because of the stringent safety standards, both public and environmental, set by statutory authorities across the world, it has become imperative to develop better FR materials with improved FR efficiency that are economical and, at the same time, halogen free (Thirumal *et al.*, 2010).

1.3 Polymer Combustion, Flammability Process and Flame Retardancy

In general, there are two major approaches to gain flame retardancy in polymer composites;

- Additive type,
- Reactive type.

More economical and simpler way to improve flame retardancy is the incorporation of FR into polymer, physically called *additive* type. In spite of the simplicity of incorporation, the compatibility and the mechanical and rheological properties are poor when this type is preferred. These include chlorinated paraffins, brominated organics, phosphate esters, aluminum trihydrate, magnesium hydroxide, borates, and antimony trioxide (Murphy, 2001).

An advanced and alternative type to additive type is the *reactive* flame retardants. The polymer is modified with the FR through copolymerization and the unit prevents flame retardancy is presented in the chain. The composite preparation process in reactive type is uneconomical however the improvement in flame retardancy is spectacular (Lu and Hamerton, 2002). Typical examples are tetrabromobisphenol A, dibromoneopentyl glycol, vinyl chloride, and bromo- or dibromostyrene (Murphy, 2001).

The combination of two factors; reducing agents (combustibles) and an oxidizing agent (combustive) are needed for the combustion reaction. The combustive is generally the oxygen in the air (Laoutid *et al.*, 2009).

Reducing agent + Oxidizing agent → Combustion Reaction

Flammability involves four processes fundamentally;

- Preheating,
- Decomposition,
- Ignition and combustion,
- Propagation.

An increase in temperature of polymeric material starts the process. The heat is supplied by an external heat source. When the material is heated sufficiently, the decomposition step takes place and it is followed by polymer bond scissions and diffusion of volatile fraction of the polymer. Thus, a gas mixture which can be called as fuel is formed. The mixture of combustible gases ignites when the auto-ignition temperature is reached. After the ignition process, the combustion becomes self-propagating and material continues to decompose. Flame is retarded when at least one of these steps is eliminated (Pearce and Liepins, 1975).

Flame retardant systems can act physically or chemically. In physical action, FRs such as aluminum trihydrate and magnesium hydroxide decomposes endothermically. They absorb heat for decomposition and reduce the temperature of reaction medium, indirectly. When ATH and MH start to decompose, water vapor is liberated at approximately 200 and 300 °C, respectively. H₂O dilutes the combustion gases with CO₂ formed. In addition, a protective char layer which isolates and protects the polymer is formed as a result of combustion. The polymeric material is separated from the fire zone by formation of an insulation layer. Such systems are called intumescent flame retardants (**Figure 1.4**) (www.budenheim.es).

In reactive FR systems, the combustion can be stopped by free-radical mechanism. Highly reactive species such as H· and OH· can be transformed into less reactive or inert molecules when released radicals (Cl· and Br·) incorporate into them in the gas phase. This action leads to a decrease in temperature and a reduction in the fuel produced.

The comparisons between the materials prepared with and without FRs pointed out the necessity of them clearly according to the test results of National Institute for Standards and Technology in Washington DC, USA. The results making difference in flame retardancy for flame retardant composites were presented below;

- 15 times more available escape time,
- Only 25% of the heat released,
- 50% less material consumed by the fire,
- One third of the toxic gases (expressed at CO equivalents) released.

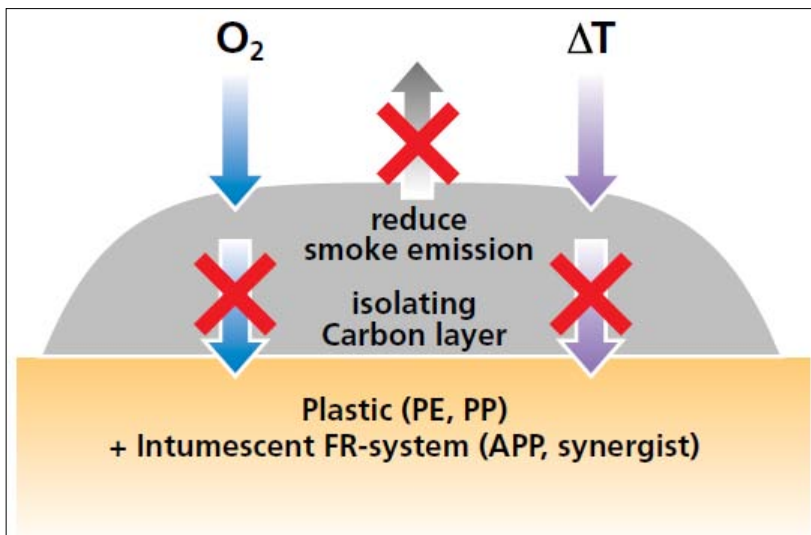


Figure 1.4 The mechanism of Intumescent flame retardant systems (www.budenheim.es)

1.4 Flame Retardant Fillers used in Cable Industry

Flame retardants used in the industry can be classified into groups; non-halogenated, halogenated and more popular type: nanometric particles.

1.4.1 Halogen-free flame retardant additives

HFFR additives cover a diverse range of chemicals which are commonly classified as; inorganic FRs (most commonly; ATH and MH), phosphorus- and nitrogen-based FRs.

Flame retardant property of metal hydroxides comes from their endothermic decomposition and water release during the combustion process. However, their decomposition temperature is expected to be higher than the processing temperature of the polymers which are used together with them.

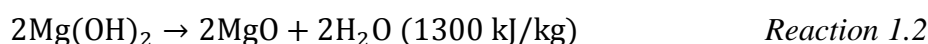
ATH, also known as hydrated alumina, is the most widely used FR additive in the low smoke free of halogens compounds representing 43% of all flame-retardant chemicals in volume but only about 29% in value (Murphy, 2001). Effects of ATH on the combustion of the polymer make ATH a very effective flame retardant material.

Fine precipitated, medium sized (0.7 – 2 μm) ATH particles are preferred in cable industry. Typical filling levels vary between 55 and 65 %wt (Sauerwein, 2002). ATH starts to decompose endothermically between 180 and 200 $^{\circ}\text{C}$ (Laoutid *et al.*, 2009). Alumina (Al_2O_3) forms and 34 wt% its chemically bonded water is released as a result of this reaction as follows (Ramazani *et al.*, 2008).

In accordance with the **Reaction 1.1**, 1050 kJ/kg energy is absorbed during the combustion. Consequently, heat energy is removed from the burning zone. Alumina forms a layer that isolates and protects the polymer from the flames. Moreover, released water vapor dilutes the combustible gases such as oxygen which surround the burning region. Aluminum trihydrate is also a good smoke suppressant since fine smoke particles are adsorbed by the aluminum oxide formed during the combustion. Thus, ATH catalyze the cross-linking reaction which helps the formation of a solid char rather than smoke (Murphy, 2001).



Another solution as halogen-free flame retardant formulations is to add magnesium hydroxide to a polymer matrix. The fire retardant behavior of MH is similar with ATH (**Reaction 1.2**) however; its endothermic degradation temperature is higher than ATH (> 300 $^{\circ}\text{C}$).



The flame retardant action of magnesium hydroxide is very effective up to 400 °C. The reaction proceeds exothermically at temperatures higher than 400 °C (Laoutid *et al.*, 2009). The sizes of MH particles, their surface area and modification of the surface directly affect the flame retardancy of the system (Lim *et al.*, 2009).

Similar to ATH, flame retardant capability of MH is very low when it is used in smaller amounts. However, a dramatic loss of mechanical and processing properties are observed when they are used larger amounts in polymer matrix. Surface modification of flame retardant is one technique to overcome this problem. Another technique which is more efficient than surface treatment includes the usage of nanosized Mg(OH)₂. Qiu *et al.* (2003), prepared the nanometric Mg(OH)₂ particles by the surfactant-mediated solution method. Their Mg(OH)₂ crystals display a needle-like morphology with a diameter of 6 nm and length of 50 nm. They measured the LOI value of Mg(OH)₂/EVA nanocomposite as 38.3. The LOI value of another composite having the same composition but filled with micrometric Mg(OH)₂ particles of 2–5 μm was measured as 24. They reported that good dispersion of nanosized MH particles in EVA matrix enhances the flammability properties of the polymer nanocomposite.

Phosphorus based flame retardants include organic and inorganic phosphates, phosphonates and phosphinates as well as red phosphorus, thus covering a wide range of phosphorus compounds with different oxidation states.

Nitrogen based flame retardants are typically melamine and melamine derivatives (e. g., melamine cyanurate, melamine polyphosphate, melem, melon). They are often used in combination with phosphorus based flame retardants.

1.4.2 Halogen containing flame retardants

Halogen containing flame retardants (HCFR) are primarily based on chlorine and bromine substances such as halogenated paraffins, chlorinated alicyclic compounds, and brominated aromatic compounds (**Table 1.1**). They act primarily by chemically interfering with the radical chain mechanism that occurs in the gas phase during combustion. These flame retardants prevent or delay the onset of ignition, and slow down the rate of burning once a fire is initiated (Morose, 2006).

Table 1. 1 The types of halogen–containing fire retardant species*

Brominated HCFR	Chlorinated HCFR
<ul style="list-style-type: none"> ▪ Brominated epoxies, polystyrene, and polyols ▪ Decabromodiphenyl ethane, and ether ▪ Ethylene bis(tetrabromo phthalimide) ▪ Hexabromocyclododecane ▪ Poly(pentabromo benzyl acrylate) ▪ Tetrabromobisphenol–A ▪ TBBPA carbonate oligomer ▪ Tris(bromo neopentyl) phosphate ▪ TBBPA (2,3–dibromo propyl ether) 	<ul style="list-style-type: none"> ▪ Chloro – paraffin ▪ Alicyclic chlorinated compound (Dechlorane plus) ▪ Hexachloroendomethylene–tetrahyrophthalic acid ▪ Tris(chloro ethyl) phosphate ▪ Tris(chloro propyl) phosphate

*Morose, 2006

Brominated flame retardants (BFRs) are the cheapest ones to improve fire resistance. Alternatives are available, such as phosphorus and metal based compounds, but these are more costly and can pose manufacturing problems.

BFRs are a highly diverse group of compounds the flame retardancy mechanism is basically the same for all compounds. With the application of heat they decompose before the matrix of the polymer, preventing the formation of flammable gases. High energy OH• and H• radicals formed during combustion are removed by bromine released from the flame retardant. Thermal stability with respect to the polymer is the critical factor in choosing a flame retardant.

The consequences of the spread of these compounds in the environment and in human health are not assessed adequately, because the information on quantities produced where used, and the quantities found in environmental samples is insufficient. The information on their toxicology is also limited, although isolated cases of the occurrence of these compounds have been related to human illnesses including cancer and mass mortality of marine mammals (Rahman *et al.*, 2001).

1.4.3 Nano structured fillers

Mechanical and flame retardant properties of EVA copolymer/organoclay/ATH nanocomposites were studied by Cardenas *et al.* (2008). Intercalated and exfoliated structures in EVA/organoclay nanocomposites with improved thermal stability and mechanical and flame retardant properties are widely published. However, EVA/organoclay alone is unable to pass the strict regulatory fire tests necessary for the use of these materials in cable and wire applications. As well, EVA/ATH and EVA/MH composites require a very high proportion of the metal hydrate filler within the polymer matrix (60 wt %) to achieve a suitable level of flame retardancy, which may lead to a lack of flexibility, poor mechanical properties and problems during compounding.

As EVA/ATH composites are compared with EVA/organoclay/ATH nanocomposites, better mechanical and fire retardant properties are observed in the nanocomposites. As the EVA/organoclay/ATH nanocomposite is heated, the modifier in the organoclay begins to degrade first, forming acid sites on the clay surface which catalyze cross linking and aromatization reactions during the EVA decomposition, resulting in a carbon char that resists combustion. This carbon char formation and the decomposition mechanism of the ATH improve the fire retardant properties of the EVA copolymer (Cardenas *et al.*, 2008).

Cardenas *et al.* (2008), studied the effects of particle size and surfaces treatment of ATH fillers' thermal stability and tensile and flame retardant properties with different EVA/organoclay/ATH nanocomposites. It was observed that smaller particle size ATH fillers lead to better elongation at break values. Good LOI and ignition time values were achieved with small particle size ATH fillers and silane coated ATH filler. Silane coated ATH fillers also lead to the best char stability in cone calorimeter test.

An *et al.* (2009), studied the surface modification of hydrophobic MH nanoparticles which were synthesized via a one-step solution precipitation method with octadecyl dihydrogen phosphate ($n\text{-C}_{18}\text{H}_{37}\text{OPO}_3\text{H}_2$, ODP). The ODP was used to control the growth of crystal and to modify the surface property of the MH particles produced from the precipitation. The samples were characterized by using field emission scanning electron microscope (SEM), X-ray diffraction (XRD), infrared (IR) analysis.

1.5 Effect of Type of Filler on Flammability Characteristics

Generally, flame retardancy is obtained by the integration of inorganic fillers such as ATH and MH with the polymer matrix.

Zhang *et al.* (2009), studied the effects of fire retardants on the fire retardancy of a polymer blend of LDPE/EVA. Different combinations, i.e., polymer blend (PB), PB/ATH and PB/MH were prepared by melt blending in a twin screw extruder. SEM results of their samples indicated that fire retardant microparticles were uniformly dispersed in the polymer matrix.

Thermogravimetric analysis (TGA) results of Zhang *et al.* (2009) showed that onset degradation temperature (defined as the temperature corresponding to 5% mass loss) was lowered when FRs incorporated into the polymer matrix due to liberation of water in the flame retardants. The highest reduction in the onset degradation temperature was observed by more than 50 °C in PB/ATH. According to the results of cone calorimeter test, flame retardant containing samples delay ignition and decrease the heat release rate due to the formation of a ceramic-like layer of $\text{Al}_2\text{O}_3/\text{MgO}$.

Haurie *et al.* (2007), investigated thermal and flame retardant properties of LDPE/EVA blends when they are filled with ATH, MH, synthetic hydromagnesite and organophilised montmorillonite (OMMT) systems. It was noted that endothermic decomposition of ATH and MH occurs in a single step between 190 – 350 °C and 340 – 450 °C, respectively. Therefore, 35% mass of ATH and 32% mass of MH is lost between these temperature range. Increasing filler content increased the LOI values from 18.7 for polymer matrix to 28.6 and 28.1 for hydromagnesite and MH filled samples, respectively.

Woycheshin and Sobolev (1975), investigated the effect of ATH mean particle size on DTA. A two step thermal decomposition reaction occurs as shown in **Figure 1.5**. First transition corresponds to 220–230 °C indicates the formation of the intermediate product, boehmite (AlOOH). As ATH particle size decreases, transition in question becomes smoother (Laoutid *et al.*, 2009).

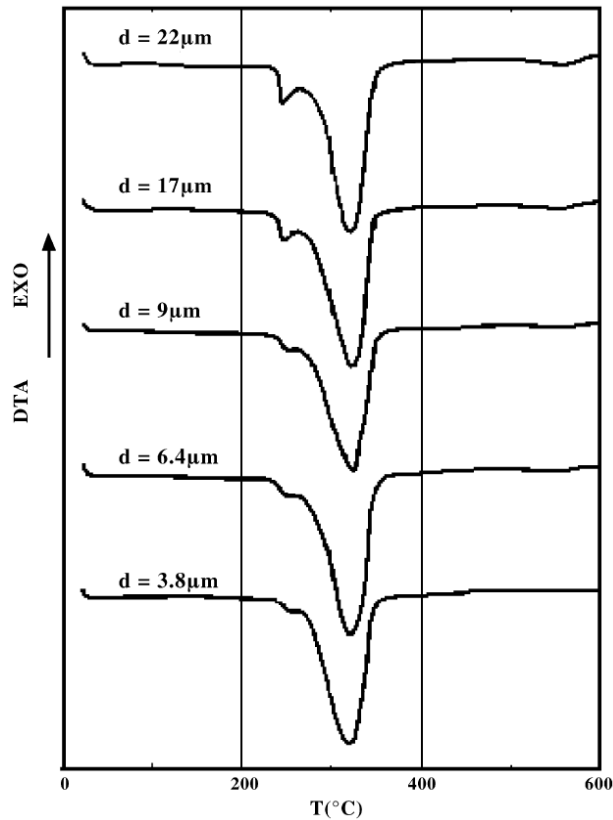


Figure 1.5 Effect of ATH mean particle size on DTA (Laoutid *et al.*, 2009)

1.6 Compatibility of Polymers and Inorganic Fillers in Composites

Polymer mixtures are defined as compatible in the polymer industry if the product has desirable properties after the mixing of polymers either as solid or in solution. Although such polymers seem to be miscible, there is only a good attraction between phases referred as compatibility, practically. In other words, compatibility is that “*a process of modification leading to creation of polymer alloy*” (Utracki, 2002).

The degree of compatibility of blends can be identified in several ways by thermal, rheological, morphological and mechanical analyses. Faker *et al.* (2008) examined the properties of LDPE/EVA blends prepared with various amounts of EVA in a laboratory batch internal mixer at a temperature of 180 °C and tested the neat PE, neat EVA and LDPE/EVA blends by using a rheometric mechanical spectrometer. The compatibility was explained by mixing rule. They stated that the compatible blends show positive deviation from the mixing rule.

Rheological properties were also discussed in the study of Faker *et al.* (2008). As presented in **Figure 1.6**, storage modulus and complex viscosity showed a positive deviation from the mixing rule for PE-rich blends, however, they show negative deviation from EVA-rich blends. Complex viscosity is calculated as given in **Equation 1.1** where ω is the angular frequency and G' and G'' symbolize the storage and loss modulus, respectively. (Jayanarayanan *et al.*, 2009). It was concluded that these positive deviations for PE-rich blends were due to the strong interfacial interaction. Viscosity and elasticity increases as a result of these strong interfacial interactions.

$$\eta^* = [(G'/\omega)^2 + (G''/\omega)^2]^{1/2} \quad \text{Equation 1.1}$$

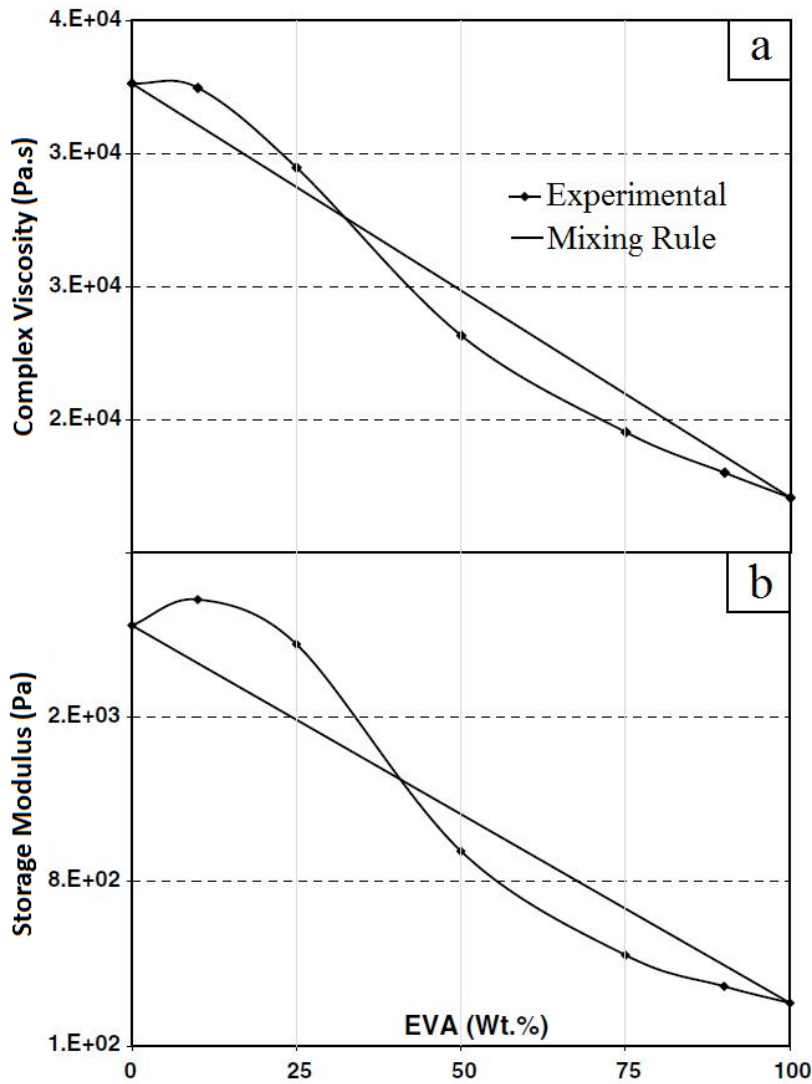


Figure 1.6 a. Complex viscosity and b. storage modulus versus blend composition of PE/EVA blend ($\omega = 0.1 \text{ s}^{-1}$, Faker *et al.*, 2008)

DMA is often used to study the miscibility in blends. This test is known with its high sensitivity for measuring glass transition and other transitions. Khonakdar *et al.* (2004), prepared LDPE/EVA and HDPE/EVA blends by melt mixing. They observed that there was a decrease in all transition temperatures with increasing EVA content in the blends of LDPE/EVA and HDPE/EVA. This indicates that the crystallinities of systems decrease as the amount of EVA in the blend increases. Morphologies of the blends were investigated by SEM and it was seen that EVA domain sizes increase with increasing EVA content for both blends (**Figure 1.7**). Above 30 wt% EVA, the irregularity in shapes of the domain sizes were observed in HDPE/EVA blends. This behavior was not observed in LDPE/EVA blends. Thus, it was concluded that LDPE is much more miscible than HDPE when blended with EVA.

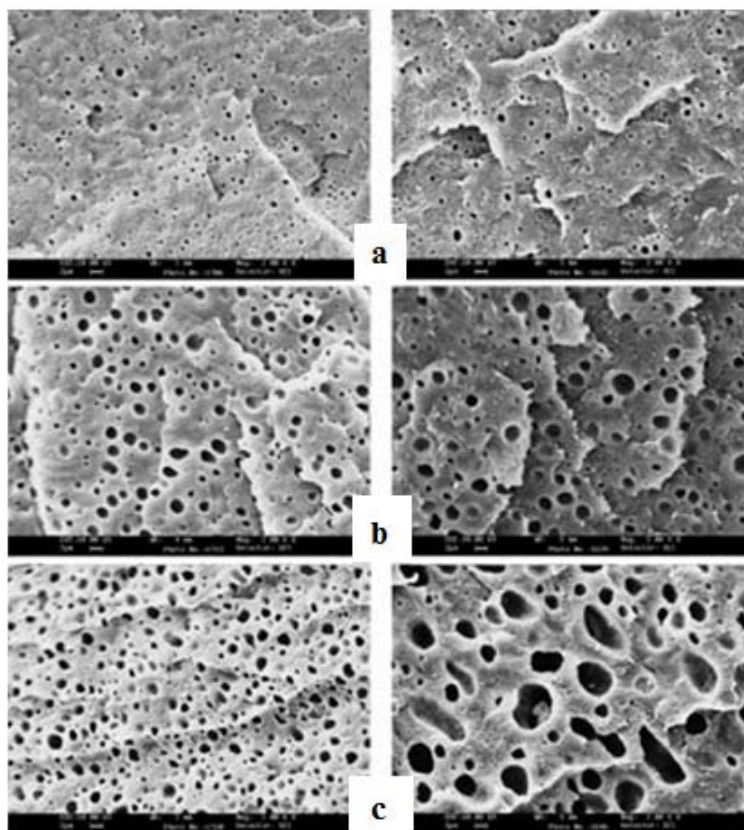


Figure 1.7 SEM images of LDPE/EVA and HDPE/EVA for various amount of EVA
a. 10 wt%, *b.* 20 wt%, *c.* 30 wt% (Khonakdar *et al.*, 2004)

The polarity is an important parameter for the compatibility of polymers, as well. VA content of EVA copolymer affects the compatibility of EVA with other polymers. The compatibility of EVA-28 (28 w% VA content) with LDPE is poor when compared to lower VA containing EVA copolymers since polarity of EVA increases with increasing VA content and therefore the affinity decreases (Takidis *et al.*, 2003).

Mineral flame retardants are the most common type of non-halogenated FRs however the mechanical properties of composites were poor prepared with $Mg(OH)_2$. To overcome this problem and increase the compatibility between MH and polyolefins, the surface of magnesium hydroxide is modified (Qu *et al.*, 2001).

The hydrophilic property of inorganic fillers makes them attract the moisture at their surface and reduce the compatibility with polymers which are hydrophobic. Surface-modified grades are used enhance the performance. Metal hydroxides surface treated with polar OH groups (fatty acids) show improved compatibility, especially at high loading levels. The polymeric material behaves like a single material when polymer matrix and FR additive is coupled. Thus, the viscosity of the material is reduced, composite is processed easier and higher loading levels are possible. Organofunctional silanes are usually preferred for modification of ATH to increase the interfacial adhesion with polymers. Electrical properties (better resistance to water permeation) are improved by this treatment in addition to enhancement in mechanical properties (Murphy, 2001).

Ulutan and Gilbert (2000) studied the effect of coating of filler on mechanical properties of polymer composites. They incorporate the uncoated and stearic acid coated MH into HDPE matrix and fit their mechanical test results to various models. Tensile and flexural properties were explained by both Pukanszky and Halpin-Tsai models.

Tensile strength as a mechanical property is affected in positively or negatively with the loading of a filler. If the transfer direction of stress is from matrix to filler, tensile strength of the composite increases. On the other hand, incorporation of inorganic fillers such as ATH and zinc borate (ZnB) decrease tensile strength because of the fragile adhesiveness in between filler's surface and matrix and their nature (Ramazani *et al.*, 2008).

One of the most widely used technology is to use of polyolefines grafted with maleic anhydride, for example PE grafted with maleic anhydride, abbreviated as PEgMA. The attachment mechanism of PEgMA to surface treated ATH is shown in **Figure 1.8** (Nabaltec, 2007).

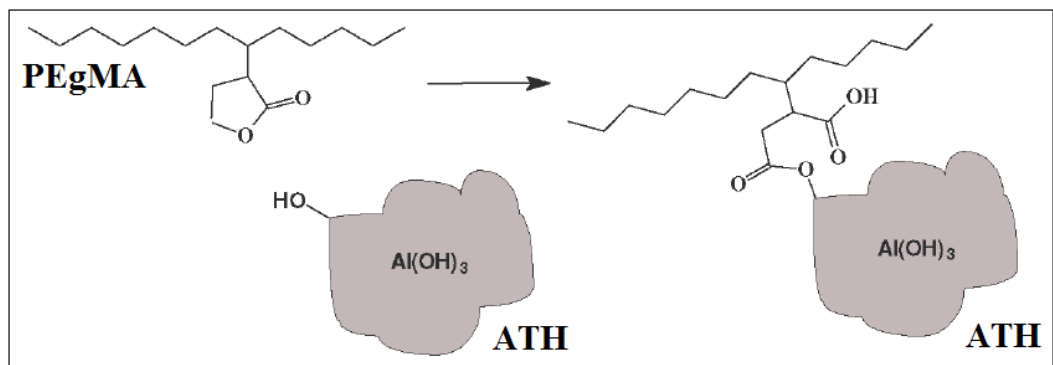


Figure 1.8 Coupling with maleic–acid–anhydride grafted polymers (Nabaltec, 2007)

Takidis *et al.* (2003), examined compatibility of LDPE and EVA containing 18 wt % vinyl acetate units. Blends were prepared by melt mixing process at 140, 160 and 180 °C with a single–screw extruder. The differential scanning calorimeter (DSC) curves of EVA blends in **Figure 1.9** show two well–separated melting peaks, corresponding to the melting temperatures (T_m) of LDPE (112 °C) and EVA (87 °C) for 25 and 50 wt % EVA–18. In other words, two immiscible blends were formed. However, the 75 wt % EVA containing blend behaves as a single phase showing only one melting peak at 85 °C. A smaller peak at 45–55 °C was also observed for all blends, indicating the melting of the crystals formed during the storage of the samples at room temperature.

DSC curves of 75 wt % EVA containing blends reveal an additional peak when melt mixing is performed at lower temperatures than 180 °C (**Figure 1.10**, Takidis *et al.*, 2003). The peak at 110 °C corresponds the melting of a separate LDPE crystalline phase. In the view of such information, it can be said that higher mixing temperature (180 °C) and large amounts of EVA (75 wt %) are required to obtain blends with a single crystalline phase.

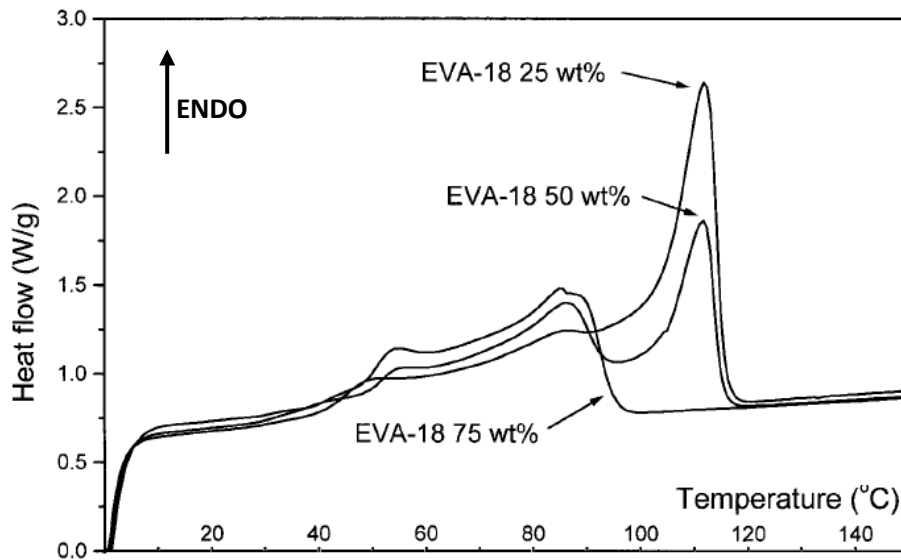


Figure 1.9 DSC curves of LDPE/EVA blends prepared at 180 °C (Takidis *et al.*, 2003)

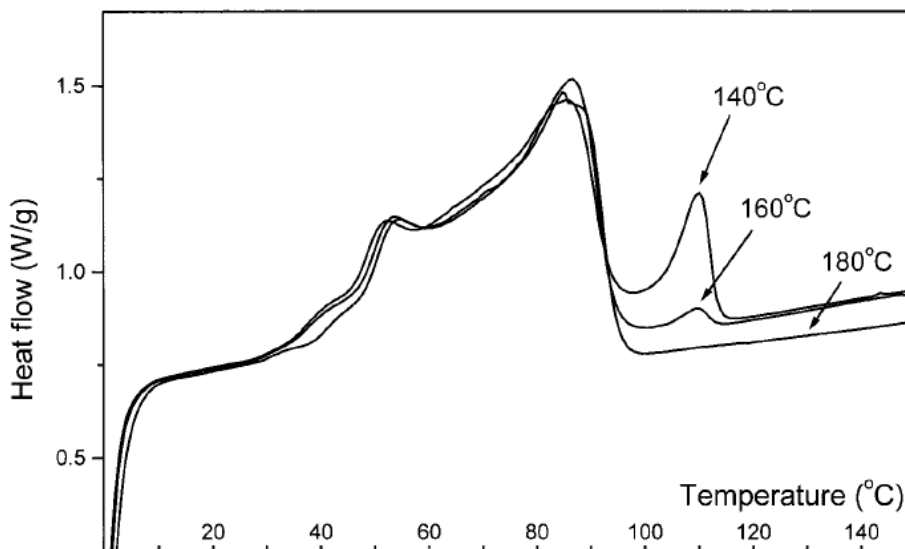


Figure 1.10 DSC curves of 25/75 (w/w) LDPE/EVA blends (Takidis *et al.*, 2003)

Khonakdar *et al.* (2007) investigated the compatibility of binary blends of low- and high-density PE, with EVA copolymer. The blends were prepared by melt-mixing in an internal mixer in different ratios of EVA content. The relationship between the EVA content and elongation at break (EB) of the LDPE/EVA and HDPE/EVA blends are presented in **Figures 1.11**. An increase in elongation at break was observed with the increasing EVA content for LDPE/EVA blends. However, increasing the EVA content resulted in a decrease in the elongation at the break for HDPE/EVA blends.

Khonakdar *et al.* (2007) used log-additive rule given in **Equation 1.2** to investigate the compatibility of blends, as well.

$$\log E = \sum \omega_i \log E_i \quad \text{Equation 1.2}$$

where E is one of the properties of the blend and ω_i represents the weight fraction of the *i*th component. Positive deviations from the log-additive rule show that the polymers are compatible. Therefore, LDPE/EVA system was much more compatible than HDPE/EVA system which showed a strong negative deviation from the mixing law (**Figure 1.11**). In addition, excellent compatibility is observed between LDPE and EVA in the region between 40–60 wt % of EVA.

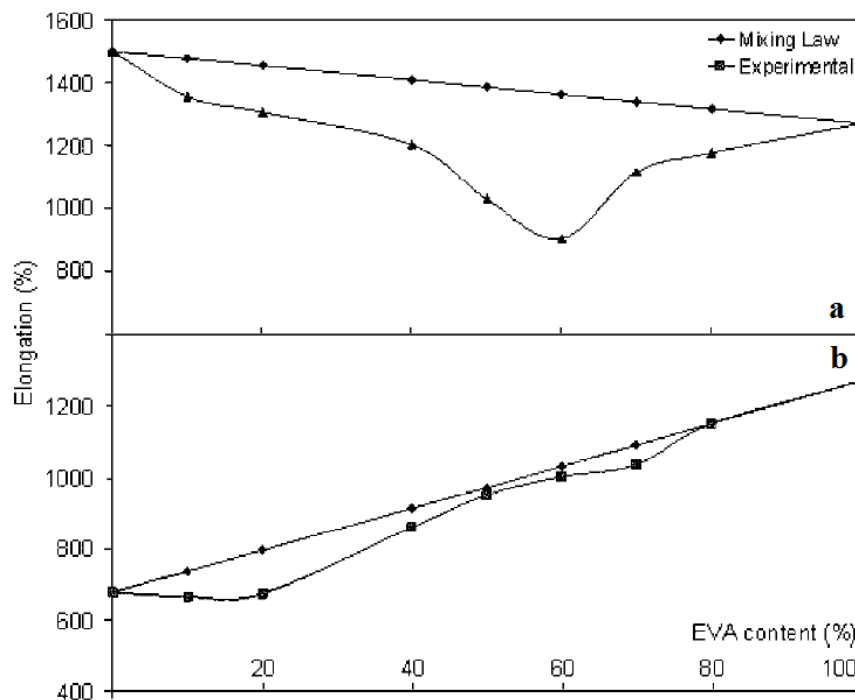


Figure 1.11 Effect of EVA % on EB of a. HDPE/EVA, b. LDPE/EVA (Khonakdar *et al.*, 2007)

1.7 Measurement of Flammability Properties

Flame retardancy of polymers is primarily characterized by their ignitability, flame–spread rate and heat release rate during combustion. It can be measured by a series of tests that material is flammable or not depending on the targeted application area (Laoutid *et al.*, 2009). There are several small, medium, and, large–scale flammability tests used in research and development and quality control laboratories. Most frequently used flammability testing methods are considered in the following section.

1.7.1 Limiting oxygen index (LOI) test

Limiting Oxygen Index test measures the minimum oxygen concentration in a flowing mixture of oxygen and nitrogen gas to support candle–like combustion of plastics. This test was standardized in France (NF T 51–071) and in United States (ASTM D 2863). The LOI test is now internationally standardized (ISO 4589). The LOI test method can be applied to solid, laminated or cellular materials however their apparent density should be greater than 15 kg/m³.

The mathematical expression of LOI value is given in **Equation 1.3** (Laoutid *et al.*, 2009);

$$\text{LOI} = 100 \times \frac{[\text{O}_2]}{[\text{O}_2] + [\text{N}_2]} \quad \text{Equation 1.3}$$

A limiting oxygen index value less than 21 means material is “*combustible*”. In cases where materials having LOI values greater than 21 are classified as “*self-extinguishing*” since the air contains 21% oxygen, the combustion does not take place without any external heat source. Flash–ignition temperatures, self–ignition temperatures and LOI values of some polymers are listed in **Table 1.2**.

Table 1.2 Ignition temperatures and LOI values of some polymers*

Polymer	Flash-ignition temperature (°C)	Self-ignition temperature (°C)	LOI (%)
<i>Polyethylene</i>	340	350	18
<i>Polypropylene</i>	320	350	18
<i>Polystyrene</i>	350	490	28
<i>Poly(vinyl chloride)</i>	390	450	42
<i>Poly(tetrafluoroethylene)</i>	560	580	95

*Laoutid *et al.*, 2009

This test method (**ASTM–D2863**) can be used to measure flammability properties of materials or products under controlled laboratory conditions. The results of LOI test do not determine the fire risk of the material under actual fire conditions.

The test set up (**Figure 1.12**) consists of a glass chimney where the gas mixture flows through, a specimen holder that holds the specimen vertically in the center of the chimney, a flame igniter and gas flow rate measurement devices. Dimensions of the specimen and properties of the components of the system are defined comprehensively in **ASTM–D2863**.

The test specimen should be 80–150 mm in length and 10±5 mm in width. The thickness of the specimen should be 4 mm with 0.25 mm tolerance for molding materials. Upper limit for burning period is 180 seconds after ignition.

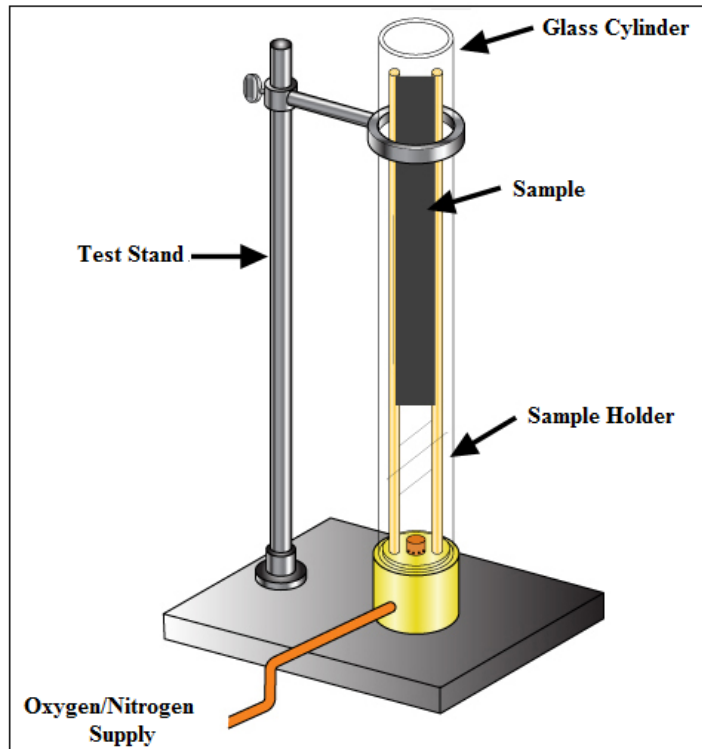


Figure 1.12 Experimental set-up for Limiting Oxygen Index Test (<http://www.wendellhull.com>)

LOI values are highly dependent on the filler content, increase with increasing flame retardant content. Filler particle size affects the LOI value directly, as well. Lim *et al.* (2009), studied the flame retardant effect of various $\text{Mg}(\text{OH})_2$ types (synthetic and natural) and revealed the particle size dependence of flammability. Their results indicated that samples prepared with smaller particle sized samples exhibited higher LOI values. LOI value was found as 28.6 when a commercial $\text{Mg}(\text{OH})_2$ sample with 20 μm average particle size was used in LDPE/EVA blends. However, with the addition of 4 μm average particle sized samples to the blends, LOI value increased to 30.9.

Synergistic effects of ZnB on LOI value of the polymer have been under investigation, recently. Ramazani *et al.* (2008), examine the synergism between ATH and ZnB in a commercial polymer matrix which is a copolymer of polypropylene and polyethylene. They accomplished the improvement of fire retardancy of the copolymer by the addition of ZnB and therefore obtained higher LOI values.

1.7.2 Cone calorimeter test

Heat release rate (HRR) is one of the most important parameters which describes the behavior of real fire conditions. The measurement of HRR makes engineers and researchers analyze flammability of material quantitatively (Morgan and Bundy, 2007). Concordantly, a cone calorimeter test device measures heat release rate, smoke production rate, carbon monoxide production and time to ignition. This test is often performed for classifying the fire behavior of cables and wires and defines the size and the characteristics of the fire. It is standardized in the United States (ASTM E 1354).

Consumed oxygen amount in the combustion process is used to determine the heat released during cone calorimeter test. The relationship between amount of oxygen consumed and released heat is that per 1 kg of oxygen consumed, approximately 13.1×10^3 kJ of heat are released (ASTM E 1354–04a). Huggett (1980), showed this proportionality between released heat and oxygen consumption for various polymers as shown in **Figure 1.13** (Lindholm *et al.*, 2008).

The cone calorimeter test (ASTM E1354–04a) set up consists of a conical radiant electric heater, specimen holders, an electric ignition spark plug, a load cell for measuring specimen mass loss, exhaust gas system with oxygen monitoring and flow measuring instrumentation and a data collection and analysis system as shown in **Figure 1.14**. Temperature and moisture of test specimens should be conditioned before the test is performed at an ambient temperature of 23 ± 3 °C and a relative humidity of 50 ± 5 %.

Elliot *et al.* (1998), investigated the fire behavior of four commercially available wires having different thicknesses and compositions with a scientific cone calorimeter. The tests were performed according to ASTM E1354 standards. Three of them were flame retarded with metal hydroxide based (halogen-free) systems, they only differ in thickness. The last sample had a chlorinated polyethylene (CPE) insulation with antimony trioxide based flame retardant system.

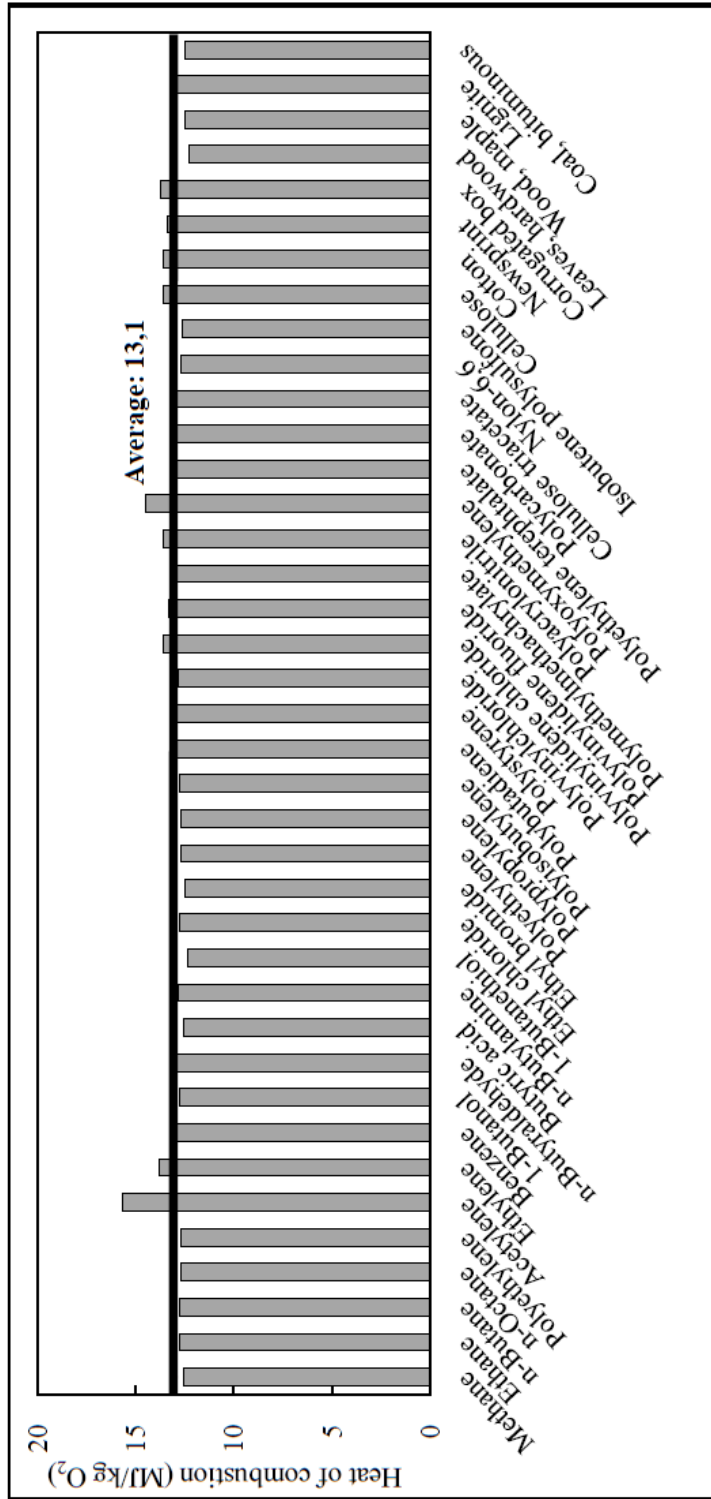


Figure 1.13 Heat of combustion for a range of different fuels (Lindholm et al., 2008)

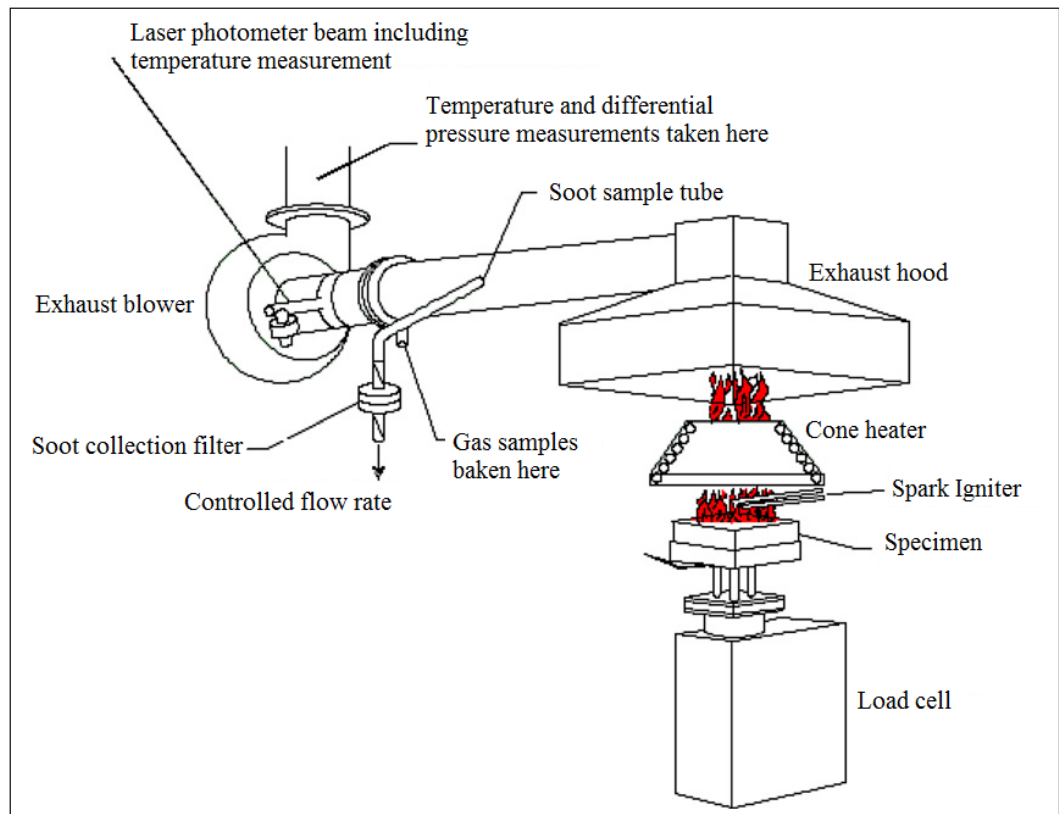


Figure 1.14 Experimental set-up of cone calorimeter test (Laoutid *et al.*, 2009)

According to the test results in **Table 1.3** (Elliot *et al.*, 1998), chlorine/antimony flame retarded wire was found more smoky and toxic than the halogen-free wires under fire conditions. It is observed that there is a linear correlation between the wall thickness of insulation and smoke, heat release and CO values, as well. The harmful products of fire are expected to be great for thicker wires since there is more flammable material available to burn.

Table 1.3 Cone calorimeter data of various thicknesses for chlorine/antimony flame retarded wire*

	HFFR wire (thin wall)	HFFR wire (med. wall)	HFFR wire (thick wall)	CPE/Sb FR (med. wall)
<i>Peak heat release rate/kW</i>	1.66	2.24	3.28	2.06
<i>Total heat release/kJ</i>	99	289	653	261
<i>Peak CO concentration/ppm</i>	21	84	138	991
<i>Peak smoke production rate/cm²s⁻¹</i>	256	537	795	1510

* Elliot *et al.*, 1998

1.8 Present Study

Nowadays, there has been a growing demand on halogen-free cables in Turkey, as well as in the world. On the other hand, it is known that there is no plant producing halogen-free flame retardant cable material in Turkey and national cable industry produces HFFR cables by using ready-to-use formulations. In the present study, HFFR cable formulations have been investigated to offer an occasion to develop own compositions to the Turkish cable producers.

Formulation of the HFFR having composites were determined to find out the convenient type of LDPE and amount of EVA and LDPE. The type of EVA copolymer, amount and type of fire retardant filler, and, coupling agent were kept constant. The composites were prepared with two types of LDPE, one of them has low MFI and other has high MFI. For each series, low (L-series) and high (H-series), 4 composites were prepared which differ in EVA content (26–65 %mass). Three commercial formulations were studied, as well.

Thermal behavior of samples was examined by DSC and TGA methods. In addition, mechanical and rheological properties of composites were investigated by tensile tests and a rheometer with parallel plates geometry, respectively. Finally, their flame retardancy was determined by LOI tests.

2.0 MATERIAL and METHODS

2.1 Description of Materials

i. Polymers

The polymers used in the present study were LDPE and EVA which were kindly supplied by PETKİM and DuPont, respectively. Their grades and properties are given in **Table 2.1**.

Table 2.1 Grades and typical properties of polymers used in the present study

Grades	EVA		LDPE	
	ELVAX [®] 260	ELVAX [®] 40L-03	H2-21T [®]	I22-19T [®]
MFI (g/10 min)	6	3	2.1 - 2.9	17 – 29
Density (g/cm ³)	0.955	0.967	0.919	0.917
Vinyl Acetate content (%w)	28	40	-	-
Supplier	Dupont-Germany		PETKİM-Türkiye	

ii. Coupling agent, flame retardant additives and antioxidant

PEgMA; Coupling agent, polyethylene grafted with maleic anhydride (grade Fusabond[®] E226, highly grafted, MFI: 1.5 g/10 min, density: 0.93 g/cm³; kindly supplied from DuPont) has been used herein (**Figure 2.1**).

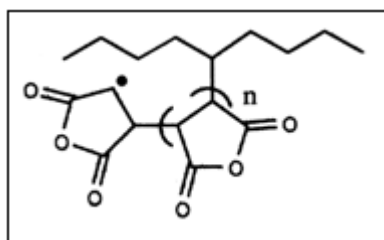


Figure 2.1 Polyethylene grafted with maleic anhydride

ATH and MH; fine precipitated, untreated aluminum tri hydrate (ATH, grade Apyral[®] 40CD; particle size = 1.3 μm) and stearic acid coated magnesium hydroxide (MH, grade Apymag[®] 60S, particle size 4 μm) were kindly supplied by Nabaltec-Germany. The chemical purities of ATH and MH are 99.5 and 92 %, respectively. The market share, cost and thermal properties of flame retardants were taken into consideration and ATH was chosen and used in composite formulations.

Antioxidant (A.O.) used in this study is a non-staining and nondiscoloring hindered thiophenol antioxidant mainly used for wire and cable applications. Its trade name is Lowinox TBP-6 and it is a product of Chemtura-US.

iii. Commercial HFFR resins

Three types of commercially used resin for producing halogen-free flame retarded cables in electrics and electronics industry were collected and characterized during this study. They were coded as Com-H, Com-K and Com-L. No further purification or modification processes were applied.

2.2 Organization of Experiments

The organization of experiments performed in this study is presented in **Figure 2.2**. The composites were processed with given formulations in **Table 2.2** using internal mixer in the line with the demands from the cable industry and then compression molded to 2 mm thick sheets to examine thermal, mechanical and rheological properties and 4 mm thick sheets to test fire properties.

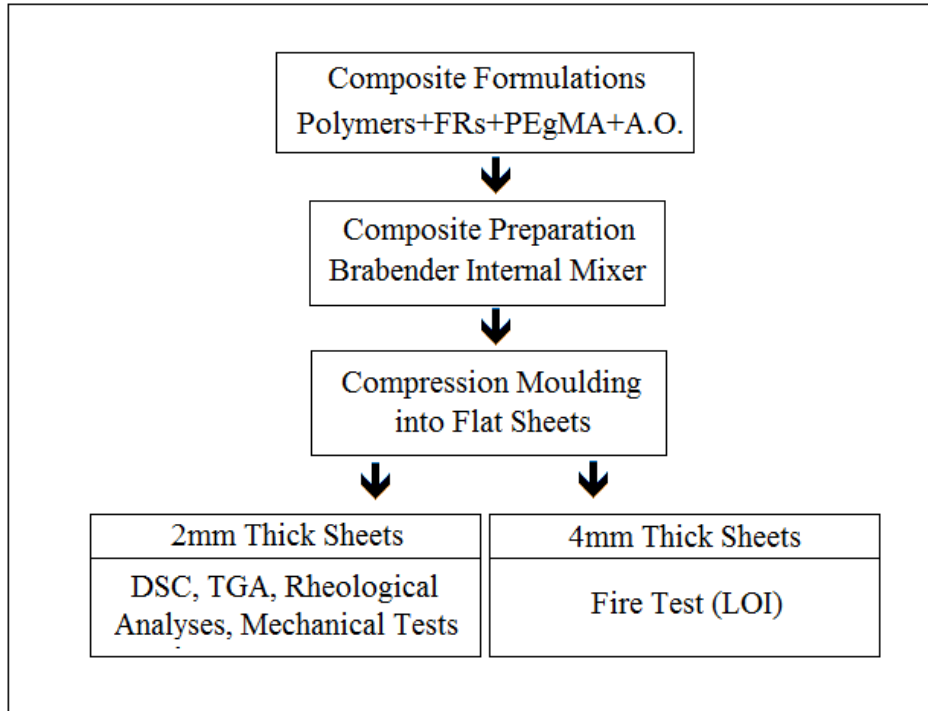


Figure 2.2 Organization schema of the experiments

Table 2.2 Composite formulations

Sample Code	<i>EVA-28</i> (%, in the polymer matrix)	<i>EVA-28</i> (%, in the composite)	<i>LDPE</i> (H2-21T)	<i>LDPE</i> (I22-19T)	<i>ATH</i>	<i>PEgMA</i>
<i>L13/25</i>	65	25	13	–	60	2
<i>L18/20</i>	52	20	18	–	60	2
<i>L23/15</i>	39	15	23	–	60	2
<i>L28/10</i>	26	10	28	–	60	2
<i>H13/25</i>	65	25	–	13	60	2
<i>H18/20</i>	52	20	–	18	60	2
<i>H23/15</i>	39	15	–	23	60	2
<i>H28/10</i>	26	10	–	28	60	2

2.3 Sample Preparation

Composite preparation was done by using a Brabender measuring mixer W30 EHT. The mixer was operated at 200 °C for 10 min with a mixing speed of 25 min⁻¹. First, the polymers and compatibilizer, PEgMA were fed and mixed during 2 minutes. Then, flame retardant additive, ATH and antioxidant were added and allowed to mix for the remaining 8 minutes (**Figure 2.3**).



Figure 2.3 Composite production in the mixer. **A:** Overall set-up of computer controlled mixer, **B:** A closer view of mixing chamber, **C:** demounted state of the mixer; pushing part (1) feeding hopper (2) and outer cover (3), **D:** Mixer in open position, **E:** Mixing blades and produced pieces of composite, **F:** Compression molded composite samples.

Samples were compression molded to flat sheets, using Shinto SFA-37 Automatic Molding Press, at a temperature of 190 °C for 6 min for pre-heating and at the same temperature for 3 min under 40 kg/cm² pressure in 2 and 4 mm thicknesses for mechanical tests and fire tests, respectively.

- The dog-bone test specimens used in tensile tests were prepared with an automatic hollow die punch, a product of CEAST, in accordance with related ASTM and ISO standards.
- LOI tests samples were prepared by cutting 4 mm thick plates in 1 cm wide specimens according to related ASTM standards. The plates were kept 5 minutes in 70 °C oven before cutting to soften the plates and facilitate the cutting process.

2.4 Analyses Performed

A series of experiments were performed during this study. Resin amounts are fixed totally to 40 gram. Amount of EVA is taken in between 10-25 gram while PEGMA, a LDPE resin based coupling agent, is kept constant as 2 gram and LDPE amount is chosen to complete the resin amount to 40 gram. The amount of ATH was kept constant as 60 grams to complete the amount to 100 gram. In addition, 200 ppm antioxidant was added to each sample to prevent the oxidation. In this part of the experimental study, it was desired to determine the convenient type of LDPE (H2-21T or I22-19T) and amount of EVA as given in **Table 2.3**, with a detailed description of sample compositions. The percentage of EVA copolymer in polymer fraction in composite varies between 26 and 65%.

Before performing the tests of mechanical, thermal and fire properties, samples were conditioned at 23 °C and 50% relative humidity for 3–5 days.

DSC tests were performed with Shimadzu DSC-50 (Japan) at 10 °C/min from 23 to 500 °C, encapsulated in aluminum pans. The amounts of the samples were around 10 mg. Nitrogen atmosphere with a flow rate of 30 ml/min was used.

Table 2.3 Formulation of the samples in terms of the mass% of EVA in LDPE

EVA/LDPE(w/w)	25/13	20/18	15/23	10/28
% EVA	65	52	39	26

Mettler Toledo TGA/SDTA-851 thermal analyzer was employed to evaluate the thermogravimetric behavior of neat polymers, fillers, commercial HFFR resins and synthesized composites. Samples of 10 mg were heated at 20 °C/min from 23°C to 1000 °C in nitrogen flow.

Particle sizes of flame retardant fillers were measured by a Micromeritics, 2280 particle size analyzer.

Tensile properties were determined by using an Instron 4411 universal testing machine with a cross head speed of 50 mm/min.

Rheological measurements were carried out on circular samples of 25 mm diameter and 1000 µm thickness by using a TA Instrument AR2000 rheometer with parallel plates geometry at 230 °C using 1% strain for Com-H and Com-L and 3% strain for Com-K samples.

Fire properties of composite samples were characterized mainly by their LOI corresponds to the minimum oxygen percentage required for the combustion of specimens measuring 75×10×4 mm in an oxygen nitrogen atmosphere in accordance with ASTM D2863 standard.

The system used for coding the prepared composites consists of 5 digits, totally. The letter L or H indicate type of LDPE used, L is used for low melt flow-PE and H is used for high melt flow-PE. The following segment including four digits separated by a slash refers the LDPE and EVA copolymer percentage in the composite, respectively. In the sample coded as “L13/25”, 13 % of PE-L and 25 % of EVA were used. The contents of ATH and PEgMA are 60 and 2% mass, respectively and constant for all composites.

3.0 RESULTS and DISCUSSION

The influence of LDPE/EVA ratio and flame retardant filler; ATH on flammability of polymeric composites and the effect of MFI of LDPE on various properties of composites have been investigated by means of calorimetric, thermal gravimetric, rheometric, mechanical analyses and fire tests.

First the components; polymers and FR, then prepared composites and finally commercial samples were characterized in the following sections.

3.1 Characterization Studies on Raw Materials, Composites and Commercial Samples

Neat polymers; LDPE and EVA, and flame retardant used; ATH, were tried to characterize calorimetrically and thermal gravimetrically.

3.1.1 Characterization of components

In this part, DSC and TGA analyses performed on LDPE, EVA copolymer and flame retardants; ATH and MH, were given. EVA-40 which is a product of DuPont containing 40% of VA was analyzed thermally together with EVA copolymer in order to discuss the effects of VA content on thermal properties. In addition, particle size distribution of ATH and MH was determined.

The temperatures corresponding to the melting points of LDPEs are approximately 106 °C for PE-H and 108 °C for PE-L. The heat required for melting (ΔH_m) of PE-L type LDPE is higher than that of PE-H type as seen from **Figure 3.1**. The area of the curves indicates that the degree of crystallinity is lower for PE-H which has higher melt flow index. Furthermore, the density of PE-L is higher than PE-H and higher densities usually mean higher stiffness and a higher glass transition temperature.

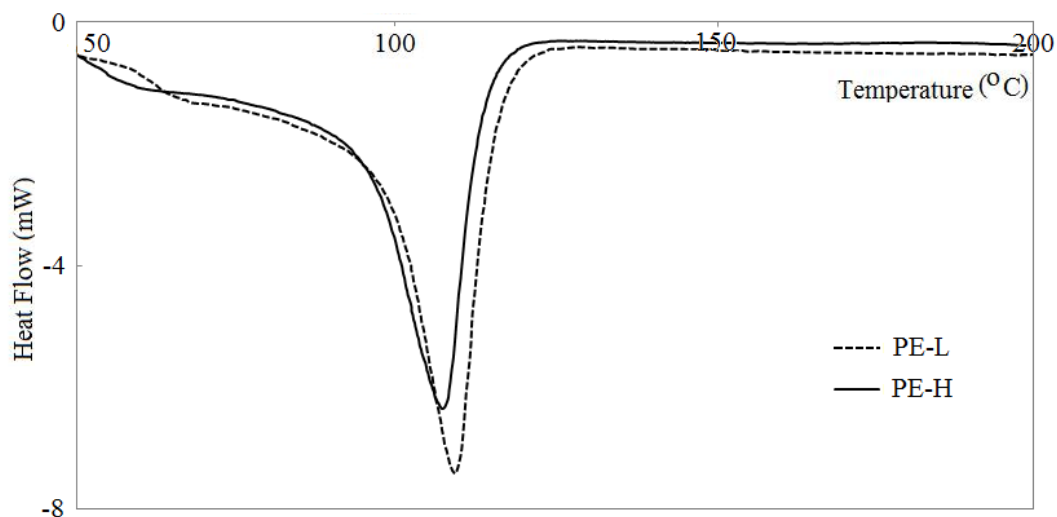


Figure 3.1 DSC curves of polyethylenes of types PE-L and PE-H

It can be seen from **Figure 3.2** that both LDPE types exhibit single step decomposition in nitrogen atmosphere over a relatively short temperature range (380–500°C). Hinsken *et al.* (1991), reported that the random scission is the main way of degradation of PE and polymer branching occurs, simultaneously resulting in a single mass loss step (Roy *et al.*, 2007).

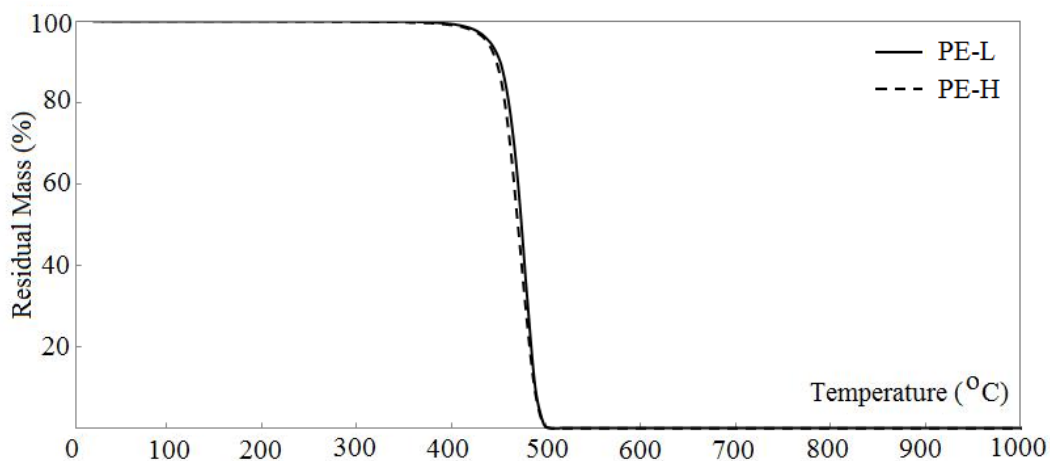


Figure 3.2 TGA curves of neat LDPE polymers, PE-L and PE-H

Figure 3.3 shows the results of DSC measurements of EVA and EVA-40 copolymers. The curves exhibit two and one endothermic peaks for EVA-28 and EVA-40, respectively. The area of these endothermic peaks corresponding to the crystalline phase presents in the copolymer increases with decreasing VA content. With increasing proportion of the polar comonomer VA, the products change from modified PE to rubber-like products. The degree of crystallinity decreases when VA content increases. In addition, determination of the melting temperature (T_m) is difficult for EVA copolymer containing high amount of VA content (i.e. EVA-40).

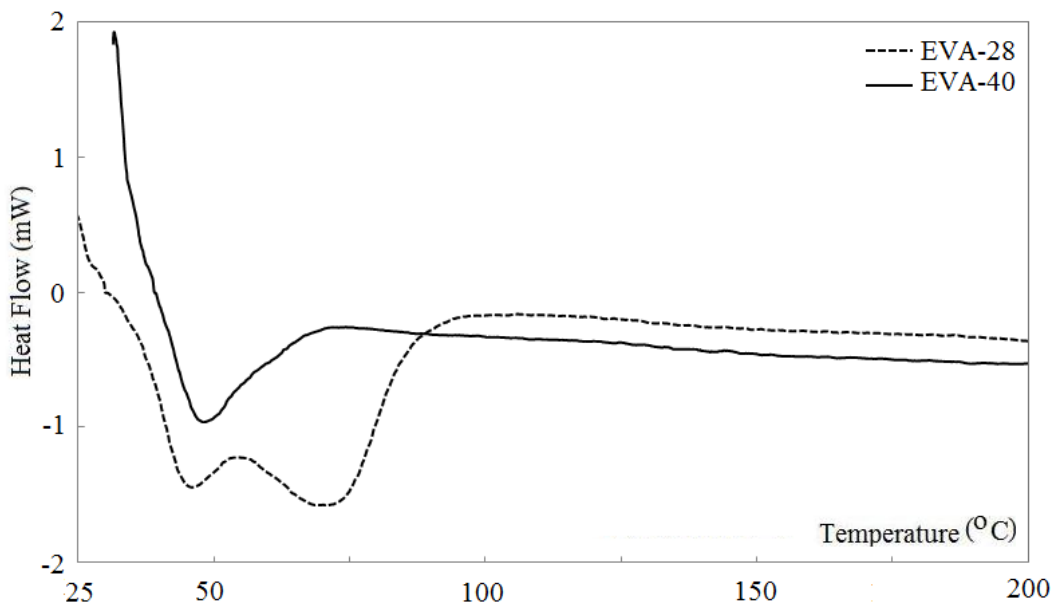


Figure 3.3 DSC curves of EVA-28 and EVA-40

Typical two step mass loss processes were observed in **Figure 3.4** for both EVA-28 and EVA-40. The first step completed at 395 °C for EVA-28 and at 383 °C for EVA-40, involves the loss of vinyl acetate fraction. As expected, while vinyl acetate content in EVA increases from 28 to 40 %, the mass loss within the interval of 290–399 °C (first step of degradation) increases from 20.1 to 28.3 %, respectively. The second step indicates the degradation of remaining main-chain.

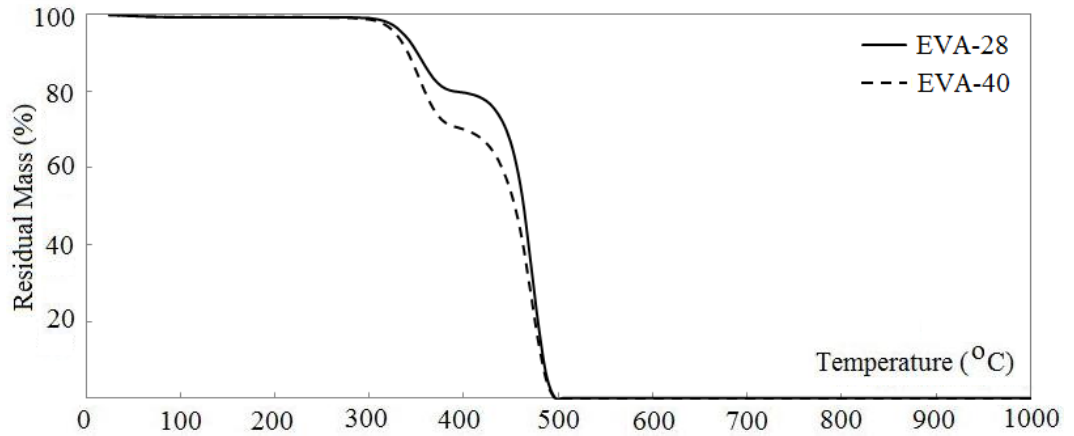


Figure 3.4 TGA curves of neat EVA copolymers, containing 28% and 40% VA (w%)

In **Figure 3.5**, calorimetric behavior of both PE-L and EVA-28 is presented. Compared to PE, EVA is more polar and less crystalline due to the acetate groups. The great difference between peak areas shows the difference in degree of crystallinity.

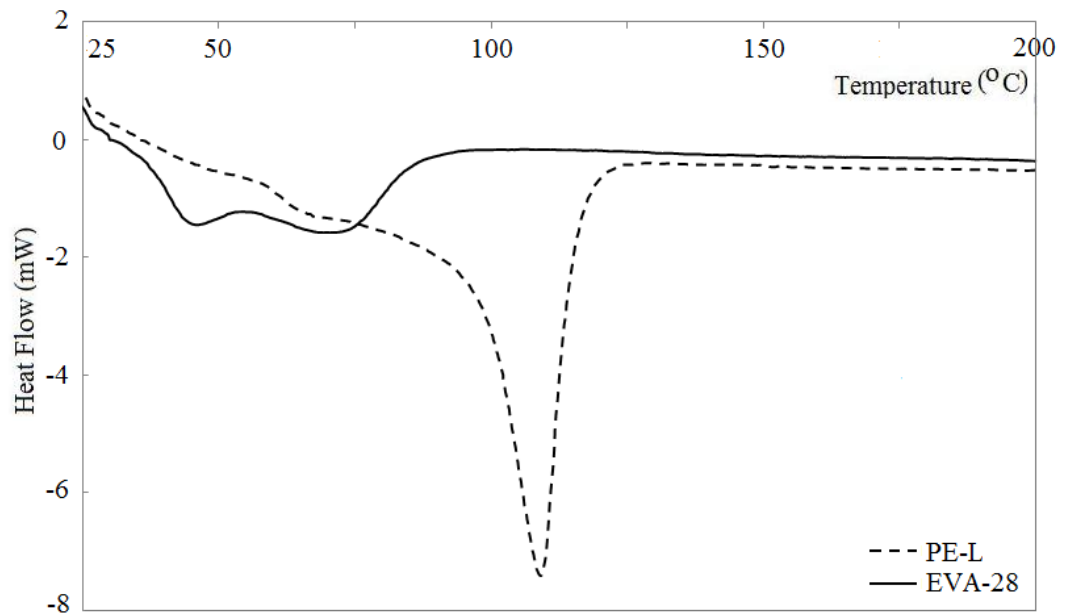


Figure 3.5 DSC curves of PE-L and EVA-28

In thermogravimetric studies on the major polymers; PE and EVA, presented in **Figure 3.2** and **Figure 3.4** that are used in HFFR composites decompose completely as a result of the heating up to 1000 °C under nitrogen environment.

Effectiveness of the flame retardancy depends on type of FR filler, the diameter of the flame retardant particles and their concentration. In non-halogenated cable applications, finer-sized particles of ATH is required. Many methods are available for producing such finer-sized ATH particles.

Csige *et al.* (1990) obtained 1.5–2 μm hydrate grades by grinding. However they noted that the method used for obtaining finer sized grades required high energy. Baksa *et al.* (1989) produced 0.5 μm of ATH particles by decomposing gallium–aluminum alloy with NaOH and/or H_2O .

ATH used in this study is a commercial grade and its particle size is reported as 1.3 μm in the product sheet. However, the particle size of ATH was found as 5–50 μm (**Figure 3.6**) and the mean particle size was calculated as 19.4 μm . Particle size of MH which is reported as 4 μm , was measured in the same range as seen in **Figure 3.6**. It is obviously seen that there is a great difference between reported and experimental values although conditioning process, dehumidification, was applied before particle size analysis. The possible reason of this difference is the agglomeration of the particles or charging of the particles statically during transportation, as well as the difference in the measurement method.

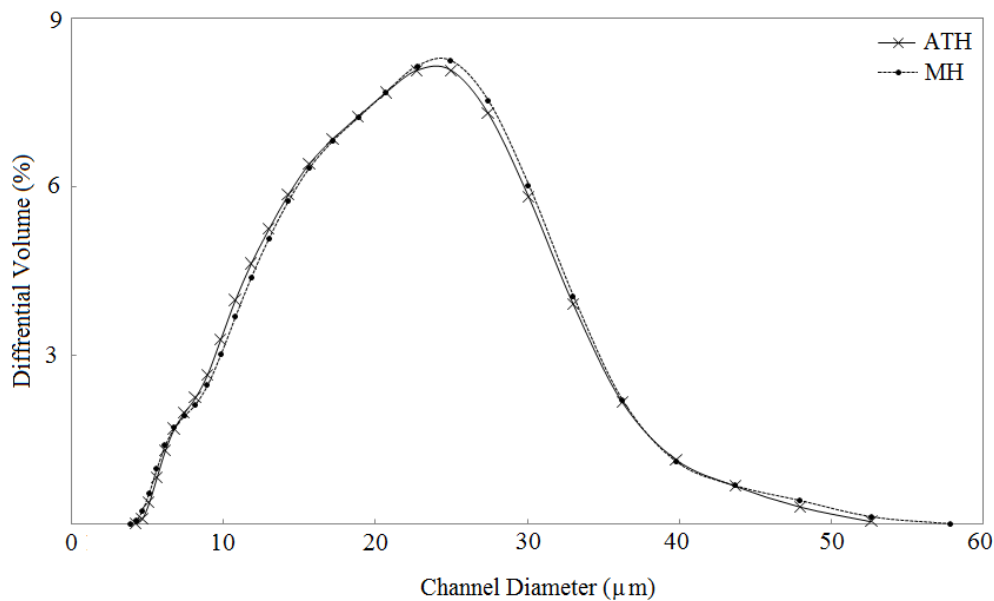


Figure 3.6 Particle size distribution curve of ATH and MH

Flame retardant effect of metal hydroxides arises when they begin to decompose endothermically. Decomposition reactions of ATH and MH (**Reactions 1.1 and 1.2**), absorb 1050 and 1300 kJ/kg energy, respectively. As a result of heat consumption, temperature of the reaction medium is reduced below the polymer combustion temperature. DSC results show that onset temperatures of decomposition are observed as 215 and 280 °C for ATH and MH, respectively (**Figure 3.7**). Laoutid *et al.* (2009), called such an endothermic reaction as “heat sink”. Since MH is a low purity product (~90%), it shows a two-step thermal decomposition while decomposition of ATH occurs in one step. The smaller peak observed in DSC curve of MH just before main decomposition peak may be due to these impurities.

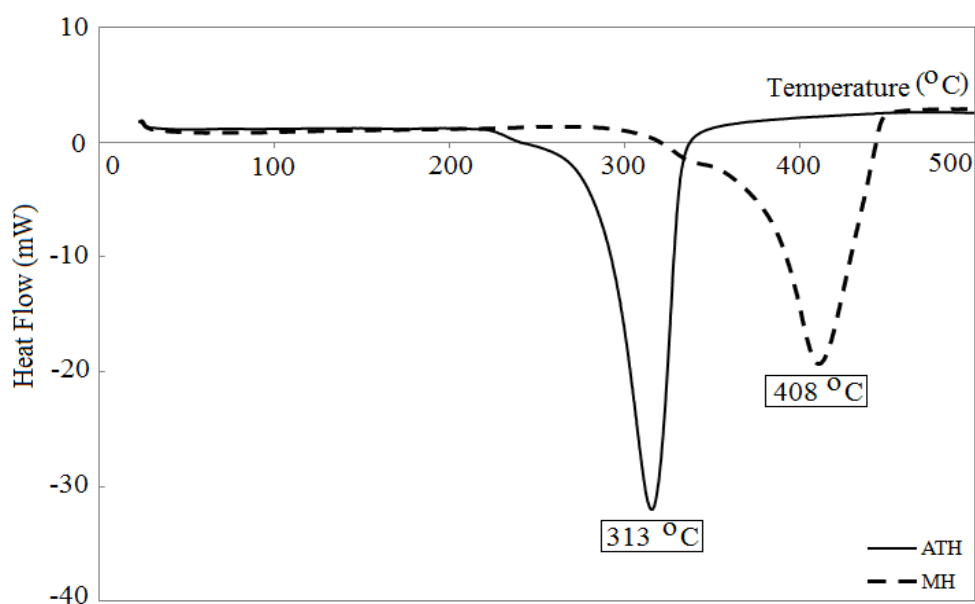


Figure 3.7 DSC curves of ATH and MH

As the released amount of water was calculated, it was found that ATH releases approximately 34% of its total mass as water vapor while MH releases 31%. In addition, onset temperature of degradation which corresponds to 5% mass loss, is lower for ATH than MH. This temperature is about 220 °C for ATH and about 320 °C for MH (**Figure 3.8**). It means that ATH acts as a flame retardant agent at lower temperatures due to its lower decomposition temperature than MH.

Liberated water amount was found to be higher than MH and a char layer forms at about 220 °C thus flame is retarded. As expected, aluminum trihydrate and magnesium hydroxide present a thermal degradation with only one-step, around 290 and 390 °C, respectively (**Figure 3.8**). The final solid residues corresponding to 65–70 % of the initial weight for both flame retardant additives were alumina (Al_2O_3) and magnesia (MgO).

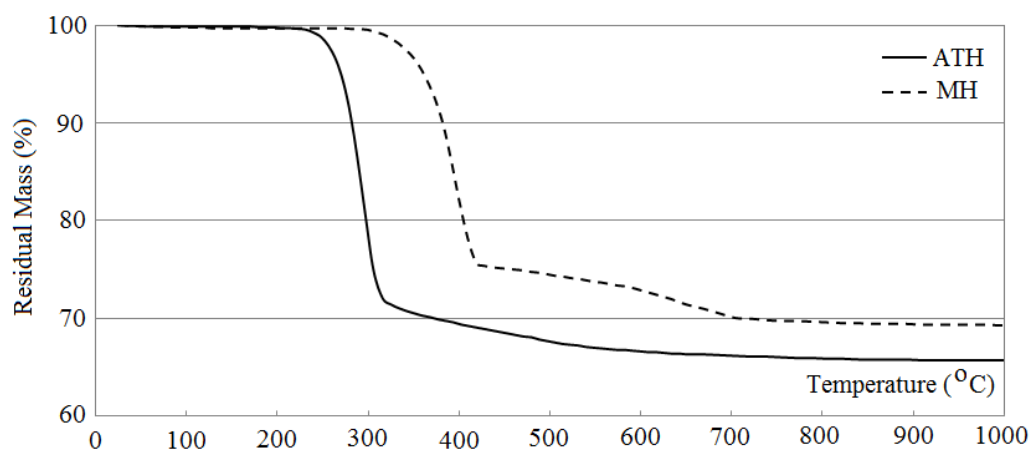


Figure 3.8 TGA curves of flame retardant minerals, ATH and MH

TGA results of polymers and flame retardants are listed in **Table 3.1**. It is seen that the polymers decomposes completely however, a great amount of FRs remains as final residue due to their inorganic structure.

Table 3.1 TGA results of LDPE, EVA, ATH and MH*

	T_1 (°C)	T_2 (°C)	M_1 (%)	M_2 (%)	R_f (%)
<i>PE-L</i>	474	–	100	0	0
<i>PE-H</i>	470	–	100	0	0
<i>EVA-28</i>	352	469	20.1	79.9	0
<i>EVA-40</i>	353	472	28.3	71.7	0
<i>ATH</i>	290	–	30.5	0	69.5
<i>MH</i>	388	–	25	0	75

* T_1 : temperature of the maximum degradation rate of step 1; T_2 : temperature of the maximum degradation rate of step 2; M_1 : mass loss in step 1; M_2 : mass loss in step 2; R_f : Final Residue

3.1.2 Characterization of composite formulations

In this part, the thermal properties of 8 different composites differing in the amount of EVA and type of LDPE; low- and high-melt flow, and are discussed. Differential scanning calorimeter curves of the composites which were prepared with PE-L and PE-H type LDPE are presented in **Figure 3.9** and **Figure 3.10**, respectively. The peaks corresponding to the melting of LDPE are around 105 °C, however thermal decomposition peaks of LDPE are observed at 475 °C. In addition, there is a large peak starts at 225 °C corresponding to the onset temperature of decomposition for ATH. At first sight, this peak seems substantially similar to the peak corresponding to the decomposition of ATH in **Figure 3.7**. However, the temperature corresponding to the onset of decomposition of ATH when used in the composite, increases from 219 to 225 °C. Onset temperature of degradation and peak temperatures for ATH are given in **Table 3.2**.

Table 3.2 Onset degradation temperature and peak temperatures for ATH*

	T_o (°C)	T_p (°C)
<i>Neat ATH</i>	219	315
<i>ATH in the composites</i>	225	324–330

* T_o : Onset degradation temperature, T_p : peak temperature

As it can be seen from both figures, **Figures 3.9 and 3.10** that the peaks referring to the melting of EVA disappeared in the composites prepared with both LDPE types. This means that high compatibility between polymers were obtained. Also, the melting peaks of LDPE, are both shifted by about 5–6 °C toward lower temperatures with respect to the peaks of the original LDPE polymers. In the literature, it has been reported that a plasticizing action of polymers to each other can be the reason of this shifting due to the interpenetration of some macromolecules of one component into the phase of the other during melt mixing (Takidis *et al.*, 2003).

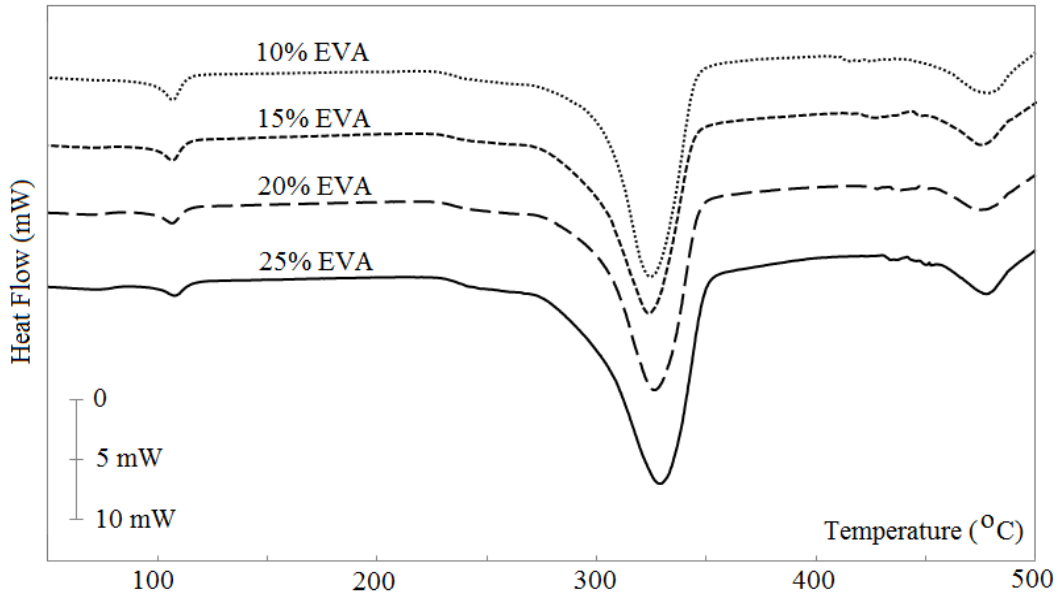


Figure 3.9 DSC curves of composites prepared with PE-L

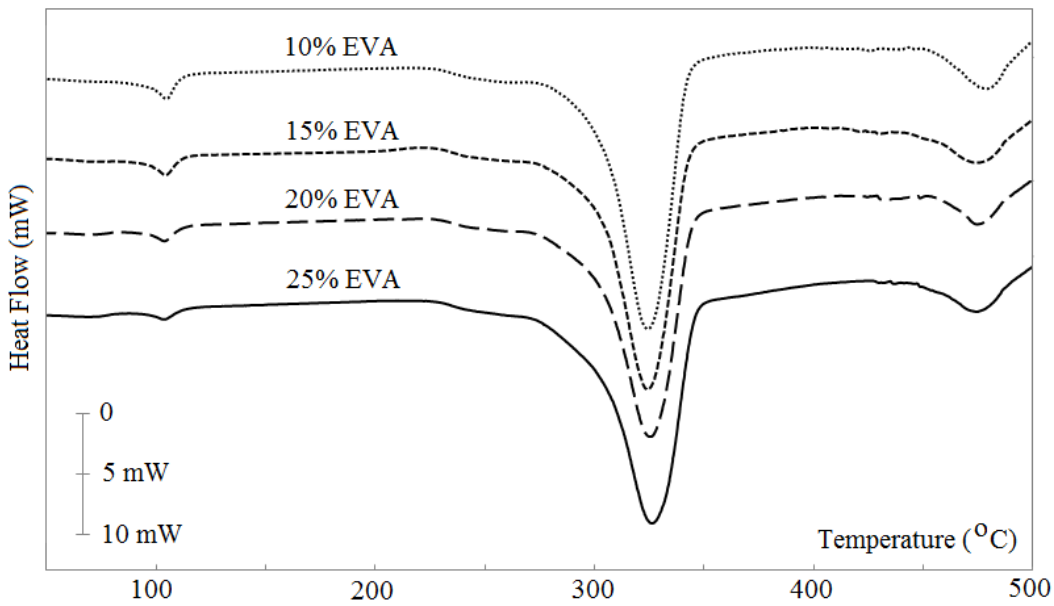


Figure 3.10 DSC curves of composites prepared with PE-H

In addition to the increase in melting peaks of LDPE when it is used in composites, it was observed that the onset temperature of degradation for ATH is shifted by about 6–7 °C toward higher temperatures with respect to the peaks of the original ATH for both composite types (L and H series). Mostly, such a shift in temperature is not a desired situation for FR filled composites since the hydrate, for example ATH, shows its flame retardant property by releasing water and lowering the temperature of combustion medium when it decomposes endothermically. Even a five or six centigrade degree shift seems to be insignificant, the performance of flame retardant filler in the composite decreases.

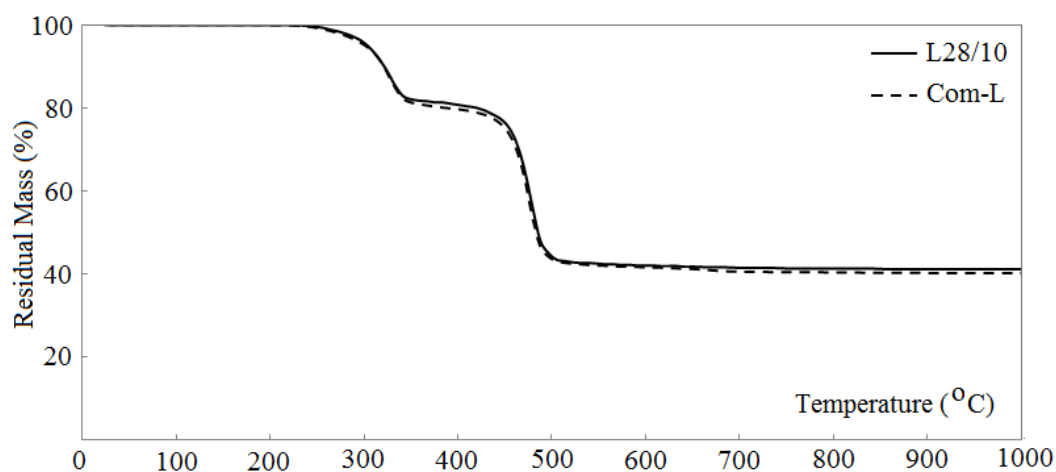
Thermal gravimetric analyzes results of prepared composite samples were given in **Table 3.3**. The temperatures corresponding to the maximum degradation rate of second step are very close to each other for nearly all of the samples. Although amounts of ATH added are the same as 60% by mass in all composites prepared and it was expected to form the same amount of alumina as a result of heating up to 1000 °C, the final residues; R_f , indicating the alumina formed, are different from each other ranging between 37.6 and 41.2% by mass as seen in **Table 3.3**. The possible reasons for that case may be the errors weighing the sub-gram amounts or inhomogeneity of formulations. Nevertheless, the mean value of final residue is around 40% confirming the composition intended despite the differences.

Table 3.3 TGA results of prepared composites*

	T_1 (°C)	T_2 (°C)	M_1 (%)	M_2 (%)	R_f (%)
L13/25	324	472	20	41.3	38.7
L18/20	327	475	19.5	41.2	39.3
L23/15	318	473	19.6	40.5	39.9
L28/10	321	475	18.9	39.9	41.2
H13/25	318	473	21	39.4	39.6
H18/20	323	473	19.6	39.8	40.5
H23/15	319	473	20.2	41.7	38.1
H28/10	318	473	19.9	42.5	37.6

* T_1 : temperature of the maximum degradation rate of step 1; T_2 : temperature of the maximum degradation rate of step 2; M_1 : mass loss in step 1; M_2 : mass loss in step 2; R_f : Final Residue

L28/10 and Com-L were considered to compare, thermogravimetrically (**Figure 3.11**). The TGA profiles of L28/10 and Com-L show a faster charring process between 230 and 340 °C and a higher thermal stability above 340 °C than LDPE and EVA. The decomposition temperatures of composites prepared with PE-L, are 3–5 °C higher than that of the composites prepared with PE-H nearly for all formulations (**Figure 3.12**).

**Figure 3.11** TGA curves of commercial resin (Com-L) and the prepared sample

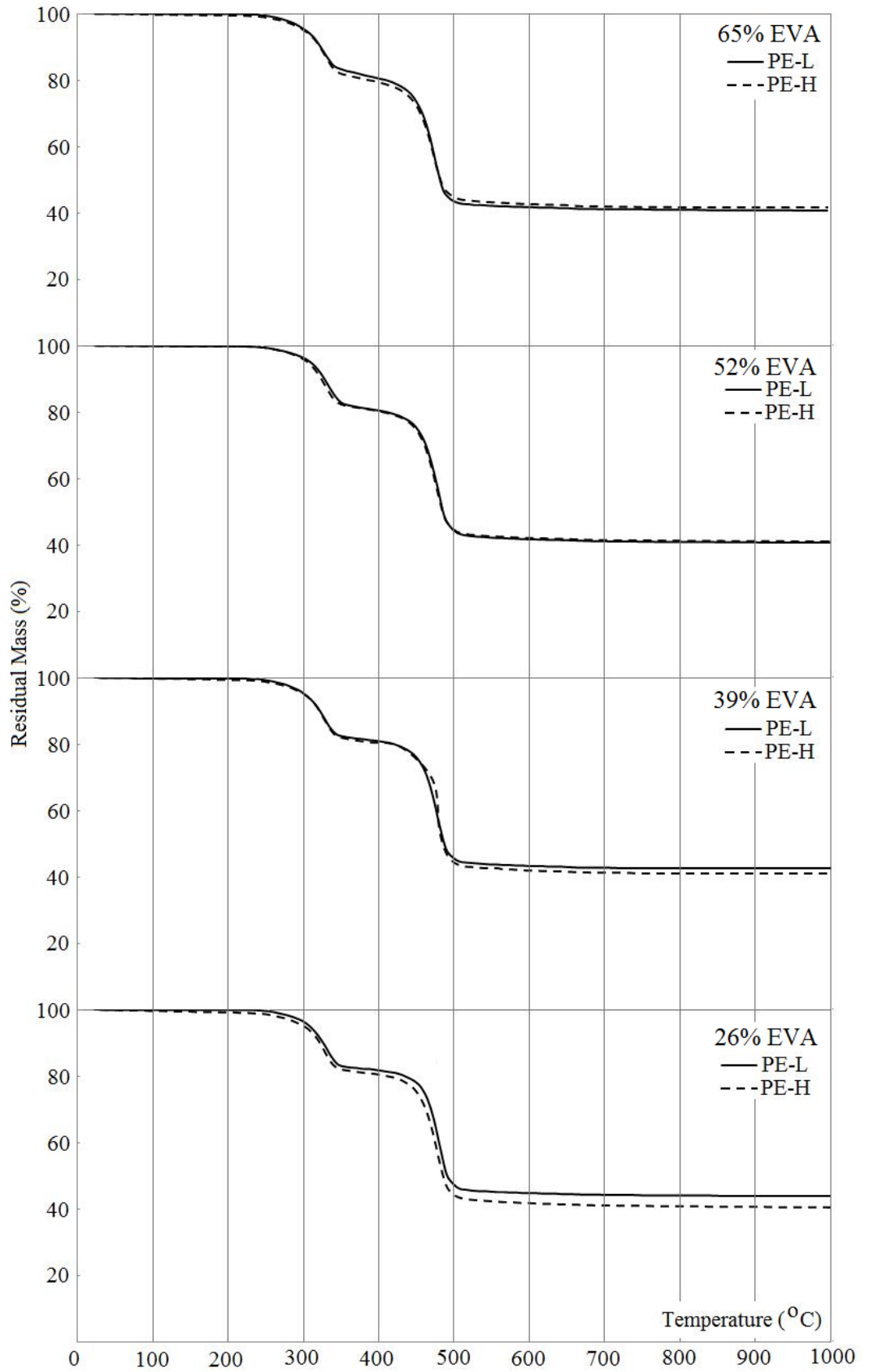


Figure 3.12 TGA results and comparison of prepared composites

3.1.3 Characterization of commercial samples

Figure 3.13 shows the DSC results obtained from the commercial resins, namely Com-H, Com-K and Com-L. Samples exhibit very similar thermal behavior having peaks around 100–120 °C and 325–330 °C and onset temperature of degradation was approximately 220 °C as neat ATH.

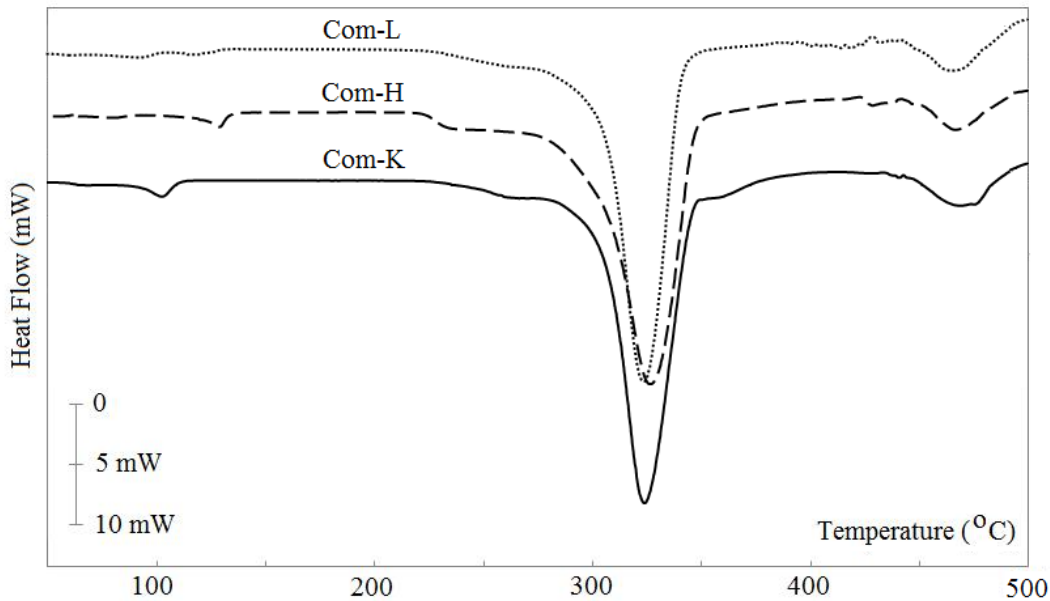


Figure 3.13 DSC curves of commercial HFFR resins

The peaks around 93 and 120 °C shows the LDPE content in the structure of the samples Com-K and Com-H, respectively (**Figure 3.13**). The difference between these peak temperatures is caused by the variety of the LDPE used in the commercial samples. The peak observed at about 108 °C for Com-L sample corresponding to the melting of LDPE is broader and less prominent than the other two. This means that there is a compatibility between LDPE and the other components used in the composite such as flame retardant fillers and other polymers for Com-L than other two commercial samples.

The thermal stabilities of commercial samples under inert environment were illustrated through thermogravimetric profiles in **Figure 3.14**. As seen, their degradation behavior is almost the same. The first step which starts at approximately 220 °C shows the degradation of ATH, while the second step presents the degradation of remaining fraction composed of polymers LDPE and EVA.

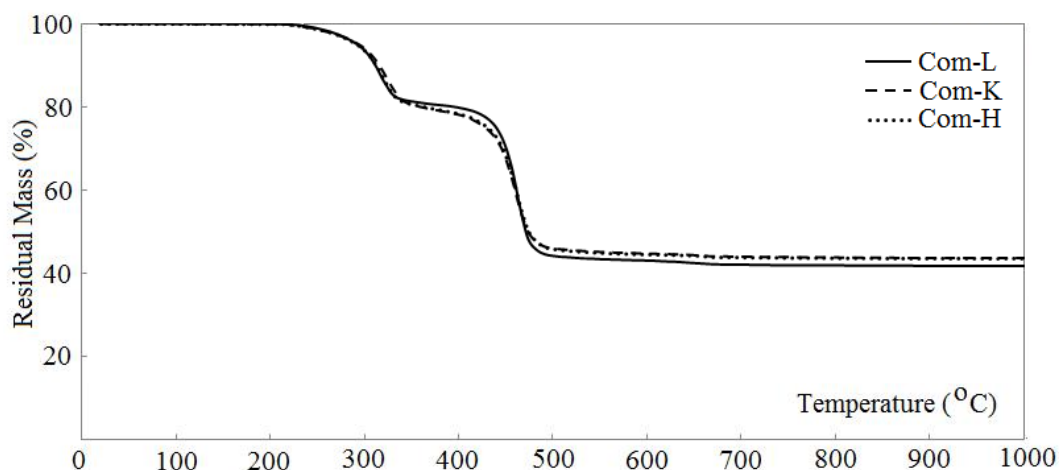


Figure 3.14 TGA curves of commercial cable formulations

TGA results of commercial samples are given in **Table 3.4**. T_1 and T_2 represent the temperature of the maximum degradation rate of step 1 and 2; respectively. Similarly, M_1 shows the mass loss in step 1 whereas M_2 refers the mass loss in step 2. Final residue is R_f .

Typical filling levels of mineral flame retardants vary between 55 and 65 wt% to obtain desired fire properties (Sauerwein, 2002). During the thermal decomposition of ATH, alumina (Al_2O_3) forms and remains as final residue under the same conditions (**Figure 3.8**). Furthermore, initial amount of ATH used in the commercial samples can be calculated and estimated by the help of decomposition reaction of ATH (**Reaction 1.1**) and amount of final residue (R_f in **Table 3.4**).

Table 3.4 TGA results of Commercial HFFR samples*

	T_1 (°C)	T_2 (°C)	M_1 (%)	M_2 (%)	R_f (%)
<i>Com-H</i>	324	473	21.1	36.7	42.2
<i>Com-K</i>	329	471	21.5	33.9	42.3
<i>Com-L</i>	321	474	19.9	39.8	40.3

* T_1 : temperature of the maximum degradation rate of step 1; T_2 : temperature of the maximum degradation rate of step 2; M_1 : mass loss in step 1; M_2 : mass loss in step 2; R_f : Final Residue

As an example, amount of ATH for the sample **Com-L** is calculated:

BASIS; total mass of composite initially : $m_T = 100$ g

- Molecular mass of ATH : $M_{ATH} = 78$ g/mole
- Molecular mass of alumina : $M_{alumina} = 102$ g/mole
- The amount of final residue (alumina) : $m_F = r_f \times m_T$

Since the residue is 40.3% by mass

$$m_F = 0.403 \times 100 = 40.3 \text{ g}$$

- Number of moles of final residue (alumina) : $n_f = 40.3/102 = 0.395$ mole

According to **Reaction 1.1**, 1 mole of alumina forms when 2 moles of ATH decompose, then;

- Number of moles of ATH initially : $n_{ATH} = 2 \times 0.395 = 0.79$ mole
- Initial amount of ATH: $n_{ATH} \times m_{ATH} = 0.79 \text{ mole} \times 78 \text{ g/mole} = 61.62$ g

The calculations above show that the composite material consists of approximately 61 percent of ATH, initially.

The mass of ATH in other commercial samples were calculated similarly. Com-H and Com-K were found to contain approximately 64 percent of aluminum tri hydrate.

3.2. Rheological Analyses Applied to the Composites

Rheology is not just about viscosity, but also about another important property, namely the elasticity. The storage modulus of a sample is a measure of its stiffness. The higher the modulus is, the stiffer the material is. It is presented in **Figure 3.15** clearly that PE-L is the stiffer than PE-H and EVA-28. The results of storage modulus as a function of angular frequency and viscosity as a function of shear rate obtained for neat LDPEs and EVA are shown in **Figure 3.15** and **Figure 3.16**, respectively.

LDPE and EVA show power-law type flow behavior (Faker *et al.*, 2008). The viscosity and elasticity of PE-L is higher than EVA in all frequency ranges and there is a remarkable difference in elasticity between two types of LDPEs at low frequencies. However, at higher frequencies, the storage modulus values approach to each other.

PE/EVA binary blends show an intermediate elastic behavior between PE and EVA. However, storage modulus curves of composites are not placed between PE and EVA. This is because, composite material become stiffer when high levels of inorganic filler; ATH, is incorporated to the polymer matrix.

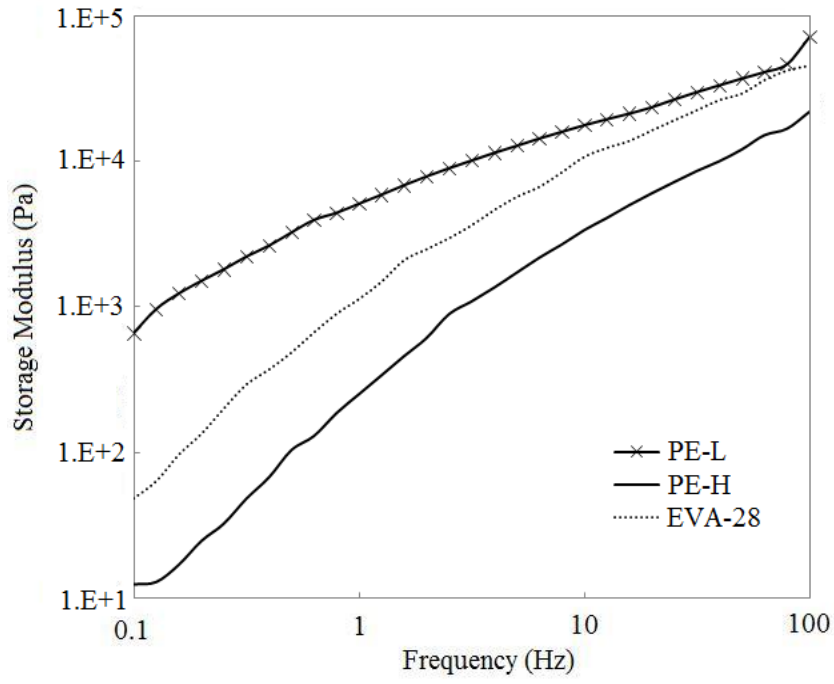


Figure 3.15 Storage modulus versus angular frequency for neat polymers

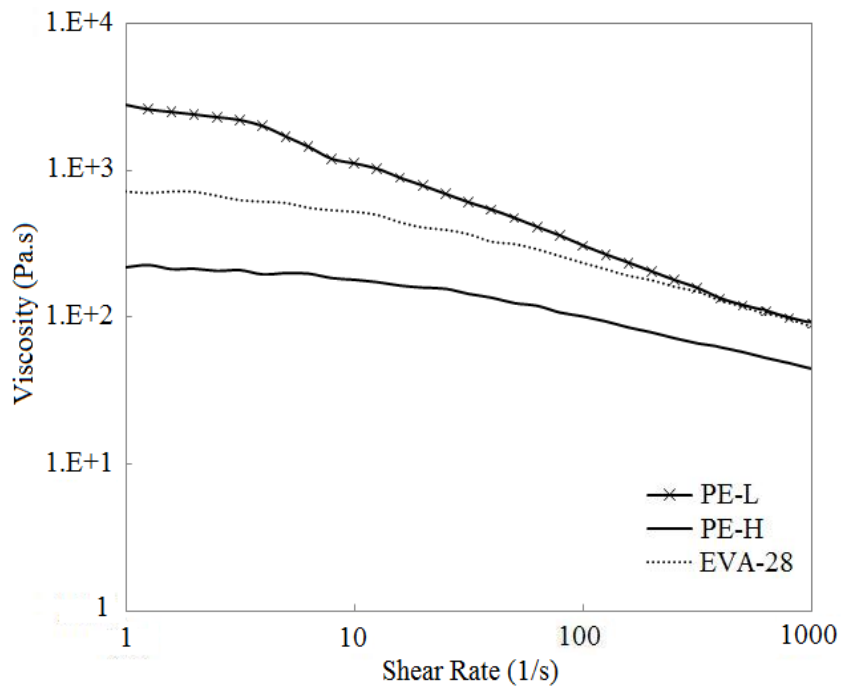


Figure 3.16 Viscosity versus shear rate for neat polymers

An increase in storage modulus was observed with the increase in EVA content for prepared composites (**Figures 3.17** and **3.18**). When 65% of EVA was used instead of using 26% in both types of composites, two times greater modulus of elasticity values were obtained for both series (H and L) of composites. In addition, it is seen that the composites containing 65% EVA approach to the commercially available one; Com-H, presented in the same figures.

In **Figures 3.17** and **3.18**, the results of storage modulus versus angular frequency for composites in different formulations prepared with both PE-L and PE-H types of LDPE are presented. As expected, the elasticity of composites increases with increasing EVA content for all frequency ranges. For H-series (composites prepared with PE-H type LDPE) the elasticity increases in a more regular manner when compared to elasticity of L series. The composites of both H- and L-series except *L13/25*, showed similar elastic behavior even if the values seem to be a little higher for L-series than H-series. It means that, an unexpected enhancement in storage modulus value was observed for the composite *L13/25* in comparison with other composites in the same series. On the other hand, an appreciable increase in elasticity could not be achieved with the increasing level of EVA content in the other composites of L-series.

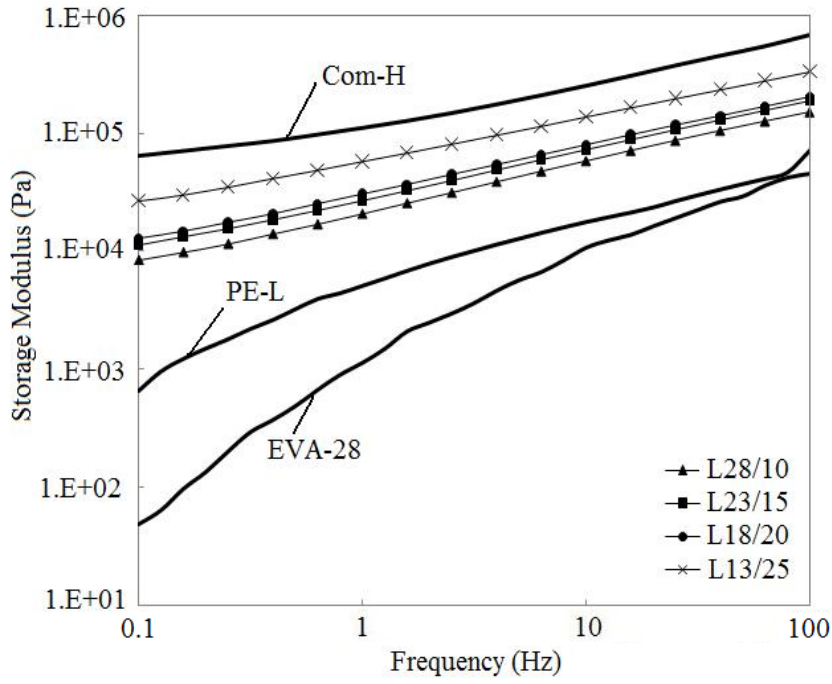


Figure 3.17 Storage modulus versus frequency for composite formulations prepared with PE-L

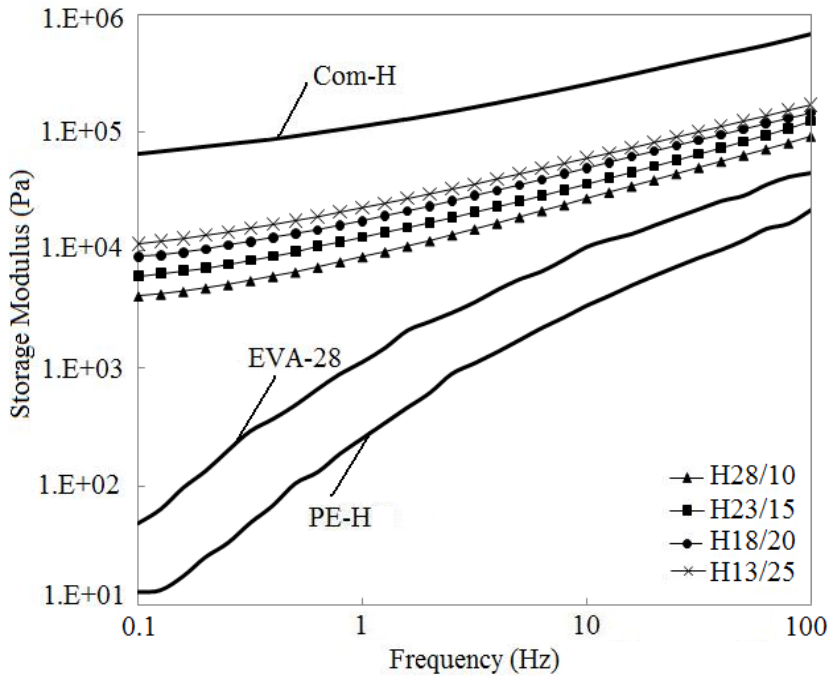


Figure 3.18 Storage modulus versus frequency for composite formulations prepared with PE-H

The viscosities of non-Newtonian fluids are affected by shear. Shear-thinning fluids are non-Newtonian, as their viscosities decrease as the applied shearing stress increases (<http://www.newton.dep.anl.gov>). The results of viscosity versus shear rate for different composite formulations are presented in **Figures 3.19** and **3.20**. As stated above, the results are indicating that the composite show similar behavior to that of neat polymers (**Figure 3.16**), all composite formulations behave as shear thinning materials.

Newtonian fluids show constant apparent viscosities against shear rate. Shear-thinning fluids show Newtonian behavior under extremely high or low shear rates. When the apparent viscosity is plotted against shear rate as in **Figures 3.19** and **3.20**, the Newtonian and non-Newtonian regions are seen, explicitly. The composites prepared with both PE-L and PE-H type, exhibit Newtonian behavior at very low shear rates. The viscosity of the composites decreases linearly with shear rates revealing power-law type behavior at high shear rates. Newtonian behavior is observed more clearly with the composites having low amounts of EVA about 26–39%.

The viscous behavior of composites is illustrated by the curves in **Figures 3.19** and **3.20**. These composites exhibit Newtonian behavior at very low shear rates, with shear thinning behavior at intermediate and higher shear rates. The structures of composites break down when the composite materials are sheared, resulting in a shear-dependent (shear thinning) behavior.

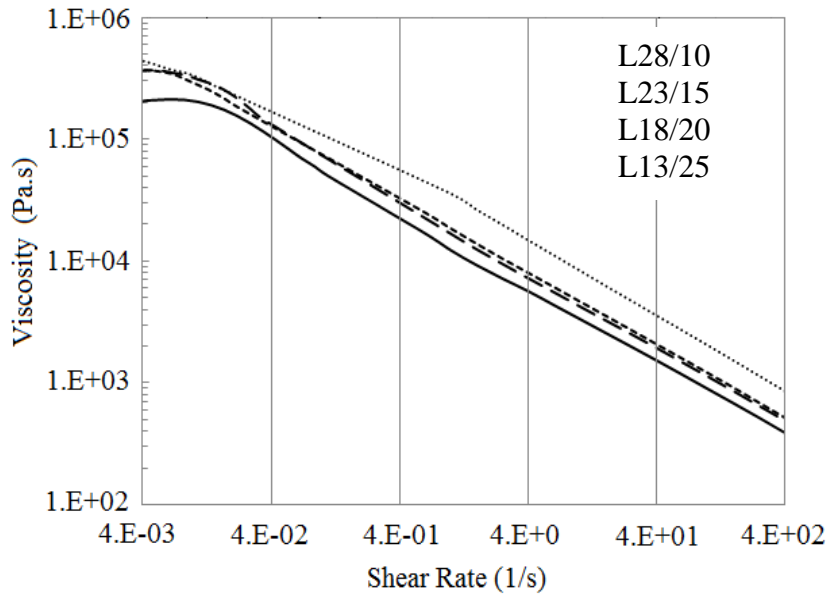


Figure 3.19 Viscosity versus shear rate of composite formulations prepared with PE-L at 230 °C

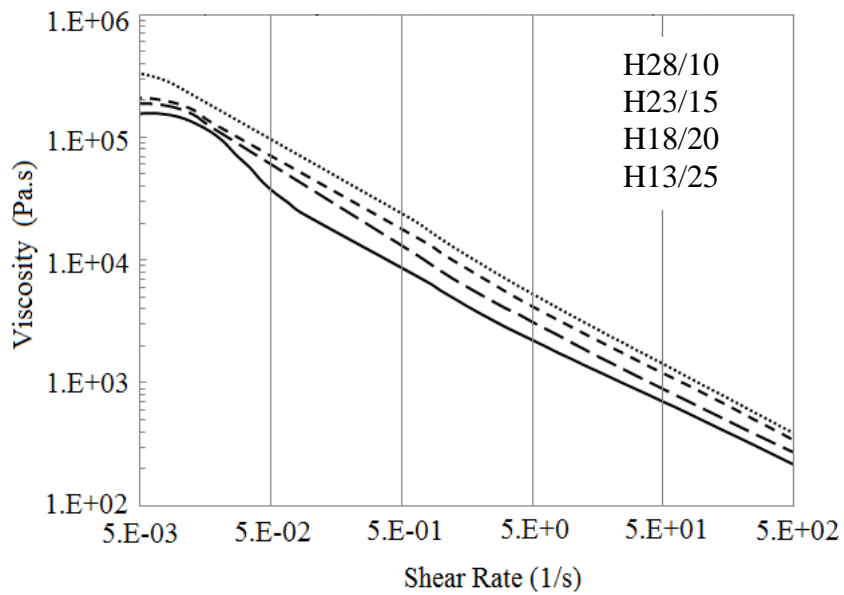


Figure 3.20 Viscosity versus shear rate of composite formulations prepared with PE-H at 230 °C

The Carreau model (**Equation 3.1**) is very useful for describing the viscosity of structural fluids:

$$\eta(\dot{\gamma}) = \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{[1 + (\lambda^2 \dot{\gamma}^2)]^p} \quad \text{Equation 3.1}$$

This model contains four rheological parameters and they are presented together with their units in **Table 3.5**. These parameters are; the low shear limiting viscosity (zero–rate viscosity, η_0), the high shear limiting viscosity (infinite–rate viscosity, η_{∞}), a time constant (consistency, λ) and the shear thinning index (p). This is a very general viscosity model and it can represent the viscosity function for a wide variety of materials.

Table 3.5 Carreau model constants calculated for composites

	η_0 (Pa.s)	η_{∞} (Pa.s)	λ (s)	p
<i>L28/10</i>	228000	78.59	89.22	0.6281
<i>L23/15</i>	412000	106.9	126.5	0.6446
<i>L18/20</i>	420100	23.26	164.1	0.6084
<i>L13/25</i>	418900	6.399E-4	63.38	0.6039
<i>H28/10</i>	510300	134.5	888.6	0.6493
<i>H23/15</i>	239100	133.1	171.2	0.6420
<i>H18/20</i>	246800	104.2	147.1	0.6142
<i>H13/25</i>	385400	102.2	181.1	0.6266

The viscosity of the composites was plotted at 1 s^{-1} shear rate as a function of EVA content (**Figure 3.21**). Similarly, the storage modulus of the composites was plotted at a frequency of 1Hz, as a function of EVA content (**Figure 3.22**). These two figures seem very similar to each other having higher values for L series samples than for H series. Increasing EVA content results in increasing viscosity and in storage modulus, due to the increasing stiffer component.

Composites with only one polymer were prepared to find out initial and final values however, these composites could not be successful in rheological measurements. Thereafter theoretical comparison using the mixing rule could not be possible.

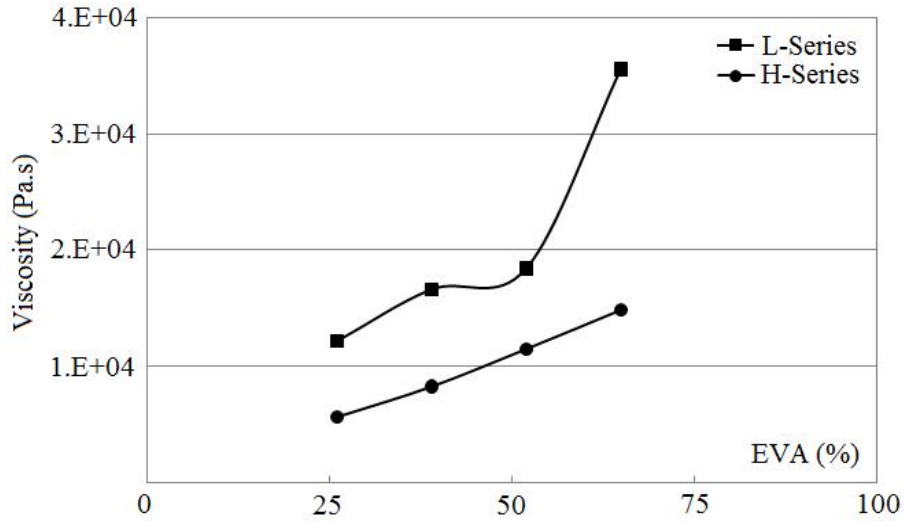


Figure 3.21 Viscosity versus EVA composition in the composites (shear rate = 1 s^{-1})

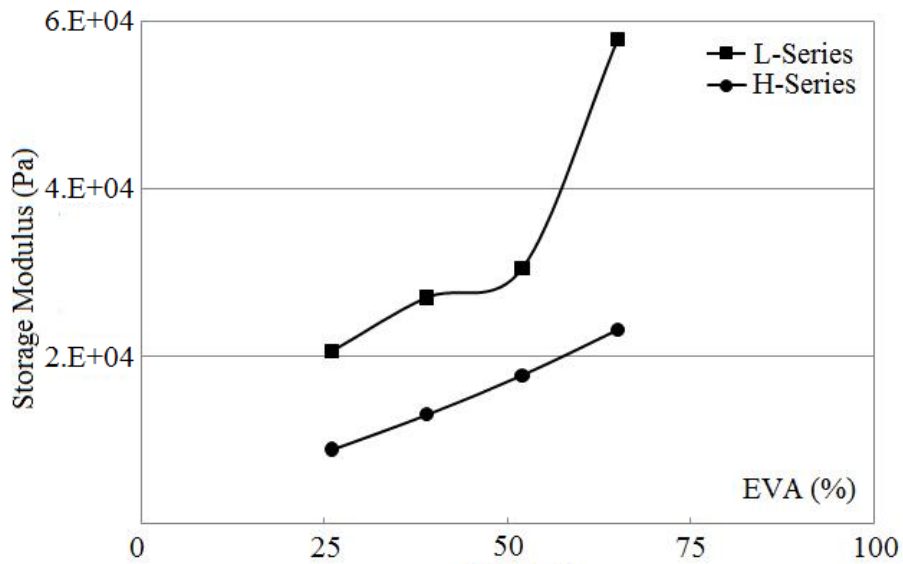


Figure 3.22 Storage modulus versus EVA composition in the composite (frequency = 1 Hz)

3.3 Mechanical Tests Applied to the Composites

Polyethylene is usually modified with the addition of EVA copolymer. The incorporation of EVA into LDPE matrix increases the flexibility, resistance to environmental stress cracking and enhance the toughness.

In the literature, the effect of EVA content on mechanical properties of LDPE/EVA blends was investigated. Serenko et al. (2001), observed an improvement in toughness of the material when LDPE is modified with EVA copolymer. They explained the reason of such enhancement as the increase of the adhesive strength at the matrix–rubber particle interface.

Mechanical properties of composites containing different amounts of EVA copolymer were investigated. **Figure 3.23** shows the dependence of elasticity (Young's) modulus on the EVA content in the composites. It is seen that the modulus sharply decreases with increasing EVA content for both series; L and H.

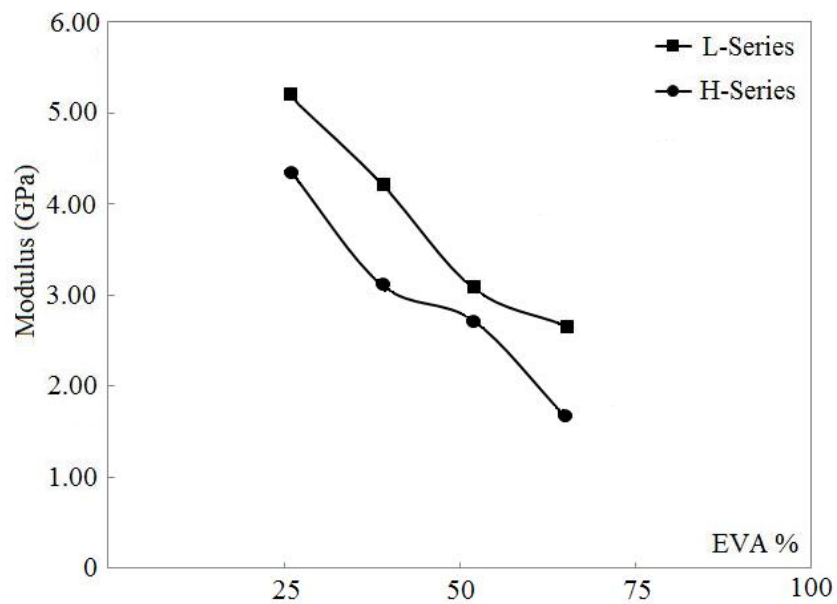


Figure 3.23 Elasticity modulus of composites as a function of EVA content

Takidis *et al.* (2003) reported that Young's modulus increases with an increasing degree of crystallinity in semicrystalline polymers. The degree of crystallinity of material directly affects the yield strength and Young's modulus. The crystallinity of EVA copolymers is lower than the crystallinity of LDPE due to its VA content. Therefore PE-rich composites have higher elasticity modulus as seen in **Figure 3.23** since crystalline regions enhance the amorphous areas by acting as physical crosslinks.

The two main mechanical properties measured in this study were; tensile strength and elongation at break. Compounds prepared with both LDPE types displayed good balance of tensile properties as presented in **Figures 3.24** and **3.25**. The composites containing lower amounts of EVA had higher values of tensile strength (**Figure 3.24**). In addition, at low levels of EVA loading, composites prepared with L-series showed higher tensile strength values. On the other hand, reversed behavior was observed in the case of higher EVA contents. At the intermediate region where EVA is used about 45% mass in the polymer matrix, the tensile strength of both type of composites showed almost similar behavior.

The elongation at break of composites improved for especially L-series with increasing EVA content up to 40% mass, as seen explicitly in **Figures 3.25**. A remarkable change in elongation at break was not observed at higher EVA contents for both series despite the drastic change obtained by the increase from 26 to 39%.

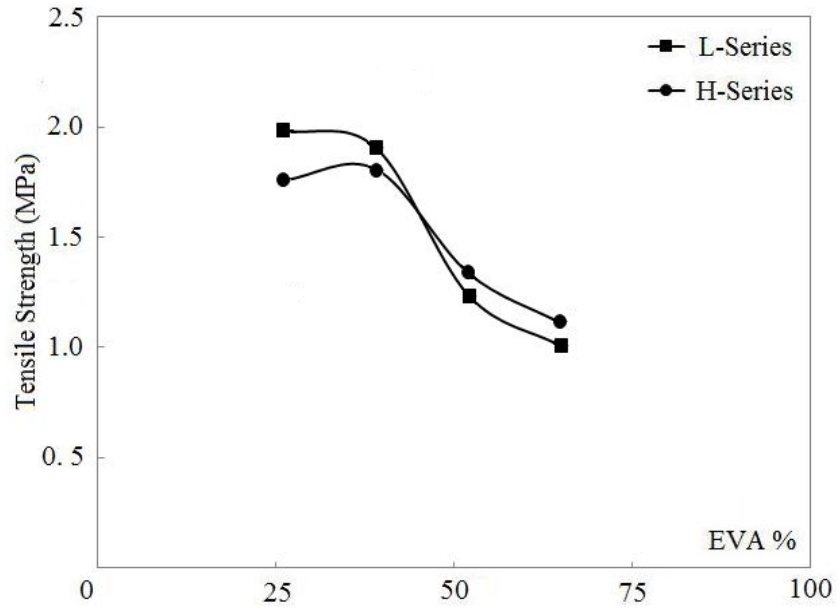


Figure 3.24 Tensile strength versus EVA% of composites

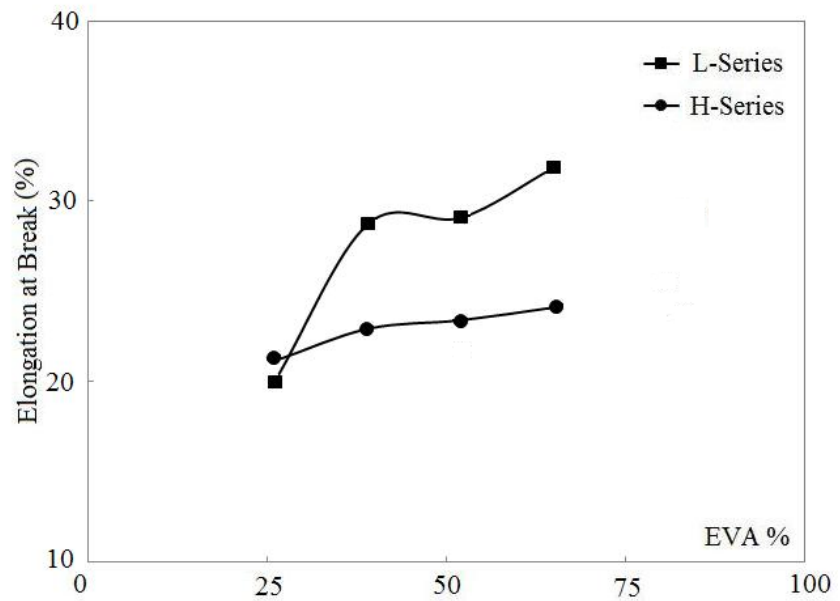


Figure 3.25 Elongation at break versus EVA% of composites

Tables 3.6 and **3.7** show modulus, elongation at the break, and tensile strength at room temperature for commercial samples and prepared composites, respectively. Com-K sample has the highest elongation and lowest modulus values as 230.69% and 0.18 GPa, respectively.

Modulus is the parameter which is mainly associated with crystallinity. Increasing amounts of EVA copolymer; having an amorphous structure, in the polymer blend, decrease the crystallinity of the blend, consequently decrease the young's modulus (Khonakdar *et al.*, 2006). It was expected that the lowest modulus value of Com-K among three commercial samples may be due to its high loading levels of EVA copolymer or the higher vinyl acetate (VA) content.

Table 3.6 Tensile Properties of Commercial Samples at 25°C, 50% R.H

	Yield Strength, (MPa)	Tensile Strength, σ_B (MPa)	Elongation at Break, ϵ_B (%)	Modulus, E (GPa)
<i>Com-H</i>	12.04	13.27	90.13	0.72
<i>Com-L</i>	7.89	6.05	48.81	0.50
<i>Com-K</i>	9.13	12.56	230.69	0.18

In **Table 3.7**, the relationship between tensile properties and EVA content which was discussed above, was listed. A remarkable difference in yield and tensile strength between the samples prepared with PE-L and PE-H could not be observed. However, higher elongation values were obtained for low-melt flow series for all EVA content except for 26% EVA. In addition, Young's modulus showed similar behavior with L-series which have higher modulus for all compositions.

Table 3.7 Tensile Properties of Composites at 25 °C, 50% R.H

PE Type	EVA %	Yield Strength, (MPa)	Tensile Strength, σ_B (MPa)	Elongation at Break, ϵ_B (%)	Modulus, E (GPa)
<i>Low MFI</i>	65	9,31	1,01	31,87	2,67
	52	10,55	1,24	29,09	3,08
	39	11,60	1,91	28,73	4,22
	26	12,34	1,99	19,99	5,18
<i>High MFI</i>	65	10,61	1,11	22,76	1,68
	52	11,19	1,34	23,41	2,73
	39	12,90	1,81	22,94	3,11
	26	13,08	1,76	21,17	4,36

In commercial applications, mechanical properties of composites play significant role together with other properties such as thermal and rheological ones. The results of mechanical studies showed that elongation at break and tensile strength of prepared composites should be improved to compete the commercially available ones which are listed in **Table 3.6**. Preparing more homogenous composites by using twin-screw extruder instead of internal mixer may result in improved mechanical properties. Another factor that directly affects the mechanical test performance is the specimen preparation method. In this study, the composite material was placed in a mould and heated. Thus, we let the material to shape the mould. However, test sample preparation by injection molding, form the specimen more homogenous. Consequently, the material can show its real mechanical performance.

3.4 Fire (LOI) Tests Applied to the Composites

The LOI is defined as the minimum oxygen concentration required for the combustion of materials. It is a significant parameter to describe the flame-retardant property of a material when the results are supported with other important flame tests such as cone calorimeter and UL-94 V test.

ATH contains some crystal water within its chemical structure. It releases 34 mass% water at temperatures between 220 °C and 450 °C during its endothermic degradation in a fire condition. Thus, it not only decreases the temperature of combustion medium and dilutes the combustion gases but also forms a protective layer against oxygen penetration which increase the limiting oxygen index value (Ramazani *et al.*, 2008).

The flame retardant performance of composites containing different EVA content was measured by the limiting oxygen index of material. The results of measurement is shown in **Figure 3.26**. LOI results obtained for composites prepared with low melt flow index-PE; PE-L were found higher than those of compounds prepared with high melt flow-PE; PE-H, independently of the EVA content.

An improvement was observed in the LOI performance of composites with increasing EVA content. While LOI value was found as 30 for composites containing 26 mass% of EVA, it increased to 32 and 34 for H- and L-series, respectively when EVA content was increased to 65 mass% (**Figure 3.26**).

In **Table3.7**, the fire properties of both commercial samples and prepared samples were given. At the beginning, the same LOI values were obtained for the composites containing 26% EVA independent of the PE type. However, LOI values increased with increasing EVA content for both series. Although, both PE and EVA have equal LOI values as 18% (Du *et al.*, 2005, Laoutid *et al.*, 2009), the flame retardant property of composites enhanced by the incorporation of EVA at higher loading levels, surprisingly.

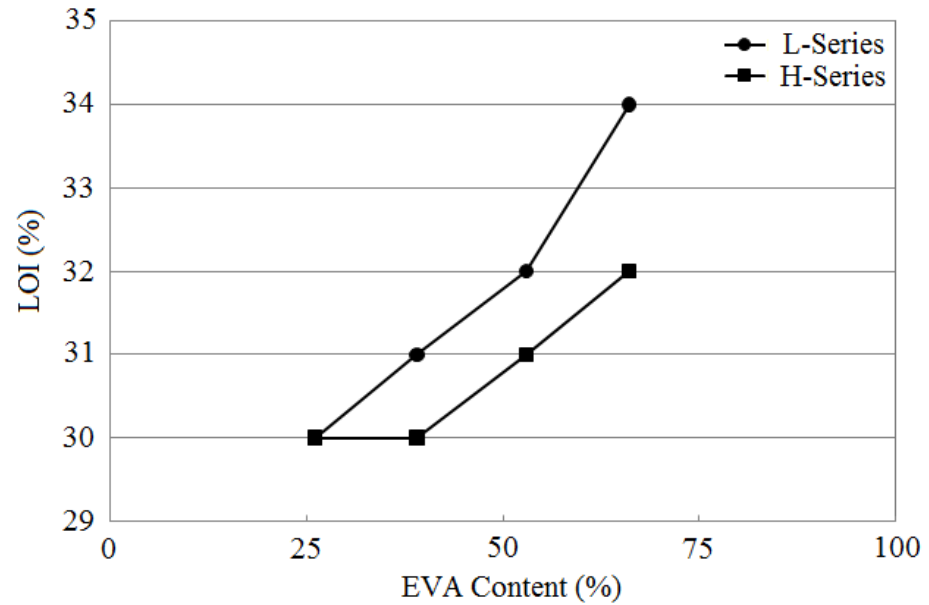


Figure 3.26 Limiting oxygen index (LOI) of composites as a function of EVA content

One of the commercial samples named as Com-H has the highest LOI value. The fire test results of prepared composites are not very close to the results of this commercial sample. However, enhanced LOI values were obtained when especially PE-L and higher amounts of EVA were used. The composite coded as L10/28 may compete with the other commercial samples with its 34% LOI value.

Table 3.8 Limiting oxygen index (LOI) of commercial samples and prepared composites

Sampe Name	EVA %	LOI	Sampe Name	EVA %	LOI
<i>L25/13</i>	26	30	<i>H25/13</i>	26	30
<i>L20/18</i>	39	31	<i>L20/18</i>	39	30
<i>L15/23</i>	52	32	<i>L15/23</i>	52	32
<i>L10/28</i>	65	34	<i>L10/28</i>	65	32
<i>Com-K</i>	–	33	–	–	–
<i>Com-H</i>	–	44	–	–	–
<i>Com-L</i>	–	36	–	–	–

4.0 THE OVERALL ASSESMENT of RESULTS

The peaks on DSC curves corresponding to the melting of EVA disappeared in the composites prepared with both LDPE types. This means that high compatibility between polymers was obtained. The melting peak of LDPE shifted by about 5–6 °C toward lower temperatures with respect to the peaks of the original LDPE polymers. A plasticizing action of polymers to each other is thought to be the reason of this shift due to the interpenetration of some macromolecules of one component into the phase of the other during melt mixing.

The TGA results exhibit that the onset of decomposition of ATH in the composite increases from 219 to 225 °C. ATH shows its flame retardant property by releasing water and lowering the temperature of combustion medium when it decomposes endothermically. Even if a five or six centigrade degree shift seems to be insignificant, the performance of flame retardant filler in the composite decreases.

The decomposition temperatures of composites prepared with PE–L, are 3–5 °C higher than that of the composites prepared with PE–H nearly for all formulations.

The ATH amount used in the commercial samples was calculated as approximately 61–64 mass percent.

In rheological measurements, the viscosity and storage modulus of PE–L was found higher than EVA in all frequency ranges and there is a remarkable difference in storage modulus between two types of LDPEs at low frequencies. The storage modulus increased with the increase in EVA content and the composites containing 65% of EVA exhibited two times greater values than those of 26 % EVA containing ones for both series (H and L).

The storage modulus of composites increases with increasing EVA content for all frequency ranges. An enhancement in storage modulus value was observed for the composite containing 65 mass percentage of EVA, named L13/25, in comparison with other composites in the same series.

The Carreau model was applied for describing the viscosity of composites and parameters of this model were presented. The results of viscosity versus shear rate for composites showed that similar with neat polymers, all composite formulations behave as shear thinning materials.

The Young's modulus sharply decreases with increasing EVA content for both L and H series. The composites containing lower amounts of EVA and prepared with L-series showed higher tensile strength. At higher EVA contents, reversed behavior was observed and the tensile strength of both type of composites showed almost similar behavior at the intermediate region where EVA is used about 45 mass % in the polymer matrix. The elongation at break of composites were improved with increasing EVA content and a remarkable change in elongation at break was not observed at higher EVA contents for both series despite the drastic change obtained by the increase from 26 to 39%.

The crystallinity of EVA copolymers is lower than the crystallinity of LDPE due to its VA content. Thus, PE-rich composites have higher Young's modulus since their crystalline content is higher. Among commercial samples, Com-K sample has the highest elongation and lowest modulus values as 230.7 ± 16.6 % and 180 ± 6 MPa, respectively. Similar with composites, Com-K may contain high loading levels of EVA copolymer or the higher vinyl acetate (VA) content.

The flame retardant performance of composites prepared with low melt flow index-PE; PE-L, were found higher than those of compounds prepared with high melt flow-PE; PE-H, independent of the EVA content. Moreover, with increasing EVA content, an improvement in LOI performance was observed for composites. LOI value increased from 30 to 34 for L-series when EVA content increased to 65 mass%.

5.0 CONCLUSION

In the present study, cable formulations in line with the commercial samples were prepared. The effect of EVA content and melt viscosity of PE were considered as the parameters. ATH was thought to be better flame retardant than MH and chosen due to its lower decomposition temperature and low cost. Some conclusions drawn are presented as follows:

As EVA content increased from 26 to 65% mass;

- Storage modulus of L- and H-series increased by 220% and 180%, respectively,
- Viscosity of L- and H-series increased 61% and 107%, respectively,
- Tensile modulus of L-series decreased from 5.18 to 2.67 GPa and of H-series was decreased from 4.36 to 1.68 GPa,
- Tensile strength of L-series decreased from 1.99 to 1.01 MPa and of H-series decreased from 1.76 to 1.11 MPa,
- Elongation at break value of L-series increased from 19.99 to 31.87% and of H-series increased from 21.17 to 22.76%

In addition, an improvement in fire properties of composites was observed for both series;

- At 26% EVA content, the LOI value was 30% for both series however, it was increased to 34 and 32% for L- and H- series, respectively when EVA content increased to 65% mass.

The assessment of the results obtained was done in comparison with the commercial samples. Since the results exhibit that the mechanical, rheological and fire retardant properties are comparable that those of commercials, these formulations can successfully be used in industry. This project hopefully will help Turkish cable manufacturers to produce HFFR cable material in domestic industry.

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