DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

USE OF HUNTITE AND HYDROMAGNESITE MINERAL IN PLASTIC MATERIALS AS A FLAME RETARDANT

by
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İZMİR

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We have read the thesis entitled **"USE OF HUNTITE AND HYDROMAGNESITE MINERAL IN PLASTIC MATERIALS AS A FLAME RETARDANT "** completed by **HÜSNÜGÜL YILMAZ ATAY** under supervision of **DOÇ.DR. ERDAL ÇELİK** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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Hüsnügül YILMAZ ATAY

USE OF HUNTITE AND HYDROMAGNESITE MINERAL IN PLASTIC MATERIALS AS A FLAME RETARDANT

ABSTRACT

In this study, flame retardancy properties of huntite/hydromagnesite mineral in plastic compounds were investigated for electrical applications. Prior to production of composite materials, huntite/hydromagnesite mineral was ground at particle sizes of 10 μm, 1 μm and 0.1 μm. The ground minerals with different particle size and content levels were added to the plastic compounds to produce composite materials. After fabrication of huntite/hydromagnesite reinforced plastic composite samples, they were characterized by using DTA-TG, FTIR, XRD and SEM-EDS. Mechanical and electrical properties of the composites were also evaluated through tensile testing, hardness, multimeter and empedance machines. In addition, flame retardancy test were performed as a main objective of this research. By this way the effect of size distribution of the additives and the effect of the concent levels of the additives in the plastic compounds by means of flame retardancy are measured with this regard. It was concluded that flame retardant properties of plastic composites were improved depending on particle size and particle content of huntite/hydromagnesite minerals.

Keywords: Huntite/hydromagnesite, additive, polymeric composite, flame retardancy, size distribution effect, particle content effect.

HUNTİT VE HİDROMANYEZİT MİNERALİNİN ATEŞ ÖNLEYİCİ OLARAK PLASTİK MALZEMELERDE KULLANIMI

ÖZ

Bu çalışmada plastik kompozitlerde elektriksel uygulamalar için huntit/hidromanyezit mineralinin alev geciktirici özellikleri incelenmiştir. Kompozit malzemelerin üretimi için ilk olarak huntit/hidromanyezit minerali 10 μm, 1 μm ve 0.1 μm tane boyutlarına öğütülmüş, daha sonra bu öğütülmüş mineraller farklı tane boyutlarında ve farklı miktarlarda plastik komponentlere eklenerek kompozit malzemeler üretilmiştir. Huntit/hidromanyezit ile güçlendirilmiş plastik kompozit numunelerin üretiminden sonra, bu numuneler DTA-TG, FTIR, XRD ve SEM-EDS ile karakterize edilmiştir. Ayrıca kompozitlerin mekanik ve elektriksel özellikleri çekme testi, sertlik, multimeter ve empedans makinesi ile tespit edilmiştir. Bunların yanında alev geciktiricilik testi de bu çalışmanın ana amacı olmak üzere uygulanmıştır. Bu bağlamda eklenen mineralin boyut dağılımının ve miktarının plastik malzemelere ateş önleyicilik etkisi ölçülmüştür. Huntit/hidromanyezit mineralinin boyut dağılımına ve miktarına bağlı olarak plastik kompozitlerde alev geciktiriciliği geliştirdiği gözlemlenmiştir.

Anahtar kelimeler: Huntit/hidromanyezit, katkı malzemesi, polimerik kompozit, alev geciktiricilik, boyut dağılım etkisi, katkı miktarı etkisi.

CONTENTS

Page

CHAPTER ONE

INTRODUCTION

Fires frequently happen all over the world every day. They kill people, cause huge peculiary losses for the economy and destroy unique goods such as art works. The costs of direct fire losses are about 0.2 % to 0.3 % of the economy of European and North American countries according to statistics. In Germany, the losses are about 6,000 million euro per year and in the USA, more than USD 10,000 million (Weber, 1999). According to Turkish Statistical Institute, in Turkey the fire loss is 16,070,667 YTL for 2005.

Obviously, even more serious are fire deaths. Despite extensive fire precaution regulations for buildings, transportation, elecrical engineering and many other fields, there were stil about 1,000 fire deaths in Germany and about 5,000 in the USA per year at the beginning of the 1990s (Weber, 1999). It is illustrated the importance of the fire protection from the mentioned figures

In many application areas risk of fire cannot be ruled out, therefore products should be well-protected against fire. The open question in a lot of cases is how to ensure such levels of protection against fire attacks. Flame retardant materials play an important role in this issue. This research reviews these materials, especially plastics and their functions. We are surrounded more and more by non-flame retarded plastics in our daily life. For many years, minerals have been used in a wide variety of polymer applications. They have also been widely regarded as cost reducers and/or fillers. However, this is not necessarily the case today. Minerals are used for the flame retardancy properties for these applications. In this case, enhancements bring to polymer applications. These application properties are closely related to the physical properties of the mineral itself. Thus, in the formulation (compounding) of polymers prior to the conversion of the raw material to the finished it, ancillary materials are added that impart to the compound the required properties of; flowability of the melt, tensile strength, bending strength, resistance to

breakage by impact, resistance to the effects of oxygen or UV light, resistance to fire, suppression of smoke in the event of ultimate burning (Mureinik, 1997).

Here in this work huntite/hydromagnesite mineral is used in the polymer application for its flame retardancy properties. This mineral is one of the magnesium containing source for mineral flame retardants and it was introduced to the market in the late 1980s (Kirschbaum, 2001). At present, the commercially used deposits are located in Greece and Turkey. Especially Turkey has millions tons of reserves. The deposit normally consists of physical blends of two minerals huntite and hydromagnesite with varying ratios. The level of impurities is very low, the most important ones are other white carbonate minerals such as aragonite, calcite, and dolomite. This fact and the specific genesis of the material results in very white raw materials with microcrystalline structure. Endothermic decomposition starts at about 250 ºC liberates water steam and carbon dioxide and results in Ca and Mg oxide as solid final products.

Based on this, raw material production of final products goes through mining, analysis and selection of defined fractions, breaking, drying, milling and air classification resulting in a final product of 10 to 20 microns particle size and >95% brightness.

While being very efficient in non-flame retardant applications (eg. as replacament and extender of TiO_2 or rheology modifier in plastisols and sealants), huntite is not as an effective flame retardant as hydromagnesite. For flame retardant applications the hydromagnesite ratio should not be lower than 35 to 40%.

When the flame retardant materials are looked at related markets, the halogenated flame retardants can be seen in many areas. Nevertheless, those flame retardants are under pressure because of their significiant disadvantages related to the formation of smoke, toxic and corrosive decomposition products. In contrast, mineral flame retardants provide in part extremely low smoke values, they absorb toxic and corrosive gases, and generate nothing but water, carbon dioxide, and harmless metal

oxides. Wherever technical solutions are developed that allow the use of mineral flame retardants those formulations are preffered in many applications.

The European and the US markets account for the consumption of about 300,000 tpa of flame retardants. Markets in the rest of the world are still small. Nevertheless, markets in the Far East show a permanent annual increase on a double digit scale. The annual market development for the whole flame retardants market is estimated to be around 3%. The market share of flame retardant is estimated to increase from 38 % of the 316,000 tonnes in 1995 to 43 % of the 375,000 tonnes in 2000. Flame retardant markets are growing faster than average industrial markets and mineral flame retardants are growing twice as fast as other flame retardants. In mineral flame retardants market, Huntite/hydromagnesite products are used in flame retardant applications starting from scracth in the late 1980s, their consumption has crossed the 10,000 tonnes. They combine high purity, naturally fine particle size, and reasonable costs (Kirschbaum, 2001).

Products are used in many applications. They are used either alone or in combination with other mineral flame retardants. A review of those applications can be classified as three groups, including **(a)** wire and cable applications such as wiring in telecommunication, under the hood automotive wiring, firing in naval vessels, power stations and low smoke PVC cabling, **(b)** construction industry applications**,** such as flooring, roofing tiles, conduits, profiles, coils, sheets, films to replace brominated flame retardants and PVC, partitions and panelling and insulating foams, and **(c)** electronic/electirical applications, such as relays switches, plugs and sockets based on nylon, housing for electrical equipment, insulating and conecting parts and printed circuit boards (Weber, 1999).

Technically, huntite/hydromagnesite offers good properties and processing in a wide range of PVC compounds. Fire performance is slightly superior to other flame retardant minerals, the same applies to viscosity and product performance. PVC cable insulation and building products represent some of the most important users. The consumption is in the thousands of tpa.

Since developments for engineering plastics are underway, they most probably lead to commercial applications in the near future. The advantages of this mineral can be ordered such as being non-corrosive to processing equipments, low smoke generation, no acid gas emission, halogen free, environmental safe, recyclable, no combustion gas corrosion, no limitation in colouring and low combustion. In addition, huntite/hydromagnesite offers good cost/performance relationship in flame retardant applications. Additional effects of improved pigmentation and rheology control improve future perspectives.

As huntite/hydromagnesite is very new materials there are not so much investigations on it. The flame retardancy properties is already proved. However, there are not many sources about size distribution effects of this mineral when it is added to the polymeric materials. In the industry, normally huntite/hydromagnesite is used as an additive below 20 μm. Here in this work it is studied how the flame retardancy intensity will be changed if its size distribution is changed in the composite materials. With this regard, the main point of this research is to investigate the effect of the size distribution and the centent of the additives in the flame retardancy of the plastics. First of all the huntite/hydromagnesite material below 20 μm is ground more in the atritor mill, then this ground material is seperated into several fractions using sedimentation method. Three different size distribution is achieved; finest, medium and coarse sizes. After production of those materials the plastic samples are prepared by adding those different size of huntite/hydromagnesite. The content of huntite/hydromagnesite are changed in polimeric composite material. After fabrication of huntite/hydromagnesite reinforced plastic composite samples, they were characterized by using DTA-TG, FTIR, XRD and SEM-EDS. Mechanical and electrical properties of the composites were evaluated through tensile testing, hardness, multimeter and empedance machines. In addition, flame retardancy test were performed as a main objective of this research. According to the those results it was obvious that huntite/hydromagnesite materials gives flame retardant properties to the plastics. Also, mechanical, electrical and many other properties of the plastics became much more beneficial. On the other hand it is

observed that the finest the additive particle size of the minerals exhibited the highest values of for the flame retardancy properties of the composite materials.

CHAPTER TWO

COMPOSITE MATERIALS

2.1 Definitions and descriptions

Composite materials are formed by combining two or more materials that have quite different properties. The different materials work together to give the composite unique properties, but within the composite you can easily tell the different materials apart, they do not dissolve or blend into each other.

Composites exist in nature. A piece of wood is a composite, with long fibres of cellulose (a very complex form of starch) held together by a much weaker substance called lignin. Cellulose is also found in cotton and linen, but it is the binding power of the lignin that makes a piece of timber much stronger than a bundle of cotton fibres.

Humans have been using composite materials for thousands of years. Take mud bricks for example. A cake of dried mud is easy to break by bending, which puts a tension force on one edge, but makes a good strong wall, where all the forces are compressive. A piece of straw, on the other hand, has a lot of strength when you try to stretch it but almost none when you crumple it up. But if you embed pieces of straw in a block of mud and let it dry hard, the resulting mud brick resists both squeezing and tearing and makes an excellent building material. Put more technically, it has both good compressive strength and good tensile strength.

Another well-known composite is concrete. Here aggregate with small stones or gravel is bound together by cement. Concrete has good strength under compression, and it can be made stronger under tension by adding metal rods, wires, mesh or cables to the composite (so creating reinforced concrete).

The greatest advantage of composite materials is strength and stiffness combined with lightness. By choosing an appropriate combination of reinforcement and matrix material, manufacturers can produce properties that exactly fit the requirements for a particular structure for a particular purpose.

Modern aviation, both military and civil, is a prime example. It would be much less efficient without composites. In fact, the demands made by that industry for materials that are both light and strong has been the main force driving the development of composites. It is common now to find wing and tail sections, propellers and rotor blades made from advanced composites, along with much of the internal structure and fittings. The airframes of some smaller aircraft are made entirely from composites, as are the wing, tail and body panels of large commercial aircraft.

In thinking about planes, it is worth remembering that composites are less likely than metals such as aluminium to break up completely under stress. A small crack in a piece of metal can spread very rapidly with very serious consequences, especially in the case of aircraft. The fibers in a composite act to block the widening of any small crack and to share the stress around.

The right composites also stand up well to heat and corrosion. This makes them ideal for use in products that are exposed to extreme environments such as boats, chemical-handling equipment and spacecraft. In general, composite materials are very durable. Another advantage of composite materials is that they provide design flexibility. Composites can be moulded into complex shapes – a great assetment when producing something like a surfboard or a boat hull.

The downside of composites is usually the cost. Although manufacturing processes are often more efficient when composites are used, the raw materials are expensive. Composites will never totally replace traditional materials like steel, but in many cases they are just what we need. And no doubt new uses will be found as the technology evolves day by day.

2.2 Fabrication of a composite material

Most composites are made up of just two materials. One material (the matrix or binder) surrounds and binds together a cluster of fibres or fragments of a much stronger material (the reinforcement). In the case of mud bricks, the two roles are taken by the mud and the straw; in concrete, by the cement and the aggregate; in a piece of wood, by the cellulose and the lignin. In fibreglass, the reinforcement is provided by fine threads or fibres of glass, often woven into a sort of cloth, and the matrix is a plastic.

In Figure 2.1 it is demonstrated simply the steps of preparation of the polymer compounding operations (O'Driscoll, 1994).

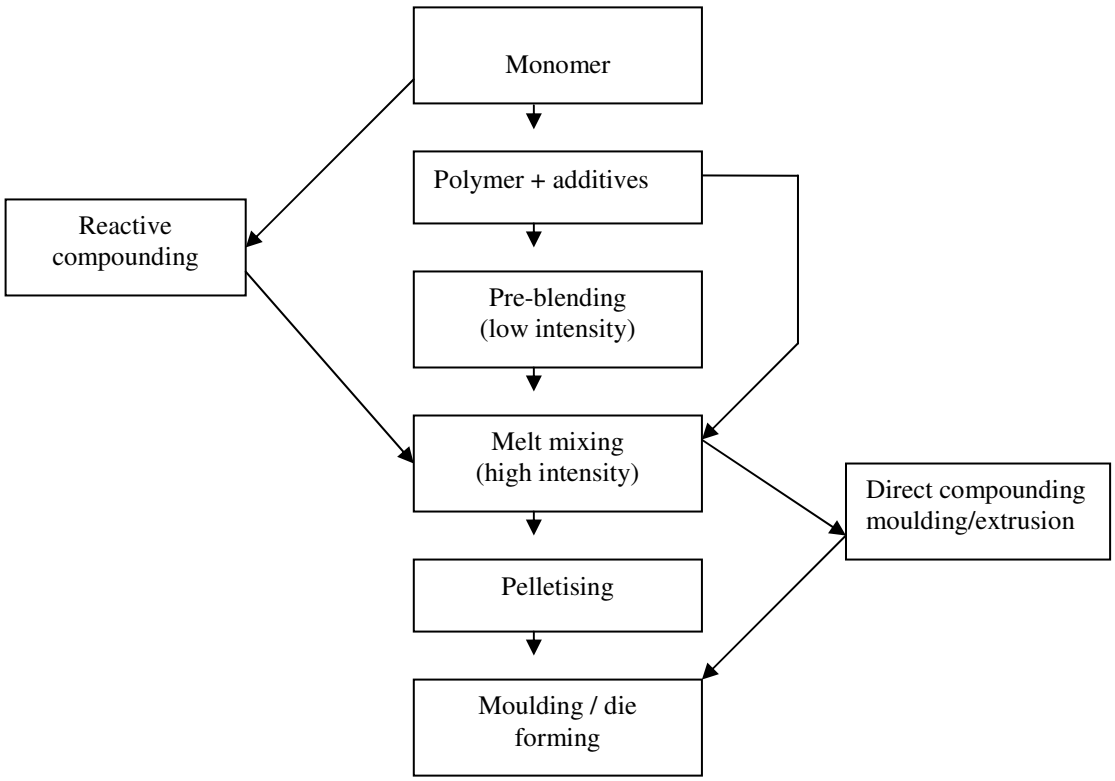


Figure 2.1 Scope of polymer compounding operations (O'Driscoll, 1994)

The threads of glass in fibreglass are very strong under tension but they are also brittle and will snap if bent sharply. The matrix not only holds the fibres together, it also protects them from damage by sharing any stress among them. The matrix is soft enough to be shaped with tools, and can be softened by suitable solvents to allow

repairs to be made. Any deformation of a sheet of fibreglass necessarily stretches some of the glass fibres, and they are able to resist this, so even a thin sheet is very strong. It is also quite light, which is an advantage in many applications.

Over recent decades many new composites have been developed, some with very valuable properties. By carefully choosing the reinforcement, the matrix, and the manufacturing process that brings them together, engineers can tailor the properties to meet specific requirements. They can, for example, make the composite sheet very strong in one direction by aligning the fibres that way, but weaker in another direction where strength is not so important. They can also select properties such as resistance to heat, chemicals, and weathering by choosing an appropriate matrix material.

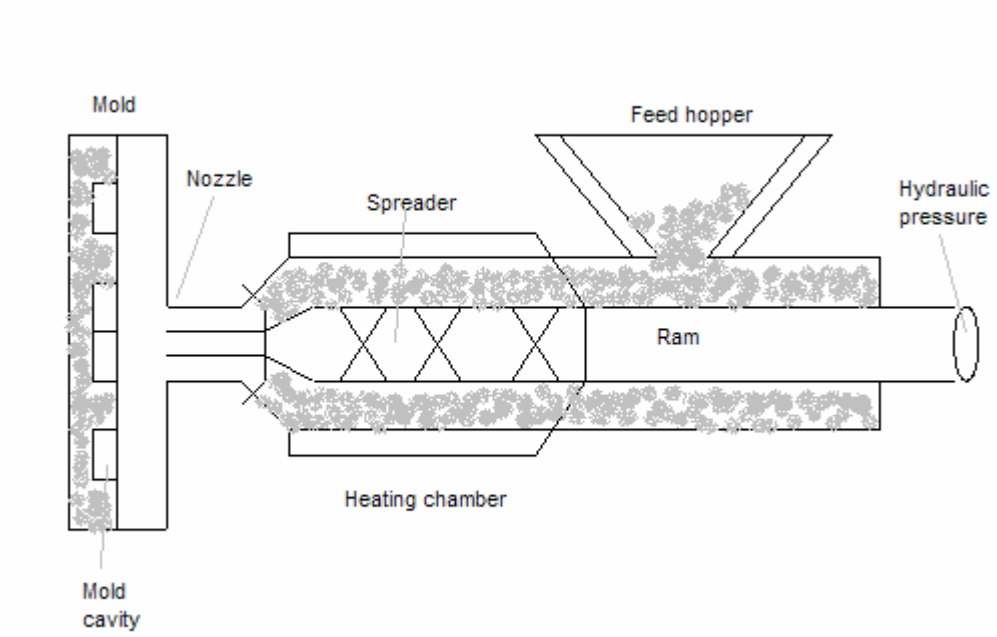


Figure 2.2 Schematic diagram of an injection molding apparatus (Callister, 2003)

The process explained above can be performed by using injection molding technique. This tecnique is widely used technique for fabrication polymer compounds. A schematic crosssection of the apparatus used is shown in Figure 2.2 (Callister, 2003).

2.2.1 Choosing materials for the matrix

For the matrix, many modern composites use thermosetting or thermosoftening plastics (also called resins). The use of plastics in the matrix explains the name 'reinforced plastics' commonly given to composites. The plastics are polymers that hold the reinforcement together and help to determine the physical properties of the final product.

Thermosetting plastics are liquid when prepared but harden and become rigid (i.e., they *cure*) when they are heated. The setting process is irreversible, so that these materials do not become soft under high temperatures. These plastics also resist wear and attack by chemicals making them very durable, even when exposed to extreme environments.

Thermosoftening plastics, as the name implies, are hard at low temperatures but soften when they are heated. In spite of the fact that they are less commonly used than thermosetting plastics they do have some advantages, such as greater fracture toughness, long shelf life of the raw material, capacity for recycling and a cleaner, safer workplace because organic solvents are not needed for the hardening process.

Ceramics, carbon and metals are used as the matrix for some highly specialised purposes. For instance, ceramics are used when the material is going to be exposed to high temperatures (e.g. heat exchangers) and carbon is used for products that are exposed to friction and wear (e.g. bearings and gears).

2.2.2 Choosing materials for the reinforcement

Eventhough glass fibres are by far the most common reinforcement, many advanced composites now use fine fibres of pure carbon. Carbon fibres are much stronger than glass fibres, but are also more expensive to produce. Carbon fibre composites are light as well as strong. They are used in aircraft structures and in

sporting goods such as golf clubs, and increasingly are used instead of metals to repair or replace damaged bones. Even stronger (and more costly) than carbon fibres are threads of boron.

Polymers are not only used for the matrix, they also make a good reinforcement material in composites. To illustrate, kevlar is a polymer fibre that is immensely strong and adds toughness to a composite. It is used as the reinforcement in composite products that require lightweight and reliable construction (e.g. structural body parts of an aircraft). Composite materials were not the original use for kevlar, it was developed to replace steel in radial tyres and is now used in bulletproof vests and helmets.

2.2.3 Choosing the manufacturing process

Making an object from a composite material usually involves some form of mould. The reinforcing material is first placed in the mould and then semi-liquid matrix material is sprayed or pumped in to form the object. Pressure may be applied to force out any air bubbles, and the mould is then heated to make the matrix set solid.

The moulding process is often performed by hand, but automatic processing by machines is becoming more common. One of the new methods is called pultrusion (a term derived from the words 'pull' and 'extrusion'). This process is ideal for manufacturing products that are straight and have a constant cross section, such as bridge beams.

In many thin structures with complex shapes, such as curved panels, the composite structure is built up by applying sheets of woven fibre reinforcement, saturated with the plastic matrix material, over an appropriately shaped base mould. When the panel has been built to an appropriate thickness, the matrix material is then cured. In many advanced composites such as those used in the wing and body panels of aircraft, the structure may consist of a honeycomb of plastic sandwiched between two skins of carbon-fibre reinforced composite material. Such sandwich composites

combine high strength, and particularly bending stiffness, with low weight. Like everything to do with aircraft, they can be very costly.

2.2.4 Ceramic-Matrix Composites

Ceramic materials are inherently resilient to oxidation and deterioration at elevated temperatures; were it not for their disposition to brittle fractures, some of these materials would be ideal candidates for use in high-temperature and severe-stress applications, specifically for components in automobile and aircraft gas turbine engines. The fracture toughnesses of ceramics have been improved significantly by the development of new generation of composites. Ceramic-matrix composite materials have extended fracture thoughness to between about 6 and 20 MPa (Callister, 2003).

2.2.5 Fillers

Particulate-filled polymer composites have a long history and consequently newcomers to the field usually expect to find an area of well-understood science with few intellectual challenges remaining. However, they are usually amazed to find that this is far from the truth in many areas, with few reliable generalisations (but several unreliable ones) available and much basic information yet to be established. This is largely due to the way in which the technology has developed, with different filler and polymer combinations tending to be developed to meet the specific demands of various industries. The initial, and to some extent continuing, emphasis on cost reduction has also meant that many fillers have been poorly characterised.

In developing a particulate-filler composite, the basic charactersitics of particulate fillers need to be indicated. It can be started with answering the following questions:

- What property benefits are being sought?

- What deleterious changes may also occur and can they be tolerated?

- How easy is the filler to handle and how might it affect processing?

- Are special additives needed?

- What is the true cost of using the filler, is it justifiable, and are there more cost effective alternatives.

Important information for answering the above questions includes, cost, purity, particle size and shape, density, hardness, optical and thermal properties and chemisty.

2.2.5.1 Cost

Although it seems to be a simple topic, it causes considerable problems for the unwary. It is widely assumed that polymers are expensive and fillers are cheap, and many articles on filled polymers start with the statement that fillers are used primarily to reduce cost. These savings are frequently not as great as anticipated and, in quite a few instances, compound costs, even with the lowest cost filler, can be higher than unmodified polymer.

2.2.5.2 Chemistry, Composition and Impurities

Chemical nature of the fillers is frequently of little direct importance to its use in composites, this plays two important roles, in that it determines the structure of the mineral, and also the nature of the interaction between polymer and flller. Nevertheless, away from these a prior considerations, only in a few cases does the chemical reactivity of the filler play a significiant role in the properties of a composite.

2.2.5.3 Bulk Chemistry

As reactive and inert, fillers can be divided into two types. Reactive fillers will react with their environment. A good example of this is gibbsite (aluminium hydroxide), which will react with both acidic and basic substances. Aluminium hydroxide also loses its water of crystallisation at around 200ºC and this enable it to provide fire retardancy in polymer formulations. The silicate Minerals including kaoline, mice, talc and quartz are in classical chemical terms, virtually inert, only

being attacked by very strong acids and alkalis. The carbonate minerals and the hydroxide minerals are very reactive to acids. The interactions between the constituent elements in a filler determine its molecular structure and hence crystallinity, which the dictates all the intrinsic properties of the filler.

2.2.5.4 Surface Chemistry

Filler surface chemistries are of more important than the bulk ones, as they determine both the rate of wetting and the strength of interaction with polymers. They are different from bulk chemistry but, unfortunately, they are poorly characterised for many fillers.

2.2.5.5 Surface interactions

Polymers have a higher (20-30 times) thermal expansion coefficient than mineral fibers. Thus, in many well-dispersed, hot processed composites, a radial compressive stress develops as the polymer cools leading to an intimate interaction between matrix and filler. Based on both polymer and filler, the value of this stress can be calculated. Due to this, the interaction will at the very least be mechanical, but other types will exist depending on the surface chemistry of the filler and also the chemistry of the polymer.

Table 2.1 Surface energies of fillers and plastics (Schlumf, 1991)

Material	**Surface energy (m/Jm^{-2})**
Diamond	10,000
Mica	245-500
Glass	1,200
Titanium dioxide	650
Kaolin	500-600
Calium carbonate	65-70
Stearate coated calcium carbonate	25-30
Talc	65-70
Polymers	15-60
Polyproplene	31

Wettability of filler by polymer is an indication of compatibility between the two materials. Wettability by polymer can not be measured directly, but the effect that the material has on surface tension of a liquid is a measure of its surface energy

(Schlumf, (1991) has reported surface energies for a variety of fillers as listed in Table 2.1). There have been a wide number of claims that surface energies determine the forces between polymer chains and different phases, determining mechanical properties of the composite.

2.2.5.6 Chemical Anlaysis and Impurities

The purity of a filler is of importance both commercially and technically, i.e., the users need to know what they are buying, whether it contains components that may be detrimental to the properties of their product and whether it will cause environmental problems. Impurities include trace elemets that may be on the filler surface or in the structure of the filler and ancillary minerals, which will have been formed at the same time as the mineral. Sometimes additives from the filler manufacture may be present (e.g., surfactans). The form of the impurity can be very important in determining it's importance. Sometimes a potentially detrimental impurity can be tolerated in relatively high levels, if present in an inert form, but small traces of the same impurity, if present on the surface in an active form, can be very deleterious.

2.2.5.7 Density or Specific Gravity

Density is mass per unit volume with SI (Sytem Internationale) units of kilogram per cubic meter. Specific gravity and relative density, the weight of the substance in relation to the weight of an equivalent volume of water, are often used synonymously. They are dimensionless but have the same numerical values as density.

2.2.5.8 Hardness

The resistance of a mineral to scratching is hardness. It depends on the structure of the mineral, the strength of the chemical bonds and the density of packaging of its constituent atoms. Where mixed fillers are used, if one is much harder than the other, then abrasion of the softer one may ocur. This is of particular importance when hard particulates are used with easly damaged glass fibres.

2.2.5.9 Abrasiveness

Because of the fillers, abrasion has quite an important role in the processing of filled polymers. It has several origins. Hardness is a major factor with the harder minerals, such as quartz. Large particles and angular particles with sharp edges are particularly detrimental probably due to scratching menhanism, followed by attrition of the exposed edges. Sometimes the coarse component of a filler may be predominantly a harder impurity, which leads to combination of the two mechanisms. Chemical attack may also be caused some recative fillers, leading to etching and progressive erosion.

2.2.5.10 Optical Properties

The colour and opacity of a composite are very important, but aesthetically and functionally, and will be strongly affected by the incorporation of fillers. When light strikes any surface, it is subjected to several effects: absorpiton, scattering, reflection, polarisation and interference. The extent of each effect is dependent on the nature of both exit and entrance media, but for all practical puposes only three media, air, filler and polymer, will be considered here in a superficial treatment.

2.2.5.11 Thermal Properties

Leaving aside the special cases of phase change and decomposition, the principal thermal properties of interest are specific heat, thermal conductivity and coefficient of expansion.

2.2.5.12 Particle Shape

Particle shape is very important in determining the stiffness, or rigidity, of a composite, the flow and rheology of a melt or liquid, tensile and impact strength, and the surface smoothness of a component.

Synthetic products will have their shape determined by their chemical composition and by the production conditions. For example, precipitated calcium carbonate can be produced with different shapes by changing precipitation

conditions. These conditions can be chosen to produce single crystals or complicated aggregates, which can be modified during drying or milling.

Many fillers being extracted from the earth or rocks and processed by fairly simple mehods will exhibit the same basic original shapes. Others, however, may be extracted by complicated routes or involve intensive comminution, thus altering particle shape. This is determined by the chemical nature and strength of the bonds between the atoms and groups in the mineral. These depend on electronegative differences between atoms and the bonding can range from covalent through to ionic. Two other types of interaction or bonding are important.

2.2.6 Effects of Fillers on the Polymer Phase

To understand and predict the properties of composites, it is necessary to realise that adding filler may affect the polymer phase, both chemically and physically. Chemical changes may occur if the filler, or impurities on the filler surface, catalyse degradation of the polymer. Alternatively, various physical changes may result from the incorporation of filler. Some fillers nucleate crystal growth in certain polymers, which in turn influences manufacturing and mechanical properties.

In the literature, the possibility that the filler may have altered the polymer phase is rarely considered. It is important to realise that the polymer may be altered by the filler, especially in the case of semi-crystalline polymers (Rothon, 2003).

CHAPTER THREE

FLAME RETARDANCY

3.1 Fire Dynamics

As a process, fire can take many forms, all of which involve chemical reaction between combustible species and oxygen from the air. Properly hardnessed, it provides great benefit as a source of power and heat to meet the industrial and domestic needs, but, unchecked, it can cause untold material damage and human suffering (Figure 3.1).

Figure 3.1 A picture of fire

In the United Kingdom alone, direct losses probably exceed 1000 M pound, while over 800 people die each year in fires (Roy, 1997). In real terms, the direct fire losses may not have increased significiantly over the past two decades, but the holding action has been bought by a substantial increase in other associated costs, namely improving the technical capability of the Fire Service and the adaption of more sophisticated fire protection systems.

Futher major advances in combating wildfire are unlikely to be achieved simply by continued application of the traditional methods. What is required is a more

fundamental approach which can be applied at the design stage rather than facility relying on fire incidents to draw attention to inherent fire hazards. Such as approach requires a detailed understanding of fire behaviour from an engineering standpoint. For this reason, it may be said that a study of chemistry or material science.

Table 3.1 Properties of gaseous and liquid fuels (Lide, 1993)

Gases	Formula	Melting point (ºC)	Boiling point (ºC)	Density (liq) (kg/m³)	Molecular weight
Hydrogen	H_2	-259.3	-252.8	70	2
Carbon monoxide	CO	-199	-191.5	422	28
Methane	CH_4	-182.5	-164	466	16
Ethane	C_2H_6	-183.3	-88.6	572	30
Propane	C_3H_8	-189.7	-42.1	585	44
n-Butane	n-C_4H_{10}	-138.4	-0.5	601	58
n-Pentane	n-C_5H_{12}	-130	36.1	626	72
n-Hexane	n-C_6H_{14}	-95	69.0	660	86
n-Heptane	n-C_7H_{16}	-90.6	98.4	684	100
n-Octane	n-C_8H_{18}	-56.8	125.7	703	114
iso-Octane	iso-C_8H_{18}	-107.4	99.2	692	114
n-Nonane	n-C_9H_{20}	-51	150.8	718	128
n-Decane	n-$C_{10}H_{22}$	-29.7	174.1	730	142
Ethylene	C_2H_4	-169.1	-103.7	384	28
Propene	C_3H_6	-185.2	-47.4	519	42
Acetylene	C_2H_2	-80.4	-84	621	26
Methanol	CH_3OH	-93.9	65.0	791	32
Ethanol	C_2H_5OH	-117.3	78.5	789	46
Acetone	$(CH_2)_3CO$	-95.3	56.2	790	58
Benzene	C_6H_6	5.5	80.1	874	78

Most fires involve combustible solids, although in many sectors of industry, liquid and gaseous fuels are to be found. The range of fuels with which we are concerned is very wide, from the simplest gaseous hydrocarbons to solids of high molecular weight and great chemical complexity, some of which occur naturally, such as sellulose and others which are man made, e.g. polyethylene and polyurethane

(Table 3.1) (Lide, 1993) and (Table 3.2) (Brandrup & Immergut, (1975); and Hall (1981)).

Table 3.2 Properties of some solid fuels (Brandrup & Immergut (1975); and Hall (1981))

Materials	Density (kg/m³)	Heat Capacity (kJ/kg.K)	Thermal capacity (W/m.K)	Heat of combustion (kJ/g)	Melting point (ºC)
Natural polymers					
Cellulose	V[a]	˜1.3	V	16.1	Chars
Thermoplastic polymers					
Polyethylene –Low density	940	1.9	0.35		
Polyethylene –High density	970	2.3	0.44	46.5	130-135
Polypropylene -Isotactic	940	1.9	0.24	46.0	186
Polypropylene -Syndiotactic					138
Polymethylmethacrylate	1190	1.42	0.19	26.2	˜160
Polystyrene	1100	1.2	0.11	41.6	240
Polyoxymethylene	1430	1.4	0.29	15.5	181
Polyvinylchloride	1400	1.05	0.16	19.9	-
Polyacrylonitrile	1160-1180	-	-	-	317
Nylon 66	˜1200	1.4	0.4	31.9	250-260
Thermosetting polymers					
Polyurethane foams	V	˜1.4	V	24.4	-
Phenolic foams	V	-	V	17.9	Chars
Polyisocyanurate foams	V	-	V	24.4	Chars

a V = variable

All will burn under appropriate conditions, reacting with oxygen from the air, generating combustion products, and releasing heat. Thus, a stream or jet of a gaseous hydrocarbon can be ignited in air the oxidation process. Flame is a gas phase phenomenon and, clearly, flaming combustion of liquid and solid fuels must involve their conversion to gaseous surface, but for almost solids, chemical decomposition or pyrolosis is necessary to yield products of sufficiently low molecular weight that can volatilize from the surface and enter the flame. As this requires much more energy than simple evaporation, the surface temperature of a burning solid tends to be high

(typically 400°C). Exceptions to this rule are those solids which sublime on heating, i.e. pass directly from the solid to the vapour phase without chemical decomposition.

The composition of the volatiles released from the surface of a burning solid tends to be extremely complex. This can be understood when the chemical nature of the solid is considered. All those of significance are polymeric materials of high molecular weight, whose individual molecules consist of long 'chains' of repeated units which in turn are derived from simple molecules known as monomers (Drysdale, 1999).

3.2 Addition of Suppressants

A flammable mixture may be rendered non-flammable by the addition of a suitable suppressant. Additive such as nitrogen and carbon dioxide act as inert diluents, increasing the thermal capacity of the mixture (per unit mass of fuel) and thereby reducing the flame temperature, ultimately to below the limiting value when flame propagation will not be possible. This is illustrated in Figure 3.2 (Hertsberg, 1982) which shows the variation of flame temperature, determined by infra-red radiance measurements, as nitrogen is added to soichiometric methane/air mixtures. The limiting flame temperature (1500-1600 K) corresponds with 35-38% N_2 in aggerement with values calculated on the basis that the lower flammability limit is determined by a critical limiting temperature of this magnitude. Consequently, it is anticipated that the burning velocity at the limit will be similar to that of a limiting methane/air mixture.

However, if chemical inhibitors are present in the unburnt vapour/air mixture, there will be significant reduction in burning velocity without corresponding reduction in flame temperature. Halogen-containing species are particularly effective in this respect (Drysdale, 1999).

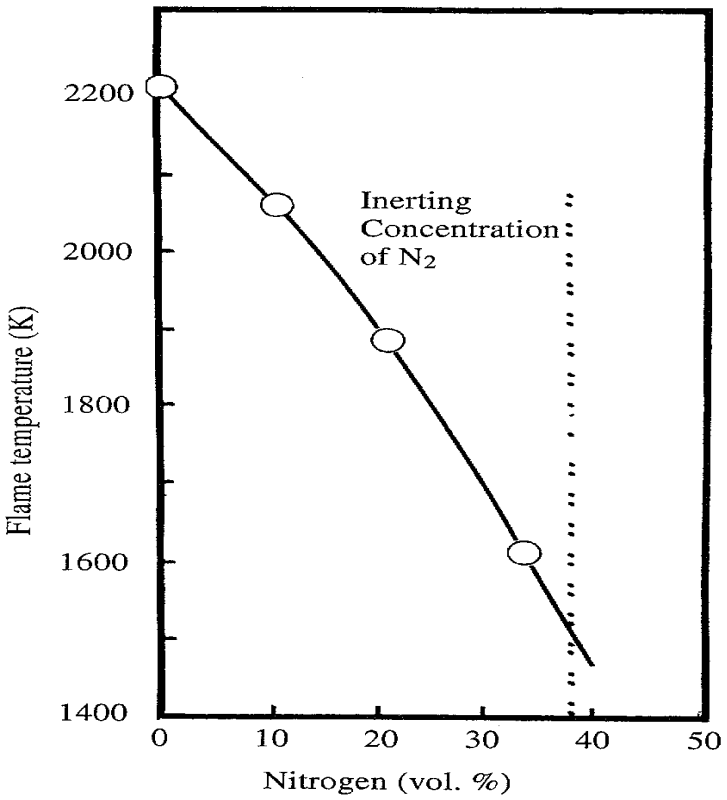


Figure 3.2 Measured premixed flame temperature during explosions in a 3.7 m diameter sphere, stoichiometric methane/air mixtures with addition of nitrogen (Hertzberg, 1982)

3.3 Introduction of Flame Retardants

Flame retardants save lives and property and protect the environment by helping to prevent fires from starting. It is possible to treat most potentially flammable organic materials in the modern world with special additives to make them more difficult to ignite and spread fire. Use of these additives - flame retardants - plays a major role in fire prevention.

Every day in Europe there are about 12 fire victims and 120 people severely injured. About 80 % of all fire deaths occur in residential buildings. The people most at risk are the very young and the elderly because they are at least able to escape in the event of a fire. The total economic damage is estimated at about 25 billion € per

year in Europe. In Germany alone, compensation costs covered by insurance coMPanies amount to 1.5 billion € per year and there are about 200 major fire incidents with damages in excess of 0.5 million €.

Flame Retardants are additives that can be added to or applied as a treatment to organic materials such as plastics, textiles and timber. Alternatively they can be used during the production process as a chemical modification of some plastic materials. Their effect is to reduce the chances of a fire starting by providing increased resistance to ignition. In the Figure 3.3, it is illustrated that the temperature increased rapidly 3 minutes after starting of fire.

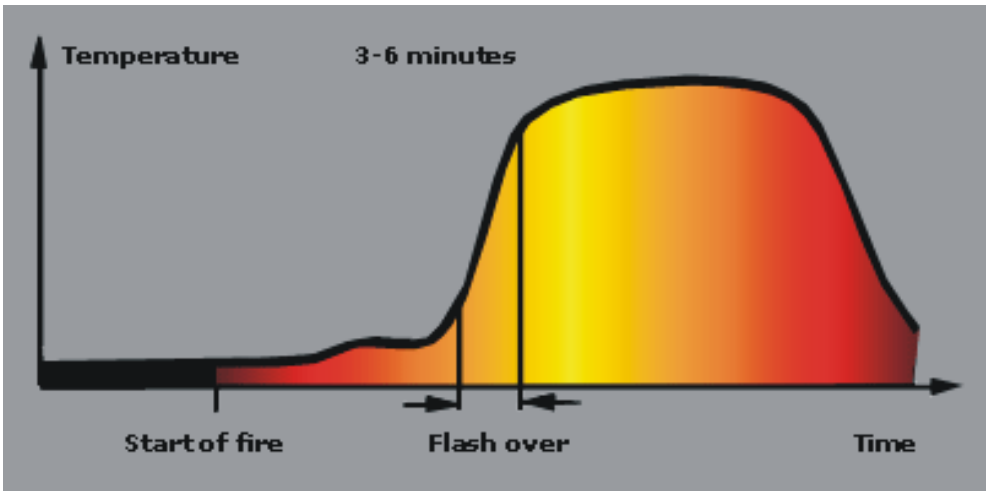


Figure 3.3 Temperature changing to time (www.cefic-efra.org, 2007)

Even if ignition does occur, flame retardants will act to delay the spread of flame, providing extra time in the early stages when the fire can be extinguished or an escape can be made. Used in combination with smoke detectors, fire alarms and sprinkler systems, flame retardants provide the most effective method available of protecting life and property.

This fact was clearly demonstrated in a series of full scale room/corridor tests carried out at the National Institute for Standards and Technology in Washington DC which coMPared the performance of a typical range of products in flame retarded

and non-flame retarded forms. The results of these tests showed, incontrovertibly, that the flame retarded products were safer than the alternative.

In the room containing the flame retarded products there was:

- 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 and
- Little difference in the production of smoke.

Over the past 20 years flame retardants have played a major role in increasing safety in all areas of our lives - at home, at work, at leisure, in transport, in the healthcare industry.

Without the use of flame retardants in all these areas, lives would be at far greater risk and some of the rapid developments which have occured during this period would not have taken place because our safety and the safety of our families would have been jeopardised.

The electronics industry is a prime example. Without the use of flame retardants in the materials used to produce modern home entertainment and domestic equipment, including TV, video and Hi-Fi, it is unlikely that the industry would have been able to move forward at such a pace. Nor would have been seen - or benefited from - the massive growth over recent years in the use of office and personal computers. Figure 3.4 shows a TV fire.

Flame retardant additives have made all these products inherently safer. This is clearly demonstrated by the number of fires caused by television sets in the UK between 1974 and 1993 - the period during which the development and use of effective flame retardants has progressed.

The UK Department of Trade and Industry published a report from the University of Surrey on Risks and Benefits in the Use of Flame Retardants in Consumer Products. The University of Surrey report emphasises the clear benefits, explaining that flame retardants bring in terms of saving lives. EFRA views this report as an important contribution to the scientific understanding of flame retardants. The report comes at a time when there are isolated proposals to phase-out the use of certain flame retardants. In this context, the report represents a clear warning against any rush to move out of individual flame retardants in view of the demonstrated benefits these products provide in terms of saving lives.

Figure 3.4 An electronic fire

In 1974 there were over 2,300 recorded TV set fires in the UK. In 1989, despite the fact that the number of TV sets in use increased many times over, there were only 470. In Europe since the early 1990s this trend has tended to level off, or even to increase again in countries such as the UK and Sweden. The range of TV set fires in Europe is 12 to 100 fires per million TV sets per year, an order of magnitude higher than in the US where the fire safety ratings for TV set enclosure materials has been historically high. TV set fires can have a dramatic iMPact on life and property. To avoid a possible future general increase in TV set fires, fire safety requirements in standards should be increased, and public awareness of the importance of fire safety

in home appliances be heightened. Figure 3.5 (www.cefic-efra.org, 2007) illustrated the trend in the UK.

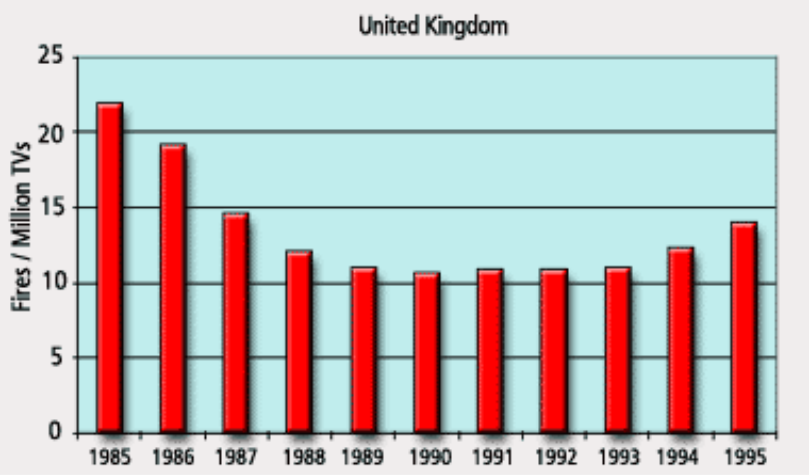


Figure 3.5 Trends in number of TV fires in the UK. Source: Home Office Statistical Bulletin, Summary Fire Statistics, UK (normalised per million TVs) (www.cefic-efra.org, 2007).

Moreover, a life-cycle assessment study recently completed in Sweden has found that over the lifetime of television set, there are less emissions to the environment from a TV set containing flame retardants in the outer casing than from a TV set without such flame retardant protection. Since flame retardants have been removed from TV set casings, TV set fires occur about 10 times more often. As fires themselves are a major source of polyaromatic hydrocarbons (PAH, a class of carcinogenic substances found in combustion smoke) and dibenzodioxin and –furan emissions, the use of flame retardants significantly decreased such environmental emissions (ca. 60 and 10 times lower respectively). Therefore, the use of flame retardants to prevent fires is beneficial from a human health and an environmental protection standpoint.

3.3.1 Flame Retardants at Work, Transport and Healthcare

Use of flame retardants inhibits the ignition of all these products and even when a fire does start they will slow down the rate of spread, giving us and our families a much improved chance of escape. This simple single fact has been demonstrated in

many tests, carried out by both coMPanies responsible for the development of flame retardants and by independent fire safety authorities.

One such test (Figure 3.6) (www.cefic-efra.org, 2007) compared the performance of an upholstered chair manufactured from non-flame retarded materials with one manufactured to comply with the UK Upholstered Furniture Fire Regulations (1988) and including flame retardants. A 30kW gas burner was used to ignite the fire in both chairs.

Within two minutes the non-flame retarded chair was burning fiercely. It took 22 minutes for the flame retarded chair to reach the same level.

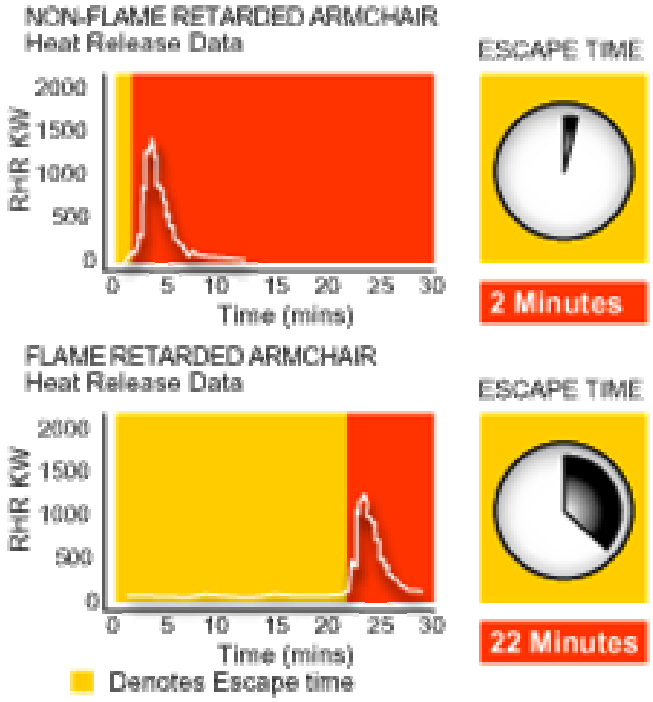


Figure 3.6 Comparison of the performance of non-flame retardant chair an flame retardant chair by means of flame retardancy (www.cefic-efra.org, 2007)

3.3.2 Fire safety standards

To reduce the toll of deaths and injuries, and the huge cost to society, fire safety standards are essential in all areas of modern life, and in particular for buildings and interior decoration, furniture, consumer equipment and transport vehicles. For the consumer, fire safety standards ensure that products offer a minimal standard of safety in use. In some cases, manufacturers also offer products with higher levels of fire safety as an element of consumer choice. For authorities, fire safety standards reduce the number of fires occurring and their gravity, thus reducing the costs to fire services and to society. For industry, fire safety standards ensure a level playing field between competitors, and provide a tool for showing that products are consumer safe.

Fire safety standards can address the fire behaviour (resistance to ignition, burning behaviour once alight) both of materials used in products and of the final product, as well as safety features of product design, fire alarms and extinguishers, emergency exits in buildings. There is an increasing tendency to develop fire performance engineering approaches to building and product fire safety standardisation: this requires the overall system (building or product) to offer a given level of fire safety, allowing designers to achieve this by optimal combinations of fire prevention (use-design, flame resistant materials), fire spread limitation (design, flame retardant materials, extinguishing) and user safety through escape and safety specifications.

Fire safety standards are defined by standardisation organisations, industrial associations, authorities or fire organisations. Conformity to standards can be obligatory (required by law or by, for example, building regulations), may be required by insurers, or can offer producers a marketing advantage. Conformity to fire safety standards can enable manufacturers to demonstrate that products fulfill the requirements of the EU General Product Safety Directive (2001/95/EEC) of being safe to be put on the market.

Conformity to fire safety regulations is tested - by product manufacturers, officially recognised testing institutes and independent experts - according to methods laid down in the standard, in particular fire tests. Certain standards specify different fire safety labels (classes) for products as a function of the results achieved in fire tests. Harmonisation of fire safety standards is a continuing process throughout the world.

In the European Union standards are now issued by the European Committee for Standardisation (CEN) and the European Committee for Electrotechnical Standardisation (CENELEC). On a global scale harmonisation of standards and recognition of test results is being undertaken by the IEC (International Electrical Commission) for electrical equipment and by ISO (International Organisation for Standardisation) for all other technical fields. In addition to these international authorities, there are fire safety standards issued by national bodies (e.g. Building Regulations, UK and ASTM in the USA), industry bodies (e.g. FAA, SOLAS, UIC) and fire safety organisations (eg. NFPA).

As part of large and small scale fire tests, which are designed to provide data on combustibility, ignitability, flame spread, heat release and smoke and gas generation both flame retarded and non-flame retarded products and components are included. Without fail, these tests demonstrate that the use of flame retardants inhibits ignition and reduces combustibility - particularly in the early stages of a fire, thus lengthening the potential escape time and providing additional time for corrective action to be taken.

Depending on the test methods specified in standards, conformity to fire safety standards can often be demonstrated by testing the complete final product, but this can involve large-scale and expensive testing, and compliance can often be achieved by instead using fire-safe materials and flame retardants (with conformity being

demonstrated using small-scale tests of material samples) (www.cefic-efra.org, 2007).

3.3.3 Fire Retardants

3.3.3.1 Combustion

Combustion can be defined as the rapid uncontrolled reaction of oxygen with a substrate. A feature of this process is that it is generally exothermic and as a consequence of the heat of combustion the reaction of the fuel with oxygen is accelerated resulting in a self propagating reaction. While the reaction can be viewed as an extreme case of oxidation, the process is more difficult to control, and as with thermal oxidative degradation of polymers, once the process is started it is extremely difficult to control or stop. Thus any fire-retardant strategy should focus on the prevention of initiation of a combustion reaction or intervene rapidly if combustion has been initiated.

3.3.3.2 Combustion of Polymers and the Combustion Cyle

The increasing diffusion of synthetic polymers into the market place has greatly increased the “fire risk” and the “fire hazard”, that is, respectively, the probability of fire occurence and its consequence either on humans or on structures.

To enable effective use of polymers, flame-retardant materials have to be added to polymer-based formulations. The role of these additives is to:

- slow down polymer combustion and degradation (fire extinction)
- reduce smoke emission
- avoid dripping of hot or burning material.

A key safety element of a fire situation is to allow people the maximum amount of time possible to escape a fire. Fire safety regulations are developed with this factor in mind. The stringency of the regulations often depends on the time needed to safely escape the environment of a fire.

3.3.3.3 Flammability of Polymers

The flammability of polymers can be determined by their reactivity with oxygen. The limiting oxygen index (LOI), defined as the minimum amount of oxygen required to sustain combustion under specified conditions, is a quantitative measure of the tendency of materials to burn (Figure 3.7) (Xanthos, 2005). In a flame-retardant system, study of the LOI can provide information on the effectivenes of flame-retardant materials.

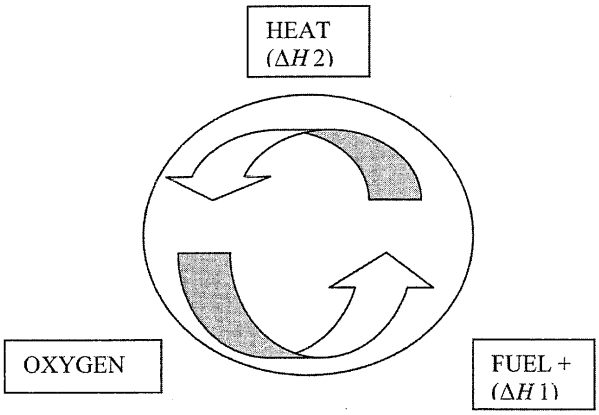


Figure 3.7 The combustion cycle (Xanthos, 2005)

Depending on the polymer and applicable fire retardance standarts, flame retardats are chosen to interfere with one or more stages of the combustion process: heating, decomposition, ignition, flame spread, smoke density. Fire retardants have to inhibit or even suppress the combustion process.

Fire retardants can be divided into halogen-containing and non-halogen-containing. This is a useful categorization as it leads into an explanation of their different modes of actions. Chief among the non-halogen fire retardants are aluminum trihydrate (ATH) and magnesium hydroxide (MOH), as well as materials such as melamine and derivatives, ammonium polyphosphates, antimony oxide, and boron-containing materials such as zinc borate.

3.3.3.4 Mechanisms of Fire Retardant Action

Flame retardants can act chemically and/or physically in the condensed phase and/or in the gas phase. In reality, combustion is a complex process occuring through simultaneous multiple paths that involve competing chemical reactions. Heat produces flammable gases from pyrolysis of the polymer and if the required ratio between these gases and oxygen is attained ignition and combustion of the polymer will take place.

Flame retardant materials consists of hydroxides (or hydrous carbonates) that endothermically decompose at temperatures between 200-400 ºC liberating water steam and/or carbon dioxide. Besides the cooling effect and quenching of the flames by inert gases, flame retardance is enhanced by formation of a kind of ceramic layer being formed on the compound surface that protects the ignitable materials from further attacks by flames and heat. Figure 3.8 (Kirschbaum, 2001) shows this mechanism of flame retardant materials in a fire.

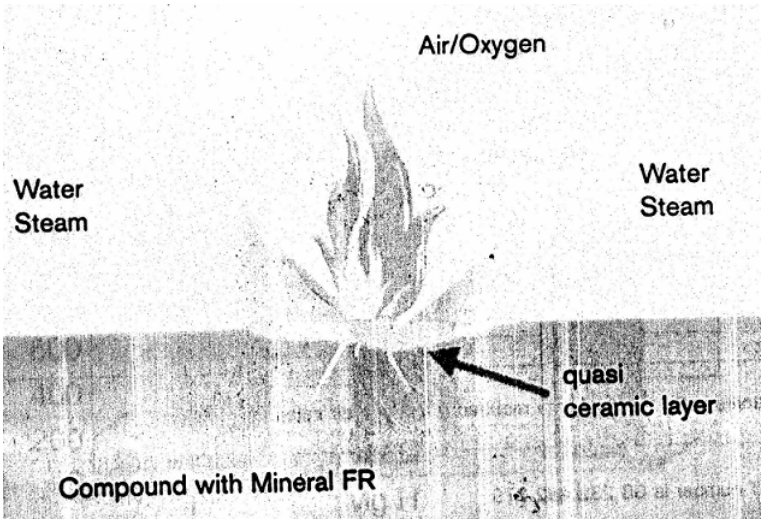


Figure 3.8 Effects of mineral flame retardants (Kirschbaum, 2001)

3.3.3.5 Condense Phase

In the condensed phase, three types of processes can take place:

- Breakdown of the polymer, which can be accelerated by flame retardants, leads to its pronounced flow which decreases the iMPact of the flame.

- Flame retardants can leave a layer of carbon (charring) on the polymer's surface. This occurs, for example, through the dehydrating action of the flame retardant generating double bonds in polymer. These processes form a carbonaceous layer as a result of cyclization and cross –linking.

- Heat absorption through materials such as ATH that have a very high heat capacity.

3.3.3.6 Chemical Effects in the Gas Phase

In the gas phase, the process of combustion is slowed by reactive species that interfere chemically with the propagation process of the fire. The flame retardants themselves or species derived from them interfere with the free radical mechanism of the combustion process. This slows or stops the exothermic processes that occur in the gas phase and results in a cooling of the system and a reduction in the supply of flammable gases. This working principle of flame retardants materials is demonstrated in Figure 3.9 (Xanthos, 2005).

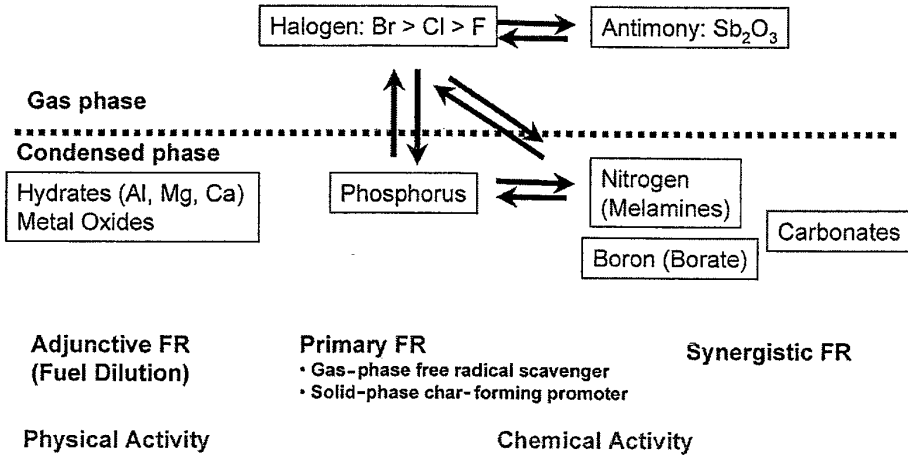


Figure 3.9 Chemical mechanism of the flame retardancy (Xanthos, 2005)

3.3.4 Classification of Fire Retardants

Fire retardant materials can be classified into two main categories; halogenated and halogen free flame retardants. Halogen containing flame retardants act in the gas phase and produce incomplete burned substances like black smoke (soot particles) and toxic CO. Thus, halogenated systems, especillay brominated systems, play an important role in North America, an explanation for the increasing percentage of people killed by smoke inhalation. Figure 3.10 shows the smoke formation of polypropylene compounds containing different flame retardants (Weber, 2000).

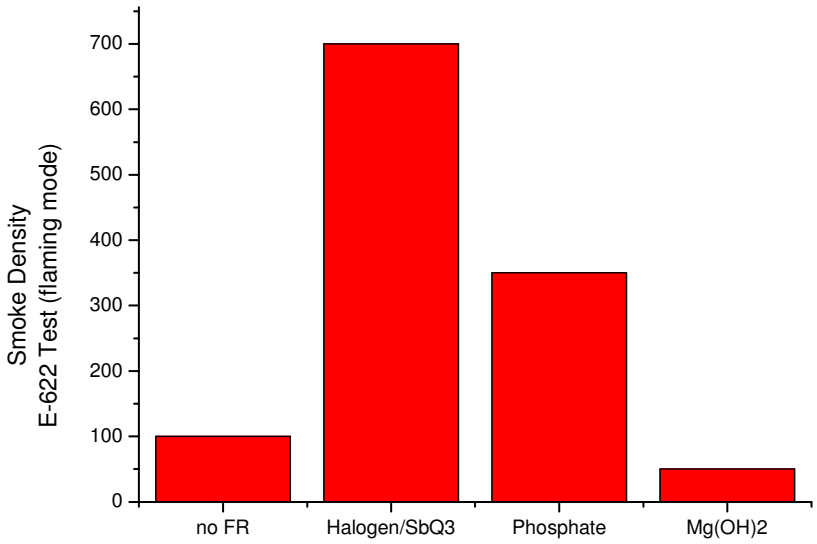


Figure 3.10 Smoke density of PP compounds with different flame retardant (Weber, 2000)

A lot of toxic gases are found in real fires. The most serious is carbon monoxide, CO, a highly toxic and non-irritating gas. The peresence of CO disturbs the respiration process immediately as it blocks the oxygen transport of the blood. Again, traditional solutions based on halogens have serious drawbacks compared to mineral flame retardants; magnesium hydroxide. Figure 3.11 illustrates the CO amounts of different flame retardants (Weber, 2000)

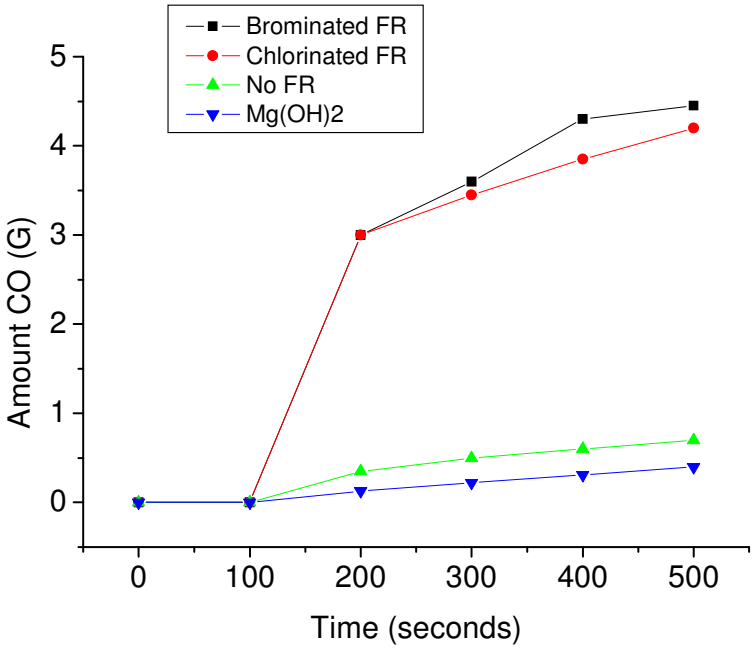


Figure 3.11 CO formation of PP compounds with different flame retardants (Weber, 2000)

Besides the CO formation, halogens may support the formation the other highly toxic substances such as dioxins and furans in fire conditions. In the most cases these compounds do not directly kill people as they are strongly bound to soot particles. However, it is time consuming and very expensive to get buildings cleaned and decontaminated from such substances after a fire. Sometimes the rebuilding is the only solution.

Halogen free flame retardant materials are much more safety when it is coMPared with the halogens. Metal hydroxide flame retardant materials are commonly used material in this matter. Metal hydroxides first decompose endothermically and release water. The endothermic decomposition serves to remove heat from the surroundings of the flame and thus cool the flame. Pyrolsis decrases in the condensed phase as a result of this action. The release of water dilutes the amount of oxygen capable of ingress to the flame and avoids the critical fuel/oxygen ratio (physical action in the gas phase). Both mechanisms combat ignition. In some fire

tests for electric/electronic cable applications, the ignition has to be significiantly delayed. Thus, metal hydroxides are suitable for these applications. Moreover, after the degradation, a ceramic-based protective layer created, which improves insulation (physical action in the condensed phase) and gives rise to a smoke suppressant effect (chemical action in the condensed phase). The ceramic-based protective layer ensures efficient protection of the polymer during combustion, leading to a severe decrease in the heat release.

- Aluminum Trihydrate: Aluminum trihydrate is well known as the largest volume flame retardant used in the world, with a consumption of around 200.000 tons per annum, representing 43% of all flame-retardant chemicals in volume (about 29% in value). ATH came into wide use as a flame retardant in the 1960s, primarily as a result of demands of consume. At room temperature, ATH is very stable but when the temperature exceeds 205ºC as could happen in a fire situation, it begins to undergo an endo thermic decomposition with a heat of reaction of -298 kJ mol^{-1}. This decomposition, as shown below, is kinetically slow between 205ºC and 220ºC, but above 205ºC.

- Magnesium Hydroxide: Magnesium hydroxide functions in a manner similar to ATH. It liberates water of crystalation in a fire situation and in so doing it forms a barrier to the ingress of oxygen required for combustion. The material is also capable of absorbing heat, although the heat capacity value of 77,0 J K^{-1} mol^{-1} (crystalline) is lower than that for ATH.

Magnesium hydroxide is produced by extraction from ores, such as magnesite, dolomite, or serpentinite, and from brine/seawater. The material used as a flame retardant is generally of high purity (>98,5%). It is most often obtained from seawater/brine, although other ore-derived products can also be very pure. Three major processes relating to magnesium hydroxide are isolation from seawater/brine; the Aman process, which involves thermal decomposition of brine to yield a high purity magnesia that is converted to magnesium hydroxide; and the Magnifin

process, in which magnesium oxide is isolated from serpentine ore and converted to magnesium hydroxide.

Magnesium hydroxide is a white powder. Median particle sizes range from 0,5 to 5 µm and specific surface areas typically range from 7 to 15 m^2 g^{-1}, depending on size and morphology. It is used at high loading levels, usually in the range 40-65 wt. %. A key difference coMPared to ATH is the higher decomposition temperature of ca. 320ºC as shown in Figure 3.12 (Xanthos, 2005). This affords an advantage over ATH in that it may be used in commodity and engineering thermoplastics as well as thermoset resin systems processed at temperatures above 200ºC. From a chemical stanpoint, magnesium hydroxide is a much more alkaline than ATH. Since slurries in water (~5% w/w) can yield pH values of 10,5 or more, this property may need to be considered in some formulation.

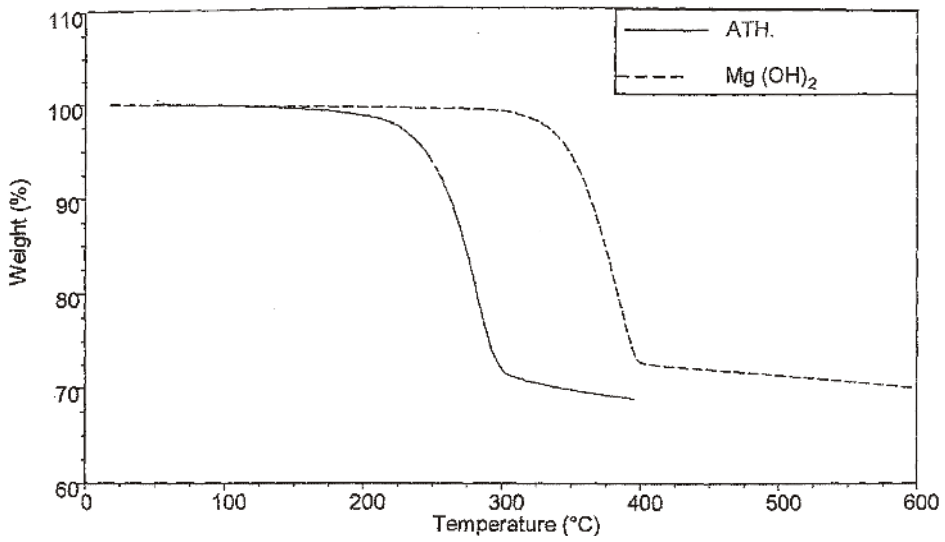


Figure 3.12 Comparison of the thermal degradation properties of magnesium hydroxide and aluminum trihydrate (Xanthos, 2005)

Magnesium hydroxide finds use in applications such as wire and cable, appliance housing, construction laminates, roofing, piping, and electrical components. Different grades are developed for different applications. The use of surface-treated grades is increasing as market demands move towards increased product and performance differentiation.

3.3.5 Nanocomposites Flame Retardancy

Nanocomposites have been demonstrated to reduce flammability, particularly through lowering peak heat release. In combination with conventional flame retardants such as magnesisum hydroxide or aluminum trihydrate, several polyolefin based wire and cable products have been developed which incorporate 5% nano clay to reduce the amount of conventional FR agents required and to improve physical properties.

3.4 Effects of Particulate Fillers on Flame Retardant Properties of Composites

Particulate fillers play a very significant role in flame retardant technologies for polymers. The main focus of this section is on those particulate fillers which function by endothermic decomposition and act as primary flame retardants in their own right. They have the advantage of a low environmental iMPact, being of low toxicity themselves, and with much lower smoke and toxic fume generation than some of the more traditional approaches. As a result, the use of this type of filler is now well established, and is continuing to expand as environmental awaresess grows.

Nano-clays are also discussed, as they are starting to show commercial promise. For completeness, fillers like antimony oxide, which work in combination with other additives, such as halogens, are also briefly discussed. This section concentrates on fire retardant effects, the synthesis and general properties of the various fire retardant fillers having already been described.

3.4.1 General Effects of Fillers on Polymer Flammability

Before discussing the special effects of fillers that are active fire retardants, it is useful to recognise that the addition of any particulate, non-combustible, filler to polymers can considerably affect their thermal stability, resistance to ignition and combustion, and the amount and nature of the combustion gases in terms of smoke, corrosion and toxicity. The main general effects are:

- Simple dilution, reducing the amount of fuel available from combustion.
- Changing the heat capacity and thermal conductivity, thus alerting the rate of heating and heat distribution.
- Various thermal effects, such as reflectivity and emissivity.
- Formation of solid residue (ash). This may possibly strengthen any polymer char.
- Slowing down the rate of diffusion of oxygen and pyrolysis products.
- Effect on polymer melt rheolgy (especially where dripping is a dripping factor).

The relative importance of these different effects is likely to vary with the polymer type, and its mode of degregation, and also with the type of flammability test.

On their own, the above effects are not usually sufficient to pass fire resistance tests and additional features are required. The main effects of this type are:

- Various solid state effects due to the chemistry of the additive, or it's surface, or shape, which promote polymer charring and the formation of a strong char.
- Heat adsorption due to endothermic decomposition.
- Release of gases such as water, which can affect solid state processes, provide a significiant dilution and cooling of the pyrolysis products, and possibly insulate the substrate from radiative energy transfer.

3.4.2 Fire Retardant Testing

Tests play a vital and somewhat controversial role in determining the effect of fillers on polymer flammability and some discussion is essential before examining the fire retardant performance of fillers.

The definition of flame retardancy needed for a specific application is often misleading. The material's behaviour, the "flammability" of the compound, is a first

hint that a finished product which uses this material may survive a real fire attack. Such material behaviour is generally and easily checked by loss on ignition (LOI).

LOI tests determine the oxygen concentration, which is needed to keep a sample of material burning. The main problem with testing conditions is that an oxygen concentration is always used which is higher than the usual oxygen concentration in the air. The LOI classification specifications are shown in the Table 3.3 (Rothon, 2003)

Table 3.3 LOI classification specifications (Rothon, 2003)

Grouping of test procedures	**LOI Classification**	
Fire propagation	<24	Flammable
Fire resistance	24-28	Limited flame resistance
Fire gases	29-34	Flame resistance
Integrity of service	>34	Extra flame resistance

Keeping in mind that oxygen is needed and used during a fire, the oxygen content of the air surrounding a burning plastic part will in any case be lower than the standard amount. Therefore it becomes clear that LOI-testing might be used as a quick test for development purposes in the lab. Here it can differentiate between samples created under similar conditions by slightly changing type and amount of ingredients.

Finished products can be better checked using full scale tests. There are many different full scale tests. In general, these tests intend to simulate potential practical fire attacks. In most cases, there is one test to check the materials behaviour against a match, a cigarette, or a lighter. A second, much more severe test, simulates an arson attempt with 20 litres of gasoline. For cables, there are single cable tests to check the burning behaviour of just one cable. Cable bundle tests simulate today's standard type of applications with more than one cable in a cable duct.

A real system test would not only include the fire retarded product, such as the cable, but also all other system parts like adhesives, paints, joints or repair kits. For cables, the after-installation of one cable after the other should also be kept in mind when judging the efficiency of a complete installation.

Every fire starts with the ignition of something which can be ignited under given circumstances. There are a lot of completely different ignition sources regarding the heat content and the time of ignition. A decision has to be made on how safe an individual part or the whole installation should be.

Large scale tests are used for assessing the real fire resistance of articles containing polymers. The construction of the article and even it's method of mounting can be important, and these tests are ususally carried out on complete items. They are also usually designed to replicate the fire hazard situation the article is likely to experience. Thus, the appropriate test for a cable jacketing will be different to that for chair upholstery or a wall covering.

Various smaller scale tests, are used for products development and quality control purposes. These are usually carried out on flat specimens, and are more related to material properties.

The main characteristics that one is trying to asses in small scale tests are:

- Ignitability: How readily a material will catch fire under certain condition.
- Propogation: How rapidly fire will travel once ignition is achieved.
- Heat Release: How much the fire will raise the temperature of the surrounding, thus causing the problem to spread.
- After glow and smouldering: This is an important, but often ignored factor, as it can cause re-ignition after a fire has apparently been extinguished.

- Dripping: Dripping can reduce the apparent flammability by removing heat from the specimen. On the other hand, it can also lead to propagation, if the drops themselves are burning.
- Smoke and toxic and corrosive gases.
- Char integrity: This is becoming of some importance for building products.

Unfortunately, all of these parameters are very dependent on the test conditions, especially the amount of radiant heat from an external source. Indeed, the rating of materials can be reversed in some tests merely by changing the radiant heat conditions.

3.4.3 Mineral flame retardants

In case of a fire, traditional mineral flame retardants react by releasing water (see box). This endothermic process cools the polymer surface and avoids fire propagation for some time. The higher the amount of water per volume of flame retardant, the more effective is the material as a mineral flame retardant. There are also other mineral functional fillers which not only evolve water, but also CO_2 or other gases. Their efficiency, however, is inferior to pure water evolving types.

Today, there are only two mineral flame retardants used in large volumes. Aluminium hydroxide ($Al(OH)_3$), also known as ATH (aluminium trihydrate) holds the lion's share of the flame retardants market with several 100,000 tonnes per year. For higher plastic processing temperatures, magnesium hydroxide is used. The world market for magnesium hydroxide as a flame retardant is around 20,000 tpa.

Table 3.4 Flame retardant reactions of huntite, hydromagnesite, ATH and MH (Schmidt, 1999)

Huntite:	$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2$
Hydromagnesite:	$Mg_4(CO_3)_3(OH)_2.3H_2O \rightarrow 4MgO + 3CO_2+4H_2O$
Magnesium hydroxide:	$Mg\ (OH)_2 \rightarrow MgO + H_20$
Aluminium hydroxide:	$2Al(OH)_3 \rightarrow Al_2O_3 + 3H_20$

For flame retardant systems there are as many requirements on the market as there are customers and applications. For each individual case, a system has to be developed in co-operation between flame retardant suppliers and the manufacturer of the finished flame retarded product. Table 3.4 (Schmidt, 1999) shows the fire retardants reactions of huntite, hydromagnesite, ATH and MH.

In some application areas such as nuclear power plants, or in public buildings where a lot of visitors are not familiar with the actual building site, the requirement is valid to have halogen-free flame retardant products to avoid smouldering conditions and smoke in case of fire. This requirement is not always technical; it is often purely political.

The same applies to the question of whether a product should be made from thermoplastics, elastomerics or thermosets. The demand to be able to recycle a product, often leads customers towards the decision to use thermoplastic materials. If the product is really recycled after use, this path is surely the right one. If the product is not recycled and the customer is not prepared to invest towards a recycling route, then the choice of the manufacturer should be based on properties or costs.

In the meantime, it is not impossible to also recycle thermosetting or elastomeric materials. It has been proven that there are better opportunities to re-use thermosetting parts than to grind and to recycle the material. The benefit of recyclable thermoplastic materials may turn to a loss in practical applications. In case of fire, the melting temperature of the thermoplastic material is easily reached and the material will start to melt and drip.

To illustrate one specific application area, let me use wire & cable again. There are as many different cables as there are applications. All cabling is sheathed with PVC-P and this market is growing by only 1%. Because new PVC-P cable developments are targeting the top level of technical properties, this one percent, and

a little bit more due to reformulation works, is made with ATH or MDH as a flame retardant and smoke suppressant.

There is an immense potential for mineral flame retardants in the short and medium term future. Just based on market development in Europe, 30,000 tonnes additional PVC-compound would consume mineral flame retardants. Usual formulations make use of 10-25% ATH and/or MDH, which accounts for an additional 3-7,500 tonnes mineral flame retardants for PVC cabling in Western Europe.

Carbon monoxide is the killer gas evolved during a fire. Smoke hinders vision and reduces the chances to escape if people are trapped. In a lot of application areas, where public traffic plays the dominating role, customers are now asking for low smoke and low carbon monoxide alternatives.

Smoke and carbon monoxide are formed because of the smouldering conditions of a fire. One potential development path is therefore to avoid materials from burning. This would mean to stop the use of plastics in such application areas; some customers try to follow exactly this route. Another option is to avoid smouldering conditions. A fire of plastic material which contains carbon and hydrogen, can be directed to create just water and carbon dioxide, if smouldering conditions can be avoided.

Mineral flame retardants are able to do this job. They are also active smoke suppressants owing to the high activated surface area created during the decomposition reaction. Because of this high efficiency, mineral flame retardants are used in halogen-containing and halogen-free material systems now and in the future (Schmidt, 1999).

3.5 Fire Retardant Fillers that Rely on Endothermic Decomposition

These fillers are of great industrial importance, and are the main subject of this chapter. They owe their fire retardant effectiveness to their ability to decompose endothermically at polymer pyrolysis temperatures, with the release of inert gases such as water. Thus, unlike some other flame retardants, they are able to combine a high level of flame retardancy, with low smoke and low toxic and corrosive gas emissions, and are thus becoming of increasing importance. One of the simplest such materials is aluminium hydroxide (also known as alumina trihydrate, ATH).

3.4.1 Potential Endothermic Flame Retardant Fillers

At first glance, there seem to be many materials that decompose endothermically and might be thought of as potentially useful, but there are other important criteria to consider. In particular, the material must be inexpensive, freely available in quantity, non-toxic, non-coloured, of low solubility and with a morphology suitable for filler use. A significiant decomposition (by experience at least 25% weight loss) is needed, if the endothermic process is to have a usefull effect. Furthermore, the decomposition temperature must be high enough to survive polymer processing, but low enough to exhibit a fire retardnig effect.

Only a few materials meet some, if not all of these criterias. The main candidates are summarized in Table 3.5 (Rothon, 2003). This list excludes other, well known materials, which have significiant endotherms, but where they are not sufficient to market the additive a primary flame retardant. These include, some clays and talc, and some stannes and borates. The materials in Table 3.5 are seen to cover a wide range of decomposition temperatures, and to include release of carbon dioxide as well as water. With such a range of materials available, it would be thought that a clear ranking of their performance would allow conclusion to be drawn, regarding the relative importance of the different parameters. Unfortunately, this is not the case at present.

Tablo 3.5 Principle candidate flame retardant fillers (Rothon, 2003)

Candidate material (common names and formula)	**Approximate onset of decomposition (ºC)** *	**Approximate entaplpy of decomposition (kj kg^{-1})**	**Volatile content % w/w**		
			H_2O	**CO_2**	**Total**
Nesquehonite $MgCO_3.3H_2O$	70-00	1750	39	32	71
Calcium sulfate dihydrate, Gypsum $CaSO_4.2H_2O$	60-130	Not available	21	0	21
Magnesium phosphate octahydrate, $Mg_3(PO_4)_2.8H_2O$	140-150	Not available	35.5	0	35.5
Alumina trihydrate, Aluminium hydroxide $Al(OH)_3$	180-200	1,300	34.5	0	34.5
Basic magnesium carbonate, Hydromagnesite $4MgCO_3.Mg(OH)_2.4H_2O$	220-240	1,300	19	38	57
Dawsonite (sodium form) $NaAl(OH)_2CO_3$	240-260	Not available	12.5	30.5	43
Magnesium hydroxide $Mg(OH)_2$	300-320	1,450	31	0	31
Magnesium carbonate sub-hydrate (MCS) $MgO.CO_2(0.96)H_2O(0.30)$	340-350	Not available	9	47	56
Boehemite AlO(OH)	340-350	560	15	0	15
Calcium hydroxide ($Ca(OH)_2$	430-450	1,150	24	0	24

* The decomposition temperatures are only approximate, as they are usually determined under dynamic conditions and depend on heating rate and sample conditions.

Despite these resevations, the presently available data suggest that, with the possible exception of nesquehonite, none of the candidate materials is a significantly more effective flame retardant than aluminium hydroxide (also known as alumina trihydrate or ATH), also magnesium hydroxide have some advantages in terms of smoke production. ATH come closest to meeting all of the criteria mentioned

previously, and this explains its current pre-eminence. It owes its relatively low cost and wide availability to its production on a vast scale as an intermediate in alumina manufacture. The main limitation of ATH is it's relatively low decomposition temperature (about 180ºC) which has restricted it's use in applicationa where processing temperatures above this, notably many thermoplastics. ATH also loses some of its cost advantages when the morphology or purity available from the alumina processes is not sufficient and special grades are required.

Nesquehonite ($MgCO_3.3H_2O$) is an effective flame retardant, as is to be expected from its large volatile content and endotherm, but suffers from a very low decomposition temperature, and is not produced commercially with attractive morphology or price. Its effect in unsaturated polyester is illustrated in Tablo 3.6 (Rothon, 2003).

Table 3.6 Contribution of various factors to the oxygen index effect (Rothon, 2003)

	% Contribution to heat balance effect		
Filler	Enthalpy of decomposition	Heat capacity of residue	Heat capacity of the evolved gases
$Al(OH)_3$	51.4	18.5	30.1
$4MgCO_3.3H_2O$	56.9	7.6	35.5

Calcium sulfate dihydrate is a low cost material with significiant fire retardant effectiveness. It is restricted by its low thermal stability, but is reported to have some applications in thermosets, such as unsaturated polyesters.

Magnesium phosphate cotahydrate appears to have interesting properties, although of limited thermal stability, and the present author has obtained excellent results with it in some thermosets. It has received little scientific or commercial interest to date. It has a relatively low specific gravity, which could be attractive in some applications. There are other magnesium phosphates with similar properties.

Basic magnesium carbonate (hydromagnesite, $(Mg_4(OH)_2(CO_3)_3.3H_2O)$ is an effective flame retardant, and can be formed from nesquehonite, although it is usually synthesized directly. It is more stable than nesquehonite and used on a small scale as a flame retardant and smoke suppressant, principally in elastomers. It is generally more expensive than ATH, and its readily available forms tend to consist of high surface area, platy particles, not ideally suited for highly filled polymer applications. This has probably limited its use.

Significiant workable deposits containing natural basic magnesium carbonate exist. These are usually associated with the mineral huntite ($3MgCO_3.CaCO_3$). Flame retardant fillers based on these deposits have been commercially developed. Unfortunately, it is not economic to remove huntite. The peresent author has found (by x-ray analysis of the ash) clear evidence that huntite decomposes under oxygen index test conditions. Even so, it does not appear to be such a good flame retardant as the basic salt and this reduces the effectiveness of the mixture (Rothon, 2003).

CHAPTER FOUR

EXPERIMENTAL PROCEDURE

4.1 Purpose

Inasmuch as huntite/hydromagnesite is very new materials there are not so much investigations on it. The flame retardancy properties of huntite/hydromagnesite is already proved. However, there is no any source about size distribution effects of it when it is added to the polymer composite materials. In the industry, normally huntite/hydromagnesite is used as an additive below 20 μm. In this research, it is studied that the flame retardant intensity will be changed if we change the size distribution. With this regard, the main objective of this research is to investigate the effect of the size distribution and the content of the mineral additives in the flame retardancy of the plastics.

Prior to production of composite materials, huntite/hydromagnesite mineral with different size particle was produced using excavating, crushing, grinding, classification and sedimentation processes. Huntite/hydromagnesite mineral was ground at particle sizes of 10 μm, 1 μm and 0.1 μm. The ground minerals with different particle size and content levels were added to the plastic compounds to produce composite materials. In the mineral processing, classification was usually water, and wet classification was generally applied to mineral particles which are considered too fine to be sorted efficiency by screening. With sedimentation, submicron or nanosize minerals were produced in the range of 1 μm and 0.1 μm. Particle size distribution of huntite/hydromagnesite particles was measured to coMPare powders in application.

After fabrication of huntite/hydromagnesite reinforced plastic composite samples, they were characterized by using DTA-TG, FTIR, XRD and SEM-EDS. Mechanical and electrical properties of the composites were evaluated through tensile testing,

hardness, multimeter and empedance machines. In addition, flame retardancy test were performed as a main objective of this research. By this way the effect of size distribution of the additives and the effect of the content levels of the additives in the plastic compounds by means of flame retardancy are measured with this regard.

4.2 Materials

In the experiment, huntite/hydromagnesite mineral was used as flame retardant reinforced particles. Commercially used escorene, solvay priex, exact and irganox polymerics were chosen in composite as matrix materials. Their properties will be explained in the next sections.

4.2.1. Huntite/hydromagnesite

There are many hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$) and huntite ($Mg_3Ca(CO_3)_4$) occurrences worldwide. The major impurities in these deposits are magnesite, aragonite, calcite and dolomite. Only a few of these occurrences are exploited for their flame retarding properties.

As it is said previosly that the main deposits of huntite/hydromagnesite minerals are in Turkey. The minerals used in this work are taken from a quarry in Denizli/Turkey region. A wiev of this quarry can be seen in Figure 4.1.

Georgiades *et al.* (1996) report that it consists of a mixture of huntite and hydromagnesite with very low iron content (Fe_2O_3<0.03%), high whiteness (~95%) relative to chemically produced MgO), the ore contains less than 8% total impurities (aragonite, calcite, magnesite, and other materials).

An average mineralogical composition, based on XRD and chemical analysis data of current ores is as follows: huntite (46%), hydromagnesite (46%), magnesite (4%), aragonite (3%), calcite (1%). A typical chemical analysis of the ore is MgO

(38.0%), CaO (9.5%), H_2O (9.1%), CO_2 (43.4%) and LOI (52.5%). In contrast to the other mineral flame retardants mentioned above, huntite/hydromagnesite has no simple metal hydroxide structure, but consists of two distinct carbonates (see Table 4.1 (Kirschbaum, 2001)).

(a)

(b)

Figure 4.1 Pictures showing huntite/hydromagnesite deposit in Turkey from different areas.

Table 4.1 Formulas and properties of huntite&hydromagnesite (Kirschbaum, 2001).

Name	Formula	Physical Density	Temperature Stability
Huntite	$Mg_3Ca(CO_3)_4$	2,70 g/cm^3	>400 ^oC
Hydromagnesite	$Mg_4(OH)_2(CO_3)_3.3H_2O$	2,24 g/cm^3	240-250 ^oC

In the Serbia basin of Kozani, beds with known ratios of huntite/hydromagnesite are selectively mined and blended to obtain a marketable product of constant composition and quality. Primary processing consists of crushing to less than 10 mm and drying to less than 1% moisture. Final processing consists of de-agglomeration and air classification to obtain desirable particle shape and particle size distribution. Depending on the specifications of the final product, additional drying and surface treatment may be required (Georgiades *et al.*,1996).

The typical end product from this locality has a huntite/hydromagnesite ratio of 1:1 and 50% of the particles are between 0.5 and 0.7 μm in diameter. Material with high huntite content is ground finer, with 50% between 0.3 and 0.4 μm. Generally, 97% of particles in both products are below 5 μm and the TAPPI brightness is over 95% (Georgiades *et al.*, 1996). The stability of the product is intermediate between that of $Mg(OH)_2$ and ATH.

4.2.2 Escorene

It is a kind of polymer, in the class of Escorene EVA Copolymers. EVA copolymers are thermoplastic materials produced by the copolymerization of ethylene with vinyl acetate monomer. There are two basic classifications of EVA copolymers when defining major application segments. These segments are concerned with copolymers designed for thermoplastic extrusion, film compounds and molding processes and with those intended as components in hot-melt adhesives and wax blending applications (www.kimyatas.com.tr, 2007).

4.2.3 Solvay Priex

Multipurpose sealing adhesive materials for sealing different components of an electrochemical cell are provided. The sealing materials are acid, acid anhydride, acid ester or metallocene modified polyolefins that are capable of providing multiple sealing functionalities in a heat activated sealing process. These sealing polymers are capable of adhering to plain and textured metal, graphite and graphite-filled polymer composite separator plates (www.freepatentsonline.com, 2007).

4.2.4 Exact

EXACT is an ethylene octene copolymer produced using ExxonMobil Chemical's EXXPOL® Technology, exhibiting both plastic and elastomeric properties. This resin is designed for modification of both polypropylenes and polyethylenes in applications such as injection molding, extrusion blow molding, blown and cast film, and profile extrusion. EXACT complies with FDA regulation 21 CFR 177.1520 "Olefin polymers" may be used in materials or articles that contain food (www.dexplastomers.com, 2007).

4.2.5 Irganox

Ciba® IRGANOX offers extreme protection against overbake yellowing by terminating free radicals in conventional solvent-based and powder coating systems. Ciba® IRGANOX anti-oxidants are phenolic based anti-oxidants that hinder thermally induced oxidation of polymers where high temperature applications are used. Unlike hindered amines, anti-oxidants are consumed - and not regenerated - in the stabilization process (www.cibasc.com, 2007).

4.3. Processing

The procedure is started from excavating the mineral, then it follows other steps as shown in Figure 4.2. This experimental procedure includes excavating, grinding, sedimentation, seperating mineral powders according to the size distribution,

fabrication of huntite/hydromagnesite powder reinforced plastic composite materials and testing composites.

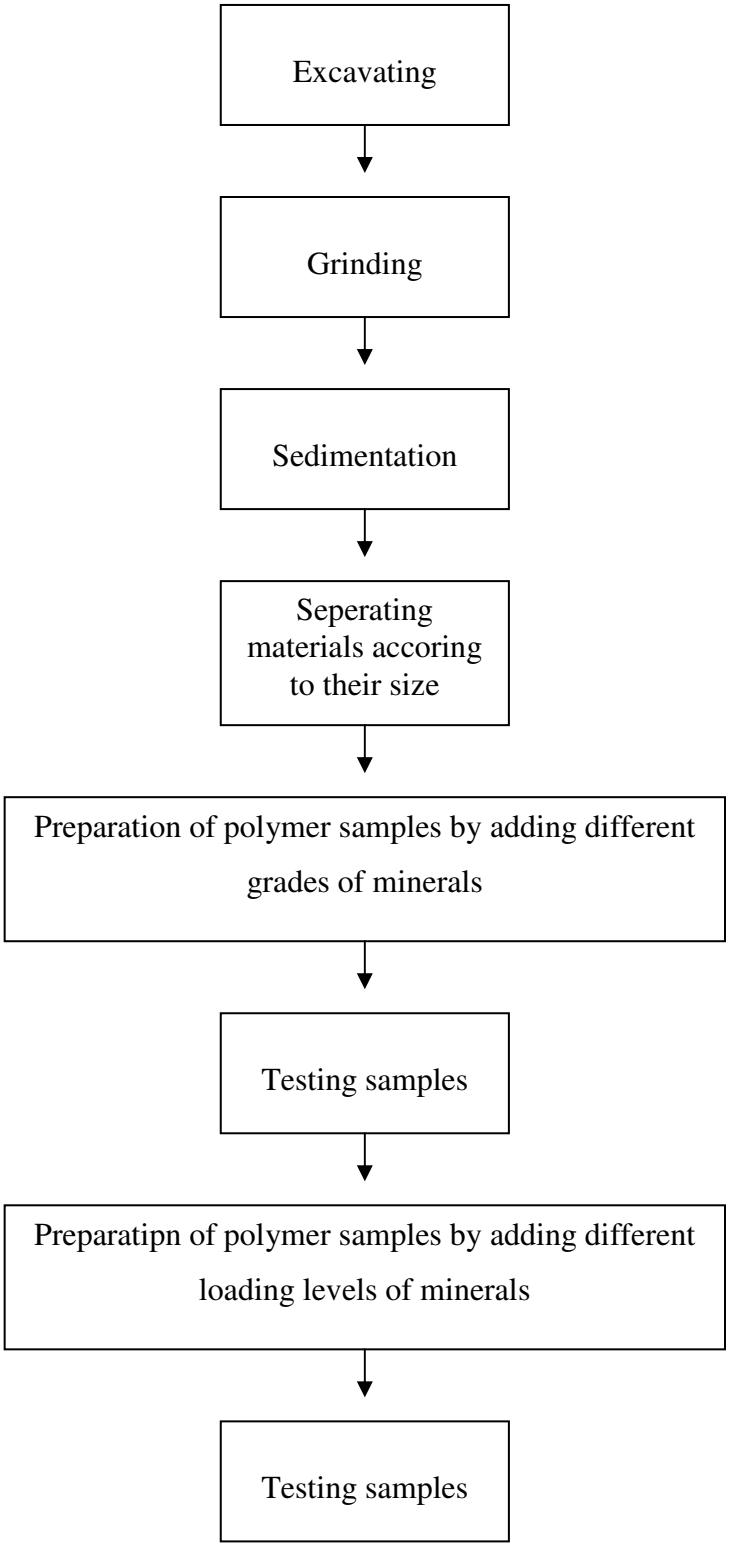


Figure 4.2 Flow chart of the experimental procedure

4.3.1 Excavating

The deposit of huntite/hydromagnesite is at around Denizli region. The technique used is open pit mining at the quarry. Open pit mining is the predominant exploitatiton method worldwide. It refers to a method of extracting rock or minerals from the earth by their removal from an open pit or borrow. Almost all nonmetallic minerals (96%), 87% of the metallic ores, and 60% of the coal in the United States are mined from the surface. In open pit a thick deposit is mined in benches or steps. (Figure 4.1.a).

Open-pit mines are used when deposits of commercially useful minerals or rock are found near the surface; that is, where the overburden (surface material covering the valuable deposit) is relatively thin or the material of interest is structurally unsuitable for tunneling (Hartman, 1987).

Open pit mines are dug on benches, which describe vertical levels of the hole. These benches are usually on 4 m to 60 m intervals, depending on the size of the machinery being used. Many quarries do not use benches, as they are usually shallow.

Most walls of the pit are generally dug on an angle less than vertical, to prevent and minimize damage and danger from rock falls. This depends on how weathered the rocks are, and the type of rock, and also how many structural weaknesses occur within the rocks, such as a fault, shears, joints or foliations. Figure 4.1-b shows the wall of the steps closely, and track of the operating machines can bee seen easily.

4.3.2 Crushing

In the this type of crushers, comminution is by impact rather than compression, by sharp blows applied at high speed to free-falling rock. The moving parts are beaters, which transfer some of their kinetic energy to the ore particles on contacting them.

The internal stresses created in the particles are often large enough to cause them to shatter. These forces are increased by causing the particles to iMPact upon an anvil or breaker plate.

Figure 4.3 (www.crusher-china.com, 2007) denotes a cross-section through a typices hammer crusher. The hammers are made from manganese steel or more recently, nodular cast iron, containing chromium carbide, which is extremely abrasion resistant. The beraker plates are made of the same material. In this study, heavy duty - hammer crusher was used in the plant. In that part mineral size was decreased from 20 cm to 1 cm which is not good enough to use a reinforced mineral material in a plastic composite.

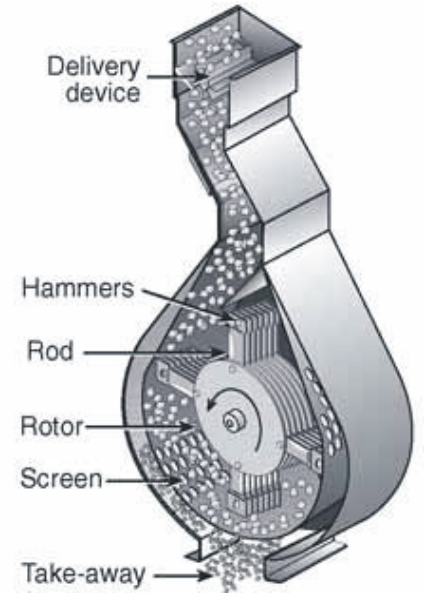


Figure 4.3 Cross section of a hammer mill.

4.3.3 Grinding

Grinding is the last stage in the process of communication; in this stage the particles are reduced in size by a combination of impact and abrasion, either dry or in suspension in water. It is performed in rotating cylinrical steel vessels known as tumbling mills. These contain a charge of loose crushing bodies-the grinding medium-which is free to move inside the mill, thus communicating the ore particles. The grinding medium may be steel rods, or balls, hard rock, or in some cases, the ore

itself. In the grinding process, particles between 5 and 250 mm are reduced in size to between 10 and 300 μm.

Grinding within a tumbling mill is influenced by the size, quantity, the type of motion, and the spaces between the individual pieces of the medium in the mill. As opposed to crushing, which takes place between relatively rigid surfaces, grinding is a more random process, and is subject to the laws of probability. The degree of grinding of an ore particle on its probability entering a zone between the medium shapes and the probability of some occurence taking place after entry. Grinding can take place by several mechanisms, including impact or compression, due to forces applied almost normally to the particle surface; chipping due to oblique forces; and abrasion due to forces acting paralel to the surface. These mechanisms distort the particles and change their shape beyond certain limits determined by their degree of elasticity, which causes them to break.

Apart from laboratory testing, grinding in mineral processing is a continuous process, material being fed at a controlled rate from storage bins into one end of the mill and overflowing at the other end after a suitable dwell time. Control of product size is exercised by the type of medium used. The speed of rotation of the mill, the nature of the ore feed and the type of circuit used.

Grinding in mining industry is almost always in closed circuit in which material of the required size is removed by a classifier, which returns oversize to the mill. Although virtually every grinding circuit has some form of classification, individual mills in the circuit can be open or closed.

In closed-circuit operation, no effort is made to effect all the size reduction in a single pass. Instead, every effort is made to remove material from the circuit as soon as it reaches the required size. When grinding to a specified size, an increase in capacity of up to 35% can be optained by close-circuit operation. The material

returned to the mill by the classifier is known as the circulating load and its weight is expressed as a percentage of the weight of new feed.

Closed circuit grinding reduces the residence time of particles in each pass, and so the proportion of finished sizes in the mill, compared with open-circuit grinding. This decreases overgrinding and increases the energy available for useful grinding as long as there is an ample supply of unfinished material present. As the tonnage of new feed increases, so the tonnage of circulating load increases, since the classifier underflow becomes coarser, but the composite mill feed becomes finer due to this increase in circulating load. Due to the reduced residence time in the mill, the mill discharge correspondingly becomes coarser, so that the diference in mean size between the composite feed and the discharge decreases (Wills, 1985).

4.3.4 Classification

Classification is a method of seperating mixtures of minerals into two or more products on the basis of the velocity with which the grains fall through a fluid medium. In mineral processing, this is usually water, and wet classification is generally applied to mineral particles which are considered too fine to be sorted efficiency by screening. Since the velocity of particles in a fluid medium is dependent not only on the size, but also on the specific gravity and shape of the particles, the principles of classification are important in mineral seperations utilizing gravity concentrators.

When a solid particle falls freely in a vacuum, it is subject to constant acceleration and its velocity increases indefinitely, being independent of size and density. Thus a lump of lead and a feather fall at excatly the same rate.

Classifiers consist essentially of a sorting column in which a fluid is rising at a uniform rate. Particles introduced into the sorting colomn either sink or rise according to whether their terminal velocities are greater or less than the upward

velocity of the fluid. The sorting colomn therefore seperates the feed into two products-an overflow consisting of particles with terminal velocities less than the velocity of the fluid and an underflow or spigot product of particles with terminal velocities greater than the rising velocity (Wills, 1985)

One of the common used classification technique is sedimentation. It describes the motion of molecules in solutions or particles in suspensions in response to an external force such as gravity, centrifugal force or electric force. Sedimentation may pertain to objects of various sizes, ranging from suspensions of dust and pollen particles to cellular suspensions to solutions of single molecules.

4.3.5 Fabrication of Composites

As shown in Figure 4.2, process is started with excavating the material from huntite/hydromagnesite quarry in Denizli. Then it is transported to the plant in Menderes. Here in that plant, material is crushed to 1 cm with the hammer mill as explained above. Then this 1 cm material is ground to 20 μm size with atritor mill.

This mill is manufactured for our material and our company specially. The grinding principle is that when the huntite/hydromagnesite mineral is subjected to a high degree of turbulent mixing in the cells created between the high velocity rotor blades, the high energy process reduces agglomeration of the mineral particles to a minimum point. To maintain grinding efficiency at an optimum level and preserving product brightness, high impact/shear forces are required.

As raw material contains 10% of moisture, burners are used in the plant for drying. The burner dries the material with a temperature of 100 ^{o}C during the material is in the mill.

Besides grinding process, this mill has a seperator inside. Therefore, before the material goes out from the mill, it is seperated by mill itself. The shear forces in the mill are sufficient to disperse all the particles during the residence time involved and

the air flow is indicated weel to classify the material the finer material than coarse. In addition, besides this seperator, there is another classifier in the plant, after grinding system. This part is a closed system; after classifier, finer material goes to the packing system but the coarser part goes back to the mill.

In that study, after the material is ground, it is seperated by seperation method to different size. By this way three fraction of the mineral are obtained getting those three fraction of the material, first step of this research is completed. Second step is to mix them with the polymer compounds. This part of the research is done in Loughboroguh University Department of Instutide of Polymer Technology and Material Enginnering. At that part, by changing the size grades of the additive mineral three different polymer compounds will be achieved, and then by changing loading levels of the additive 6 different polymer copmpound is achieved. Finally 8 polymeric composite samples were prepared.

First of all, it is indicated the ratio that how much huntite/hydromagnesite mineral is added to the plastic compound. For the finest, medium and the coarser huntite/hydromagnesite mineral the ratio was 60%. It can be obviously seen that more than half of the compound was additive. After blending plastic compound and additive well, the mixing is passed on two roll mill to obtain compression mould plaques. Those plaques are needed to do the testings. By this way, three different types of extrude tapes, which have different size distribution by means of additives, are produced. In this case reinforced materials are the same. Then the grain size of the additive is kept but content of the reinforced mineral is changed. Started from 49,75 % to 71,23%, we blend the additives to the plastic compound and then again mixing is passed on two roll mills to get compression mould plaques. After this step 6 different extrude tapes are fabricated for flame retardant materials.

4.4. Characterization

4.4.1. Powder Properties - Size Distribution

The particle size distribution of a powder, or granular material, or particles dispersed in fluid, is a list of values or a mathematical function that defines the relative amounts of particles present, sorted according to size (Jillavenkatesa, 2001). Particle size distribution is also known as grain size distribution.

The way a particle size distribution is expressed is usually defined by the method by which it is determined. The easiest-understood method of determination is sieve analysis, where powder is separated on sieves of different sizes. Thus, the particle size distribution is defined in terms of discrete size ranges: e.g. % of sample between 45 μm and 53 μm, when sieves of these sizes are used. The particle size distribution is usually determined over a list of size ranges that covers nearly all the sizes present in the sample. Some methods of determination allow much narrower size ranges to be defined than can be obtained by use of sieves, and are applicable to particle sizes outside the range available in sieves. However, the idea of the notional "sieve", that "retains" particles above a certain size, and "passes" particles below that size, is universally used in presenting particle size distribution data of all kinds.

There are different types of measuremet techniques for size distribution analysis, they are arranged as follow: (a) sieve analysis, (b) optical counting methods, (c) electrical counting methods, (d) sedimentation techniques, (e) laser diffraction methods, and (f) acoustic spectroscopy.

In this work laser diffraction method is used. These methods depend upon analysis of the "halo" of diffracted light produced when a laser beam passes through a dispersion of particles in air or in a liquid. The angle of diffraction increases as particle size decreases, so that this method is particularly good for measuring sizes below 1 μm. Advances in sophisticated data processing and automation have allowed this to become the dominant method used in industrial particle size distribution

determination. A particular advantage is that the technique can generate a continuous measurement for analyzing process streams. The machine used as laser diffraction was called Malvern Istruments, Mastersizer 2000.

4.4.2. Material Characterization

4.4.2.1 Differential Thermal Analysis-Thermograviometry (DTA-TG)

Thermal behaviours of huntite/hydromagnesite mineral, polymeric and composite material powders were evaluated to gain decomposition and phase formation at a heating rate of 10°C/min in the temperature range of 25-700 ^{o}C under oxygen atmosphere by using DTA/TG machine (DTG-60H Shimadzu). Al_2O_3 powder was used as a reference material. The enthalpies of solvent removal and combustion were obtained using TA 60WS Software of Shimadzu 60AH. This software derived the enthalpies by calculation of total area under each peak with respect to the base line from start to end temperature. In order to determine thermal behavior of materials, DTA/TG (Shimadzu DTG-60H) analyses were performed under O_2 flowing.

4.4.2.2 Fourier Transform Infrared (FTIR)

FTIR (Perkin Elmer) absorption spectra of the composite materials were only measured over the range of 4000 to 400 cm^{-1} at room temperature. FTIR (Perkin Elmer Spectrum BX) spectrums of composite materials were recorded to determine the organic components in the samples. After preparing powders at these temperatures, they were mixed with potassium bromide KBr. All of these five samples were characterized by FTIR. % Transmittance-wave length and % Absorbance-wavelenght curve can be obtained. According to the results, depending on temperature, variation of organic component's concentration can be determined by Fluka library supplied by Perkin-Elmer.

4.4.2.3 X-Ray Diffrection (XRD)

The phase analysis of huntite/hydromagnesite minerals was performed by the using a Rigaku D (Max-2200/PC Model XRD) X-ray Diffractometer equipment at 40 kV, 20 mA with a monochromatic CuK_{α} irradiation (wavelength, λ=0.15418 nm) by both θ-2θ mode and 2θ scan mode with a scan speed of 8 ^{o}/min.

4.4.2.4 Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS)

The microstructural cross-sectional areas of huntite/hydromagnesite reinforced polymeric composite materials were examined by using a JEOL JJM 6060 SEM attached with EDS. Size factors and wettability properties of huntite/hydromagnesite minerals were examined in the composites using SEM-EDS. X-ray maps of Mg, Ca, C and O in the composites were evaluated.

4.4.3. Mechanical Properties

4.4.3.1 Tensile Strength Test

The tensile strength of a material is the maximum amount of tensile stress that it can be subjected to before failure. The definition of failure can be variable according to material type and design methodology. This is an important concept in engineering, especially in the fields of material science, mechanical engineering and structural engineering.

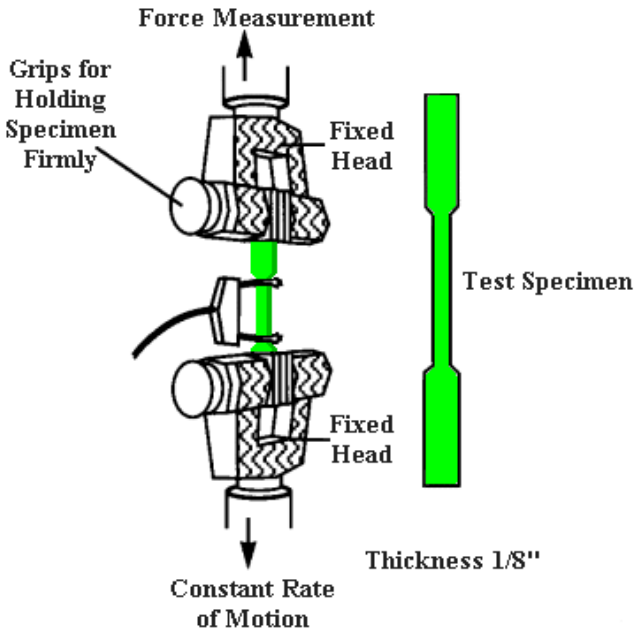


Figure 4.4 Tensile test principle
(http://www.matweb.com,2007)

Figure 4.4 from Quadrant Engineering Plastic Products, shows the test geometry. For this test, plastic samples are either machined from stock shapes or injection molded. The tensile testing machine pulls the sample from both ends and measures the force required to pull the specimen apart and how much the sample stretches before breaking.

4.4.3.2 Tear Strength Testing

Tear strength is the tensile force required to rupture a pre-slit woven fabric sample under controlled conditions. Edge tearing strength of paper is the load required to tear a sample over a V-notch fixture. Tear strength of rubber and thermoplastic elastomers are performed using the tests outlined in the standard. Special test software is used to analyze and report data. equipped to perform a constant rate of extension (CRE) compression test using standard 3 point bend fixtures or flex fixtures. The test requires measuring load and strain, or head travel of the test head. Load and deflection data can be translated into a stress-strain curve, and flexual properties extracted.

4.4.3.3 Elongation at Break Testing

The ultimate elongation of an engineering material is the percentage increase in length that occurs before it breaks under tension. Ultimate elongation values of several hundred percent are common for elastomers and film/packaging polyolefins. Rigid plastics, especially fiber reinforced ones, often exhibit values under 5%. The combination of high ultimate tensile strength and high elongation leads to materials of high toughness.

4.4.4. Electrical tests

Resistivity and dielectric constant of huntite/hydromagnesite reinforced polymeric composite materials were measured using Alpha-N high resolution dielectric analyser. Resistivity and dielectric constant of huntite/hydromagnesite reinforced polymeric composite materials were determined depending on frequencies in the range of 10^{-1} Hz and 10^{7} Hz at 1.00 AC voltage.

4.4.4.1 Conductivity

Electrical conductivity or specific conductivity is a measure of a material's ability to conduct an electric current. When an electrical potential difference is placed across a conductor, its movable charges flow, giving rise to an electric current. The conductivity σ is defined as the ratio of the current density J to the electric field strength E:

$$J=\sigma.E \qquad (4.1)$$

Due to the unavailability of large numbers of free electrons to participate in the conduction process, most polymeric materials are poor conductors of electricity (Table 4.2). The mechanism of electrical conduction in polymers of high purity is electronic (Callister, 2003).

4.4.4.2 Resistance

Electrical resistance is a measure of the degree to which an object opposes an electric current through it. Its reciprocal quantity is electrical conductance measured in siemens. Assuming a uniform current density, an object's electrical resistance is a function of both its physical geometry and the resistivity of the material it is made from:

$$R=lp/A \qquad (4.2)$$

Where "*l*" is the length, "A" is the cross sectional area, and "ρ" is the resistivity of the material. Electrical resistance shares some conceptual parallels with the mechanical notion of friction. The SI unit of electrical resistance is the ohm, symbol Ω. The resistance of an object determines the amount of current through the object for a given potential difference across the object.

$$R=V/I \qquad (4.3)$$

Where *R* is the resistance of the object, measured in ohms, equivalent to $J \cdot s/C^2$, *V* is the potential difference across the object, measured in volts and *I* is the current through the object, measured in amperes.

For a wide variety of materials and conditions, the electrical resistance does not depend on the amount of current through or the amount of voltage across the object, meaning that the resistance R is constant. Table 4.3 shows resistivities of some materials.

Table 4.2 Typical room-temperature electrical conductivities for 13 nonmetallic materials (Callister, 2003)

Material	Electrical Conductivity $[(\Omega\text{-m})^{-1}]$
Garphite	$3*10^{4}$-$2*10^{5}$
Ceramics	
Concrete (dry)	10^{-9}
Soda-lime glass	10^{-10}-10^{-11}
Porcelain	10^{-10}-10^{-12}
Borosilicate glass	~10^{-13}
Aluminum oxide	<10^{-13}
Fused silica	<10^{-18}
Polymers	
Phenol-formaldehyde	10^{-9}-10^{-10}
Polymethyl methacrylate	<10^{-12}
Nylon 6,6	10^{-12}-10^{-13}
Polystyrene	<10^{-14}
Polyethylene	10^{-15}-10^{-17}
Polytetrafluoroenthylene	<10^{-17}

4.4.4.3 Dielectric Constant

The relative static permittivity (or static relative permittivity) of a material under given conditions is a measure of the extent to which it concentrates electrostatic lines of flux. It is the ratio of the amount of stored electrical energy when a potential is applied, relative to the permittivity of a vacuum. The relative static permittivity is the same as the relative permittivity evaluated for a frequency of zero. In Table 4.4, dielectric constants of some materials are shown.

Table 4.3 Resistivities of some materials (www.wikipedia.com)

Material	**Resistivity**, ρ ohm-meter
Metals	10^{-8}
Semiconductors	variable
Electrolytes	variable
Insulators	10^{16}
Superconductors	0

Table 4.4 Dielectric constants of some materials (www.wikipedia.com)

Material	**Dielectric constant**
Vacuum	1 (by definition)
Air	1.00054
Teflon™	2.1
Polyethylene	2.25
Polystyrene	2.4–2.7
Paper	3.5
Silicon dioxide	3.7
Concrete	4.5
Pyrex (glass)	4.7 (3.7–10)
Rubber	7
Diamond	5.5–10
Salt	3–15
Graphite	10–15
Silicon	11.68
Methanol	30
Furfural	42.0
Glycerol	47–68
Water	88–80.1–55.3–34.5 (0–20–100–200 °C)
Hydrofluoric acid	83.6 (0 °C)
Formamide	84.0 (20 °C)
Sulfuric acid	84–100 (20–25 °C)
Hydrogen peroxide	128 aq–60 (−30–25 °C)
Hydrocyanic acid	158.0–2.3 (0–21 °C)
Titanium dioxide	86–173
Strontium titanate	310
Barium strontium titanate	15 nc–500
Barium titanate	90 nc–1250–10,000 (20–120 °C)
(La,Nb):(Zr,Ti)PbO_3	500-6000
High polymers	100,000
Sodium nitrate $NaNO_2$	100,000,000 (melt,600K)

4.4.5 Flame Retardancy

Flame retardancy testing was performed with Stanton Redroft FTA Oxygen Index Machine in Loughborough University Department of Instutide of Polymer Technology and Material Engineering. According to this test, oxygen index test measures the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion of a material initially at room temperature. The sample is ignited and burns from the top downwards. The rating or oxygen index is expressed in terms of this volume percent oxygen concentration.

There is no external heat provided once sample has ignited and the heat required to keep the sample burning comes from the flame itself. A useful description of the test and factors affecting results has been published by Wharton (1979). This test has been succesfully modelled. The oxygen index itself does not measure ignitability, afterglow, smoke or dripping. It is possible to observe whether after glow occurs and how much smoke is formed, but it must be remembered that this is under unrealistically high oxygen concentrations.

There is an upwards burning variant of the test, which is sometimes used. There is also a temperature index variant, in which radiant heat is used, and the temperature variation of the oxygen index is determined. The temperature index is quoted as the temperature at which the oxygen index is 20.8 (corresponging to the oxygen content of air). The temperature index is regarded by some as more relevant, especially as the oxygen concentration is more realistic, but it is more time consumineg to determine and has been little used to date (Xanthos, 2004).

CHAPTER FIVE
RESULTS AND DISCUSSIONS

In order to develop flame retardancy properties of the plastic materials, natural huntite/hydromagnesite mineral reinforced plastic composites were fabricated in this study. The effect of the size distribution and the centent of the additives in the plastics were evaluated. After huntite/hydromagnesite mineral was ground at particle sizes of 10 μm, 1 μm and 0.1 μm, ground minerals with different particle size and content levels were added to the plastic compounds to produce composite materials. In this chapter, results of powder characteristics are presented. Thermal, structural and microstructural properties of huntite/hydromagnesite reinforced plastic composite materials were given to correlate the effect of particle size in samples. Besides, mechanical, electrical and flame retardancy behaviours of the composites were discussed in details.

5.1. Powder Properties – Size Distribution

With Mastersizer 2000 the size distribution analysis is performed for each fraction of mineral. The comparision of the size distribution of those three particle sizes are shown in Figure 5.1. The powder samples were classified as HM1: huntite/hydromagnesite mineral–the finest grade, HM2: huntite/hydromagnesite mineral–the medium grade and HM3: huntite/hydromagnesite mineral–the coarsest grade. As expected from this results, it was found that HM3 sample possessed in the range of 1 μm and 30 μm. In HM2 sample, huntite/hydromagnesite mineral has the medium grade including the range of 1 μm and 5 μm. Upon investigating HM1 sample, which is huntite/hydromagnesite mineral–the finest grade, particle size distribution can be seen in the range of 0.1 μm and 1 μm. It can be roughly indicated that submicron or nanosize powders were produced from Figure 5.1. The fabrication of submicron or nanosize powders depends on production systems and parameters. Particle size distribution of as-recieved powders is like in HM3 sample after crushing

process. This sample can be used in fabrication of composite, but it causes to decrease performance of plastic materials, notably mechanical, electrical and flame retandancy properties. To eleminate these kinds of drawbacks, huntite/hydromagnesite mineral with submicron or nanosize should be used in applications.

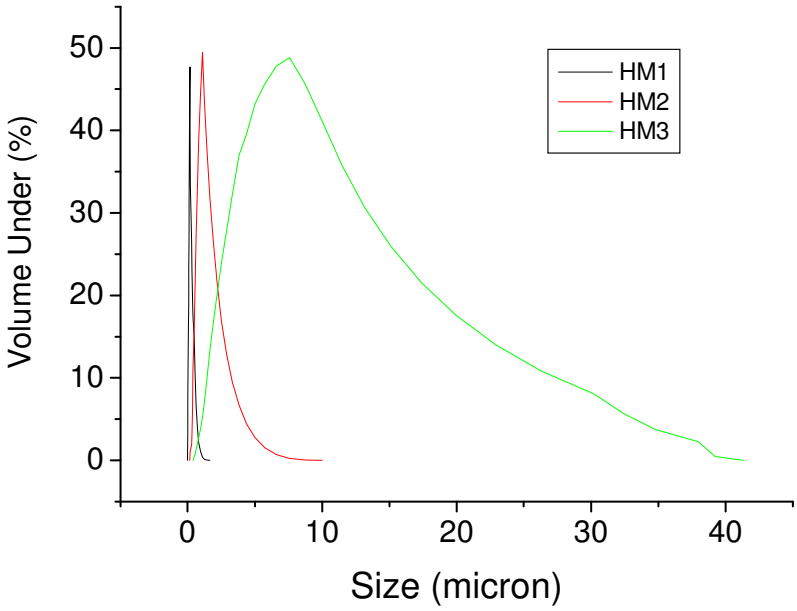


Figure 5.1 The coMParision of size distribution of three sizes of samples. HM1: Huntite/hydromagnesite mineral – The finest grade, HM2: Huntite/hydromagnesite mineral – The medium grade and HM3: Huntite/hydromagnesite mineral – The coarser grade.

As mentioned beforehand, crushing, grinding, classification and sedimantation are important processes in production of submicron or nanosize powders. With this respect, classification of powders after grinding is also important step prior to sedimantation process since classification is a method of seperating mixtures of minerals into two or more products on the basis of the velocity with which the grains fall through a fluid medium. The production way of submicron or nanosize particle is after sedimantation. Due to the fact that sedimentation describes the motion of molecules in solutions or particles in suspensions in response to an external force such as gravity, centrifugal force or electric force, various submicron and nanosizes

can be easily sedimented as explained in previous chapter. In present study, the powders with 20 μm, 10 μm and 2 μm can be taken after grinding process. Here grinding parameter is time. Submicron or nanosize powder including 0.1 μm was produced using sedimentation process. The sedimentation process was first applied for fabrication of nanosized particles after grinding process.

5.2 Material Properties

5.2.1. Thermal Analysis

Since exothermic and endothermic reactions are significant issues in flame retardancy properties, DTA-TG analysis are carried out to correlate interactions between huntite/hydromagnesite mineral and polymeric material. DTA-TG analysis are performed by heating in the range rate of a rate 10 ºC/min at temperatures between 25ºC and 600ºC.

DTA comparision between huntite/hydromagnesite mineral and polymer sample is demonstrated in Figure 5.2. It is clear from Figure 5.2 that in the mineral sample there are three thermal reactions. Huntite and hydromagnesite have $Mg_3Ca(CO_3)_4$ and $Mg_4(OH)_2(CO_3)_3.3H_2O$ chemical formulas respectively. Because of these structures, decomposition occured in these minerals at temperatures between 25ºC and 600ºC. The first thermal phenemon starts at 219,86^oC and ends at 331,89^oC and then heat releases at -3,61 J, corresponding to removal of water and OH groups. We have a good agreement with Ref. (Schmidt, 1999). According Equations 5.1 and 5.2, $Mg_4(OH)_2(CO_3)_3.3H_2O$ and $Mg_3Ca(CO_3)_4$ starts to decompose at low temperatures.

$$Mg_4(CO_3)_3(OH)_2.3H_2O \rightarrow 4MgO + 3CO_2+4H_2O \quad (5.1)$$

$$Mg_3Ca(CO_3)_4 \rightarrow 3MgO + CaO + 4CO_2 \quad (5.2)$$

After removal of water from hydromagnesite, $Mg_4(CO_3)_3$ decomposes to MgO and CO_2. It is estimated that the decomposition of $Mg_4(CO_3)_3$ become at

temperatures between 376,29°C and 490,76°C. This is the second thermal behaviour and heat releases at -5,49 J. It is difficult to seperately state decomposition phenomena of huntite/hydromagnesite because it has $Mg_4(OH)_2(CO_3)_3.3H_2O$ and $Mg_3Ca(CO_3)_4$. Finally the third one starts at 503,94°C and ends at 598,29°C. In this case, heat releases -1,43 J. Therefore, MgO and CaO are formed end of this process.

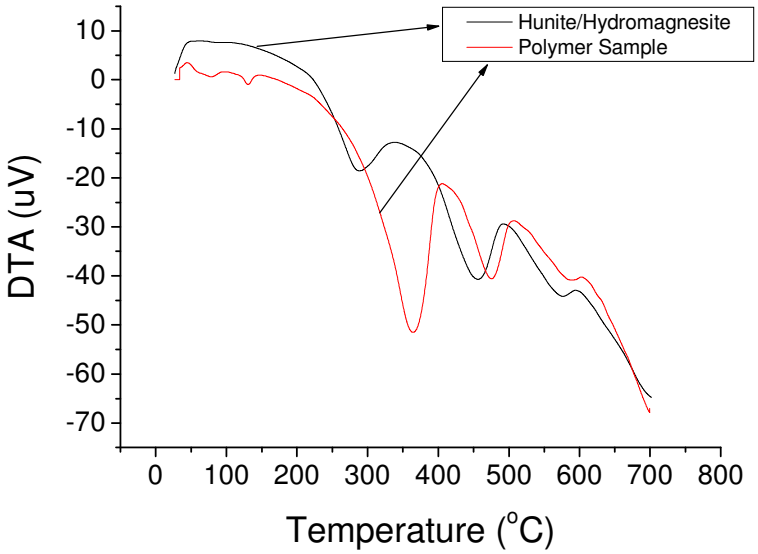


Figure 5.2 DTA curves of huntite/Hydromagnesite mineral and polymer sample

Concerning thermal behaviour of the polymer sample, four thermal reactions were determined from Figure 5.2. First exothermic reaction starts at 121,51 °C and finishes at 146,14 °C. From the first reaction, heat releases -124,21 mJ. After that, second exothermic reaction occured in the temperature range of 226,19 °C and 406,82 °C. From this reaction, heat releases -13,79 J. Third thermal phenemenon is formed at temperatures between 424,27 °C and 508,08 °C. Thus heat releases -3,41 J from third reaction. The final thermal behaviour of polymeric material occured in the temperature of 515,61 °C and 606,61 °C. Very huge amount heat having -799,71 mJ releases after fourth reaction.

Upon compared TGA analysis of huntite/hydromagnesite mineral and polymer sample, as depicted in Figure 5.3, it can be expressed that huntite/hydromagnesite material has much more consistent than polymer sample. By means of thermal

stabilities it can be seen from Figure 5.3 that as the weight losses are happened at those intervals, it is indicated that the decomposition of huntite/hydromagnesite mineral occurs at temperatures between 400 ^{o}C and 500 ^{o}C and polymer which has huntite/hydromagnesite mineral as an additive is 300-500^{o}C. Total weight losses of huntite/hydromagnesite mineral and polymer sample were found to be 56 wt. % and 72 wt.%, respectively due to the fact that combustion or decomposition of huntite/hydromagnesite is lesser than that of polymeric material. Rothon (1994) indicated the decomposition temperatures of $Mg(OH)_2$ and $AlOH_3$ are 300-400 ^{o}C and 250-350^{o}C, respectively. Therefore it can be explained that huntite/hydromagnesite or even polymer sample are much more consistent than $Mg(OH)_2$ and $AlOH_3$.

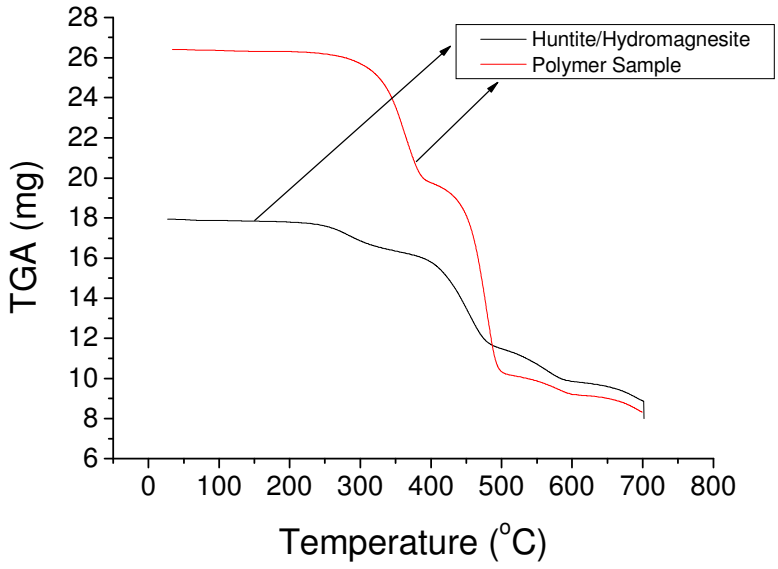


Figure 5.3 TGA curves of huntite/hydromagnesite mineral and polymer sample

5.2.2. FTIR Analysis

Figures 5.4 denotes FTIR analysis of huntite/hydromagnesite reinforced plastic composite materials including different mineral particle sizes. FTIR spectrum of calcium magnesium carbonate is quite characteristic with a very intense broad band centering at 2750-4000 cm^{-1}. This band can be illustrated by frequency of tension of

C-H bons. There is another sharp band at 3750 cm^{-1}. This could be happened due to O-H groups in the samples. Additionaly, lower intensity absorptions at 600-700 cm^{-1} can be observed from magnessium carbonate. By means of size sitribution, there are small differences in the results. As FTIR analysis is related with the molecular bondings, as the material becomes finer to nano sizes, the bond numbers decrease. Therefore, the intensity also decreases as can be shown in Figure 5.4.

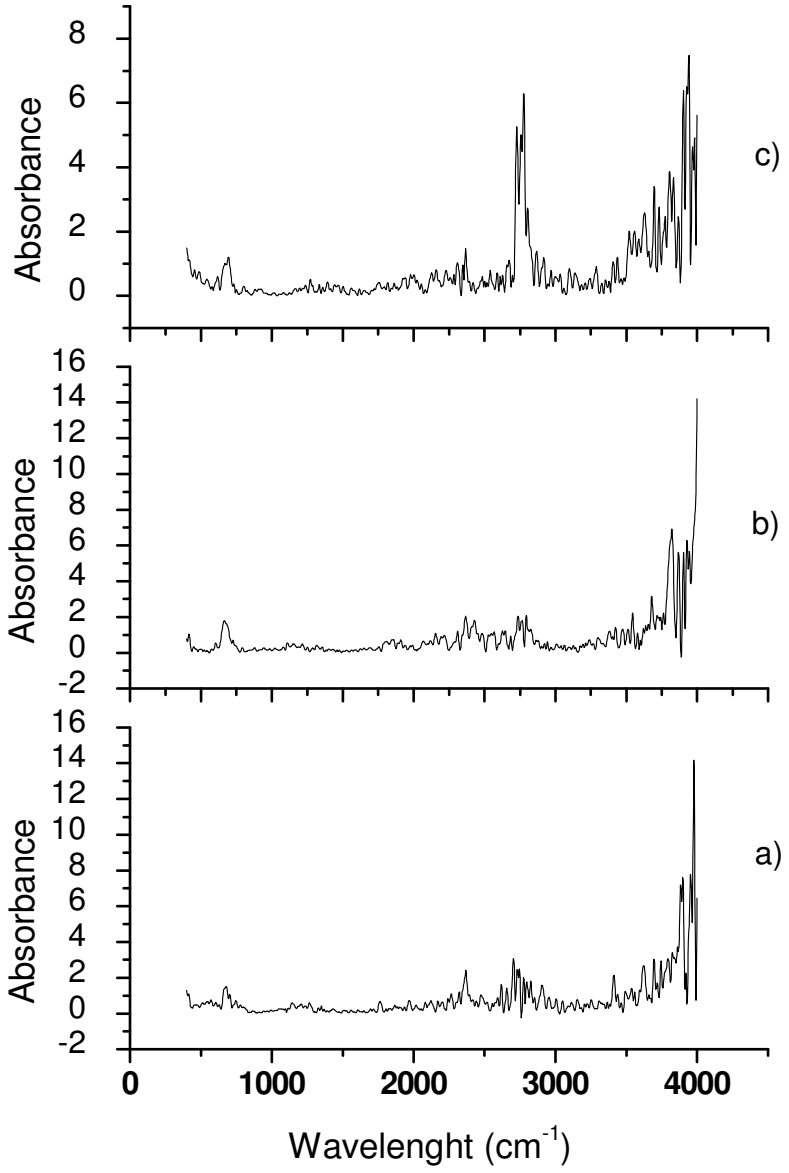


Figure 5.4 FTIR analysis of huntite/hydromagnesite reinforced plastic composite material having (a) 0.1 µm (b) 1 µm and (c) 10 µm minerals.

5.2.3. Phase Analysis

XRD pattern of huntite/hydromagnesite mineral powder is shown in Figure 5.5. It is found from this result that the basic minerals are hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$), huntite ($Mg_3Ca(CO_3)_4$) and dolomite ($CaMg(CO_3)_2$) in the raw huntite/hydromagnesite mineral which is a flame retardant material. The main phases with high intensity are huntite and hydromagnesite. In addition to main phases, dolomite having low intensity is seen from XRD pattern. As demonstrated in the literature (Kirschbaum, 2001), an average mineralogical composition, based on XRD and chemical analysis data of current ores is as follows huntite (46%), hydromagnesite (46%), magnesite (4%), aragonite (3%), calcite (1%). The current study is smiliar to Kirschbaum's research, but different phase is dolomite. In this study, magnesite, aragonite and calcite phases are not found as impurities which are influencing flame retardant properties. In contrast to another mineral flame retardant mentioned above, huntite/hydromagnesite has no simple metal hydroxide structure, but consists of three distinct phases such as hydromagnesite, huntite and dolomite.

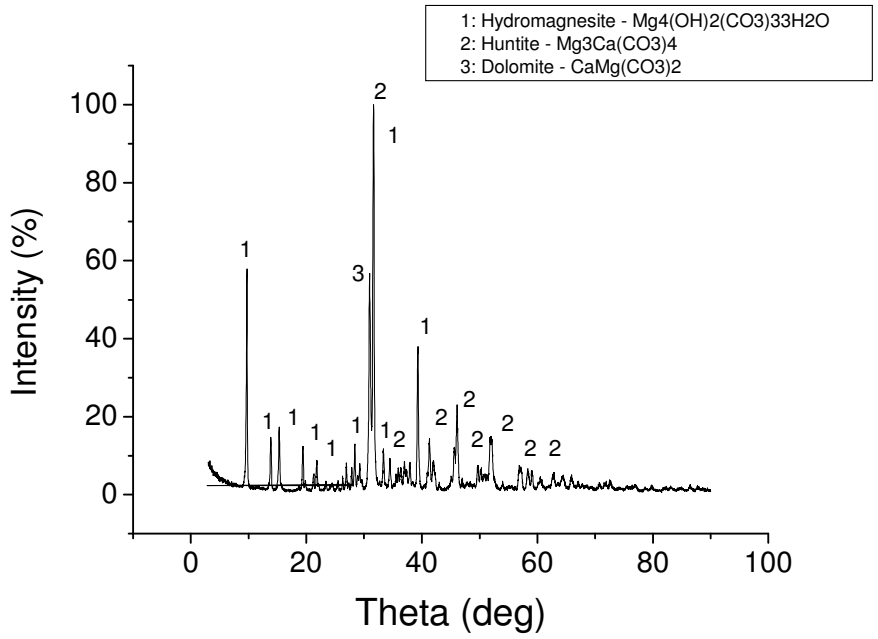
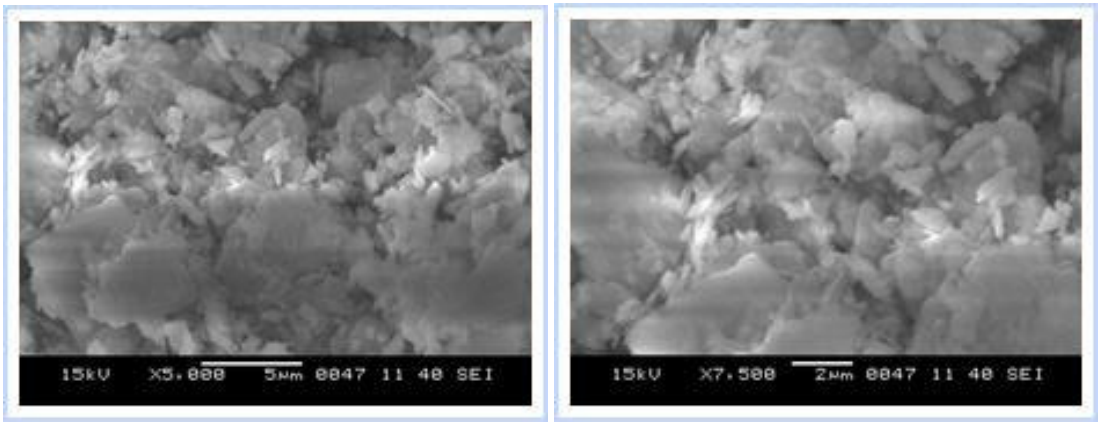


Figure 5.5 XRD pattern of as-recieved huntite/hydromagnesite mineral powder

5.2.4 Microstructure

Figure 5.6 demonstrates SEM micrographs and EDS analysis of huntite/hydromagnesite mineral particles. It is obviously seen from Figure 5.6.a that huntite/hydromagnesite mineral particles with 20 µm possess irregular shape after grinding process. EDS analysis proved XRD result because Mg, Ca, C and O elements were found and there is any other element as impurities.

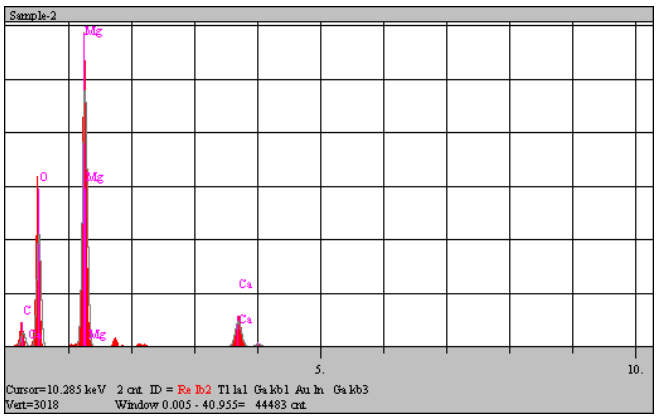


(a)

Component	Conc.		
O	51.267	wt.%	
C	30.272	wt.%	
Mg	16.498	wt.%	
Ca	1.963	wt.%	
	100.000	wt.%	Total

Elt.	Line	Intensity (c/s)	Error 2-sig	Conc		
C	Ka	12.30	0.838	30.272	wt.%	
O	Ka	90.15	1.930	51.267	wt.%	
Mg	Ka	233.86	3.116	16.498	wt.%	
Ca	Ka	30.19	1.214	1.963	wt.%	
				100.000	wt.%	Total

kV	20.0
Takeoff Angle	35.0°
Elapsed Livetime	100.0

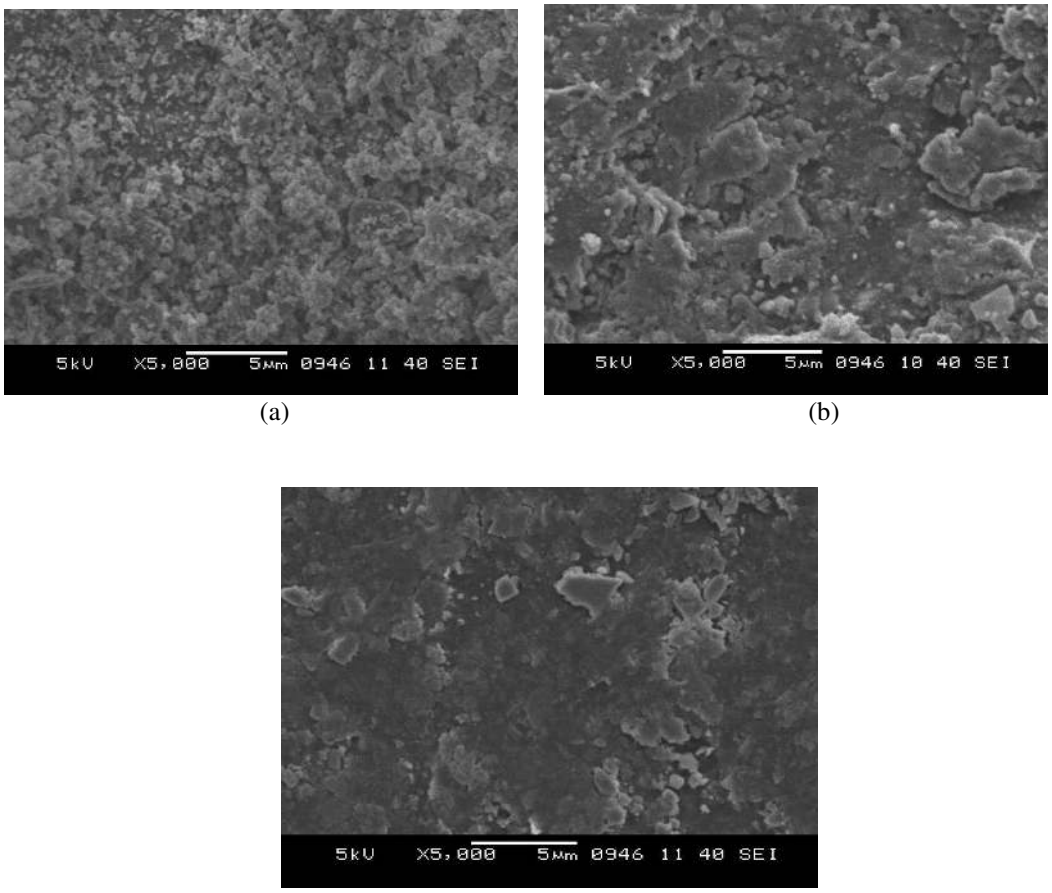


(b)

Figure 5.6 (a) SEM micrographs and (b) EDS analysis of huntite/hydromagnesite mineral particles.

Figure 5.7 demonstrates SEM micrographs of huntite/hydromagnesite reinforced plastic composite material having 10 µm, 1 µm and 0.1 µm particle size. It was found that when particle size of huntite/hydromagnesite is increased in the composite material, the particles are clearly seen. In this case, very dense structure was obtained in small particle size. Flame retardancy and electrical properties are

influenced by nanosized huntite/hydromagnesite reinforced materials since they possess 0.1 µm or 100 nm particle size as will be explained later on.

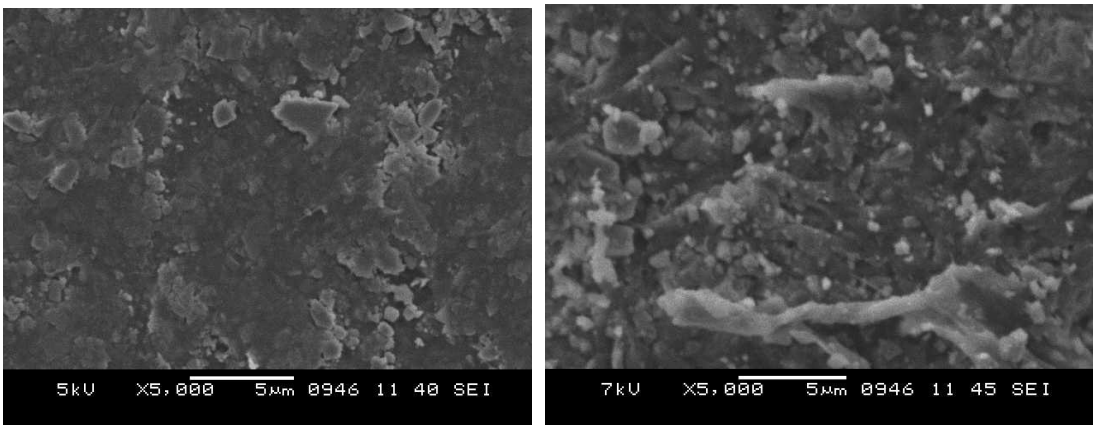


(a) (b)

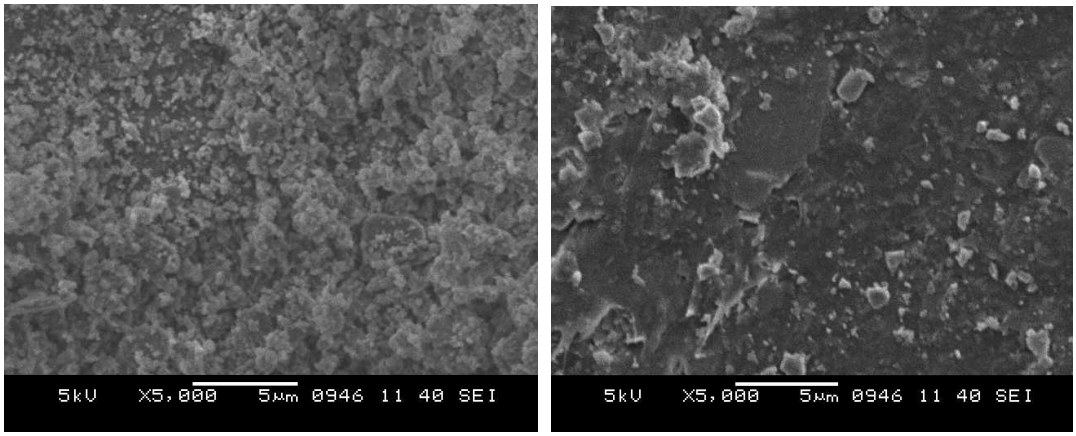
(c)

Figure 5.7 SEM micrographs of huntite/hydromagnesite reinforced plastic composite material having (a) 10 µm, (b) 1 µm and (c) 0.1 µm particle size.

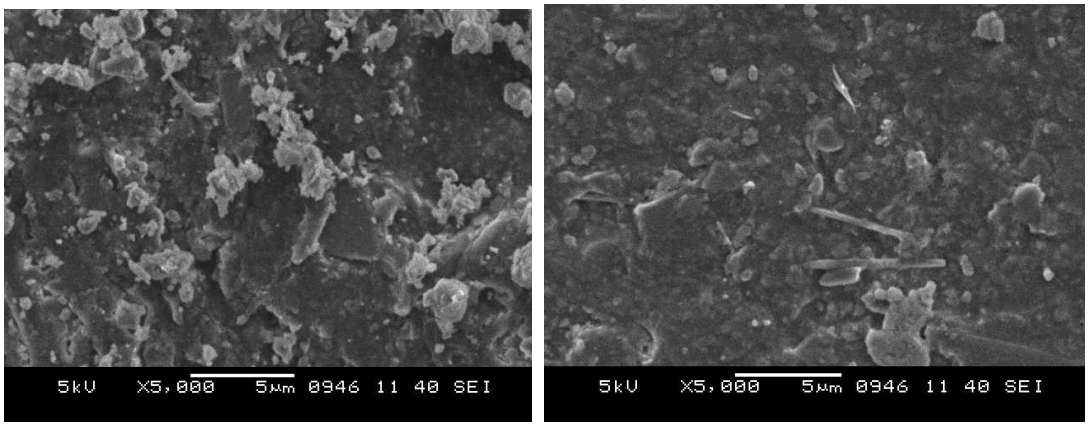
Figure 5.8 denotes SEM micrographs of huntite/hydromagnesite reinforced plastic composite material having 49%, 55%, 61%, 64%, 67% and 69% particle contents in the same particle size which is 10 µm. SEM micrographs reveal that when the huntite/hydromagnesite particle content increases, microstructure of the composite materials clearly changes.



(a) (b)



(b) (d)



(e) (f)

Figure 5.8 SEM micrographs of huntite/hydromagnesite reinforced plastic composite material having (a) 49%, (b) 55%, (c) 61%, (d) 64%, (e) 67% and (f) 69% particle contents in 10 µm size.

5.2.5 Mechanical Properties

Figure 5.9 shows tensile strength of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content. It can be seen that till level of 65%, tensile strength decreases by increasing particle content. However, up to 65 % tensile strengh is improved by increasing filler amount.

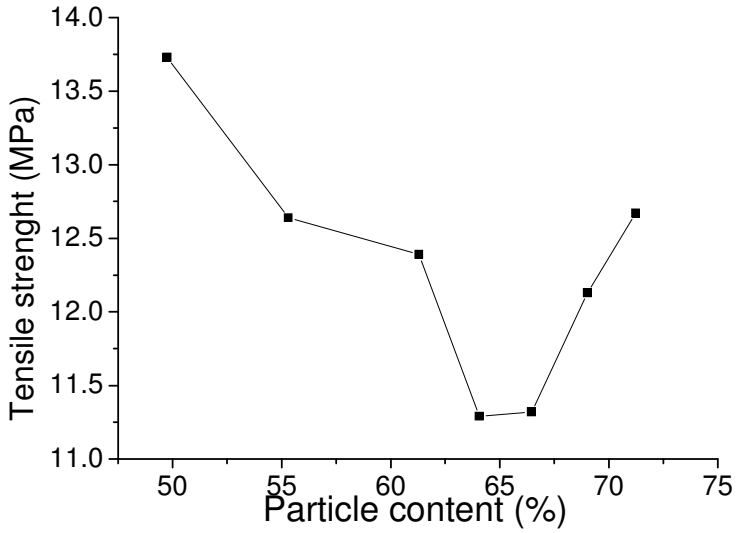


Figure 5.9 Tensile strength of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content.

Figure 5.10 demonstrates tensile strengths of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size. It is obviously seen from Figure 5.10 that increasing size of the additive mineral powder leads to decrease the tensile strength. Therefore it can be expressed that finer size gives to the polymer more tensile strength effect.

Figure 5.11 depicts tear strength of huntite/hydromagnesite reinforced plastic composite materials as a function of different particle content. It is clearly seen from Figure 5.11 that increasing particle content of huntite/hydromagnesite decreases the tear strength.

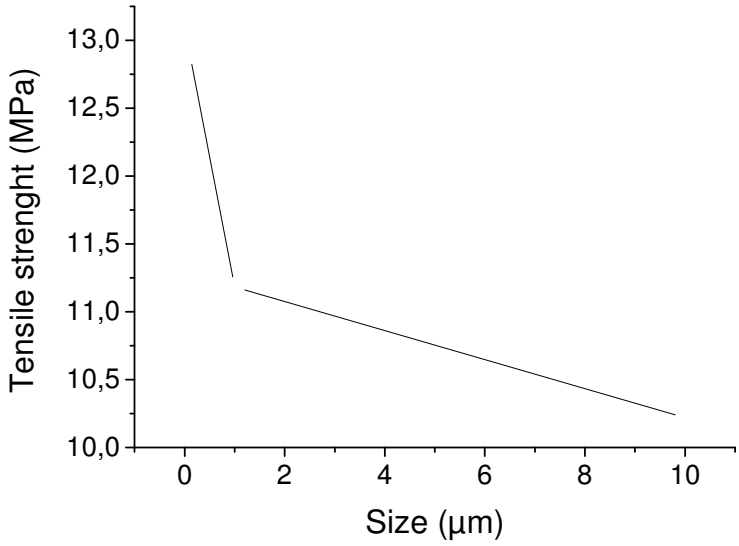


Figure 5.10 Tensile strength of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size.

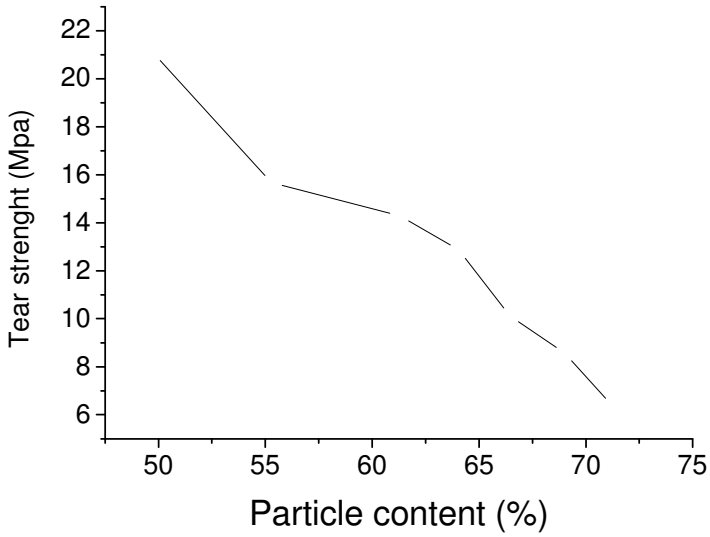


Figure 5.11 Tear strengths of huntite/hydromagnesite reinforced plastic composite materials as a function of different particle content.

Figure 5.12 shows tear strengths of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size. It is seen that increasing the size of the mineral powder decreases tear strengh. Therefore, decreasing the additive will be usefull to obtain better tear strength for flame retandancy application.

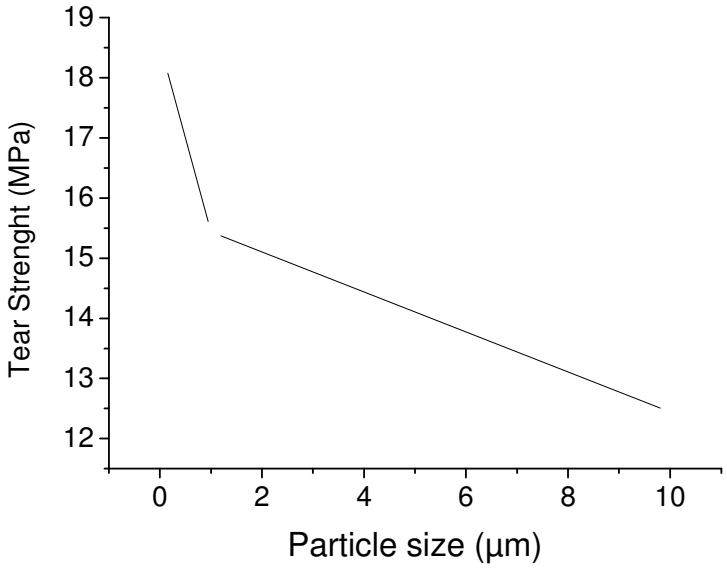


Figure 5.12 Tear strengths of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size.

Figure 5.13 denotes elongation at break values of huntite/hydromagnesite reinforced plastic composite materials as a function of different particle content. It can be stated that increasing particle content decreases elongation at break.

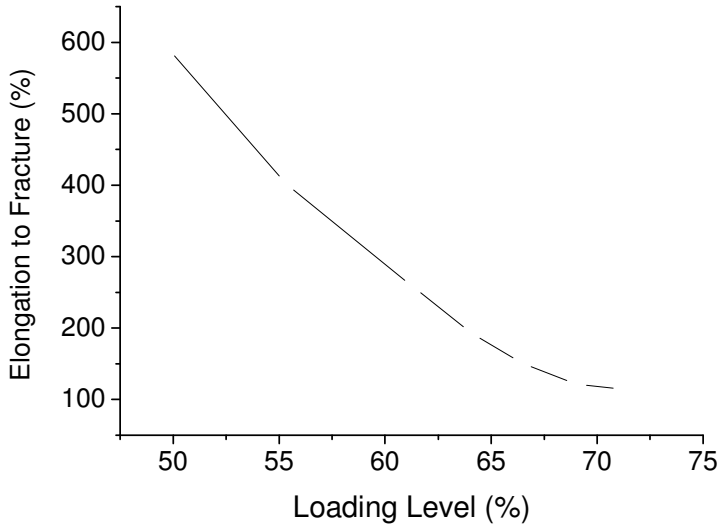


Figure 5.13 Elongation to fracture values of huntite/hydromagnesite reinforced plastic composite materials as a function of different particle content.

Figure 5.14 shows elongation to fracture values of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size. This changes regarding the sizes. The best result is achieved at the size of 1 μm. Lower or higher than 1 μm elongation at break decreases. But when we compare the two lower values, it can said that finer grades of mineral additive can improve elongation to fracture.

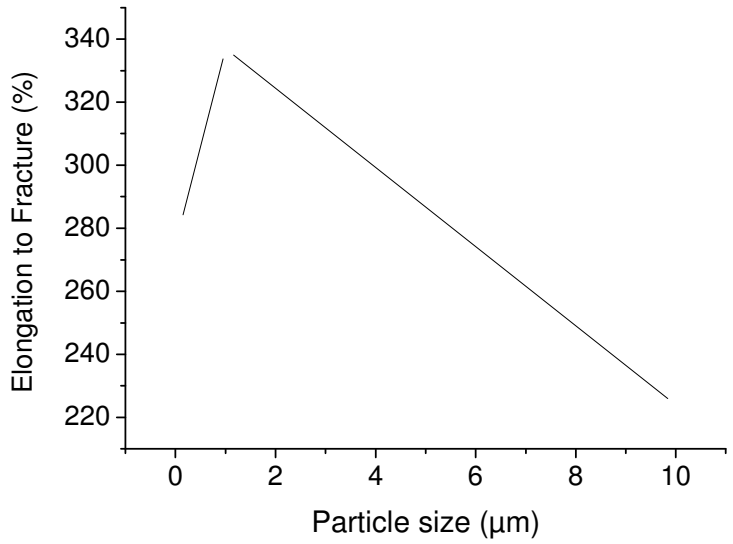


Figure 5.14 Elongation to fracture values of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size.

5.2.6 Electrical Properties

The disadvantages are alleviated by an electrically conductive, flame retardant filler comprising flame retardant particles coated with a conductive metal. In an unexpected feature, it has been found that even when flame retardant particles are coated with a conductive metal, the particles nonetheless provide effective flame retardance. Accordingly, further disclosed is an electrically conductive, flame retardant composition comprising a polymer and a filler composition, the filler composition comprising flame retardant particles coated with a conductive metal. The polymer may be an elastomer or a foam which we used in our experiments. In another unexpected feature, it has been found that the inventive

huntite/hydromagnesite particles can provide both conductivity and flame retardance without significantly adversely affecting the desired properties of the plastic materials.

Because of these reasons, conductivity, empedance, capacitance, dissipation factor, dielectric constant and specific resistance of Ag-coated and uncoated huntite/hydromagnesite reinforced plastic composite materials were investigated in details.

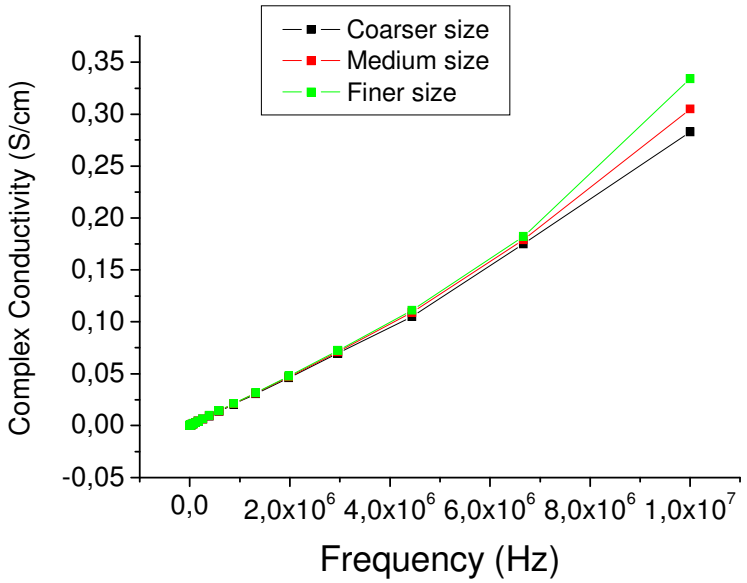
5.2.6.1 Complex Conductivity

Figure 5.15 shows conductivity values of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size and particle content. It is clearly seen from Figure 5.15.a that increasing huntite/hydromagnesite mineral additive filler amount makes the polymer more conductive. In Figure 5.15.b, conductivity values of huntite/hydromagnesite reinforced plastic materials increase with increasing particle content in the composites.

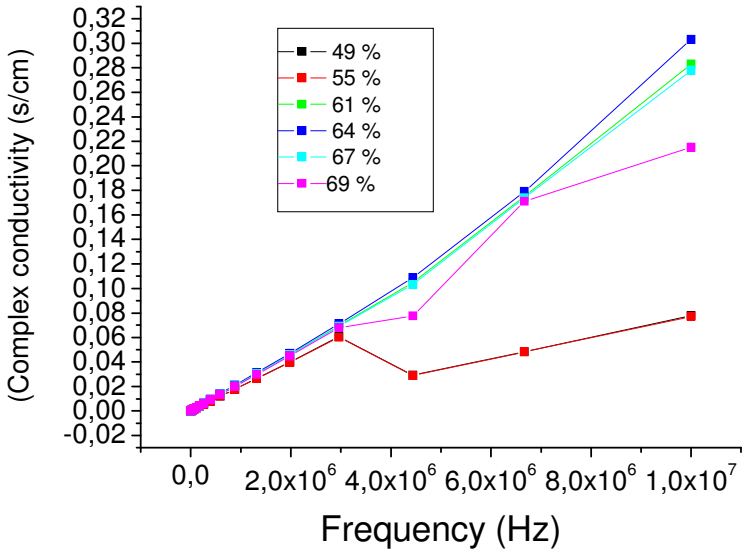
Generally speaking, reinforced huntite/hydromagnesite particles strongly influence conductivity of the composites in spite of the fact that polymeric matrix is a dielectric material. When these polymeric materials are used in electrical applications such as cables, this property is not desirable owing to its conductivity. Nevertheless, fire retardancy behaviour of cables should not be ignored.

5.2.6.2 Impedance

Figure 5.16 presents impedence values of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size and content. Electrical impedance, or simply impedance, describes a measure of opposition to a sinusoidal alternating current. Electrical impedance extends the concept of resistance to alternating current circuits, describing not only the relative amplitudes of the voltage



(a)

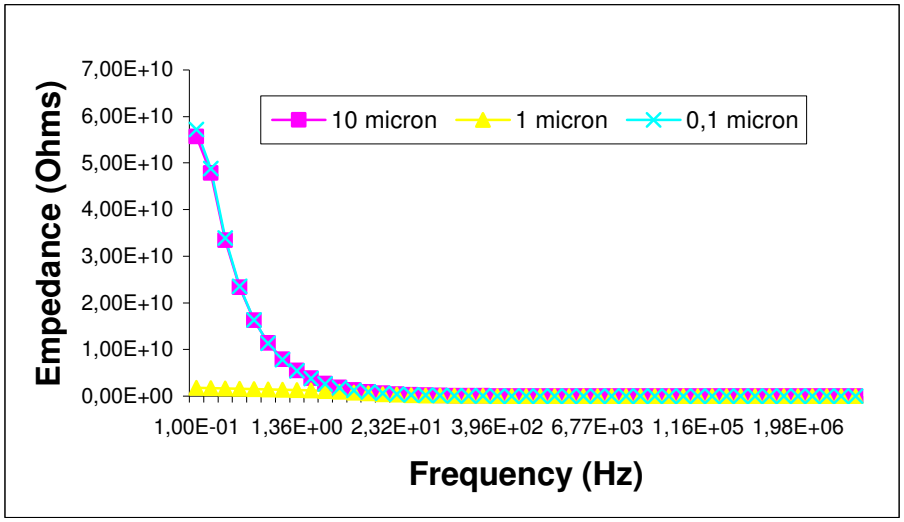


(b)

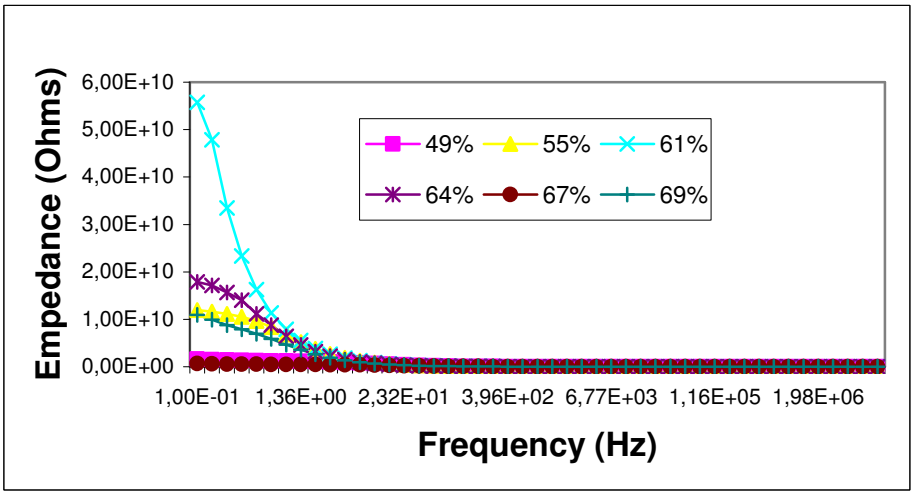
Figure 5.15 Conductivity values of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.

and current, but also the relative phases. It can be explained depending on frequency as seen in Figure 5.16. As the frequency is a significant issue, particle size and

content influencing electical impedence are also important factors in a polymeric composite. With a general statement, it can be expressed that impedence decreases with increasing particle size and content of huntite/hydromagnesite particle in the polymeric composites.



(a)



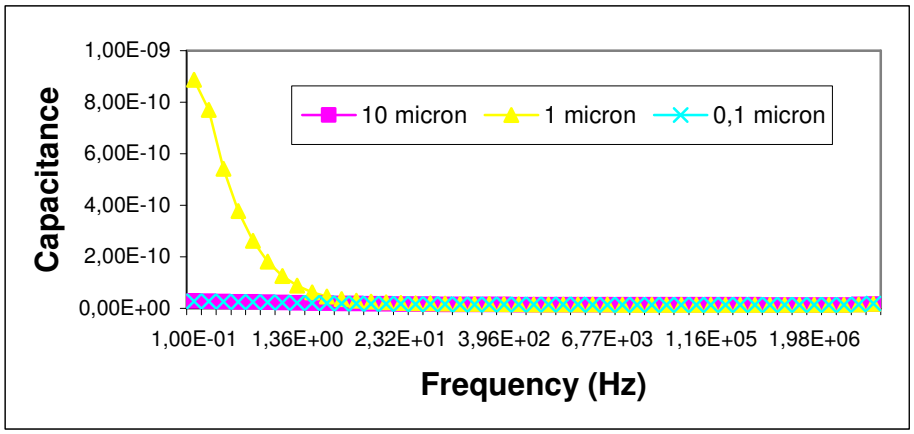
(b)

Figure 5.16 Impedence values of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.

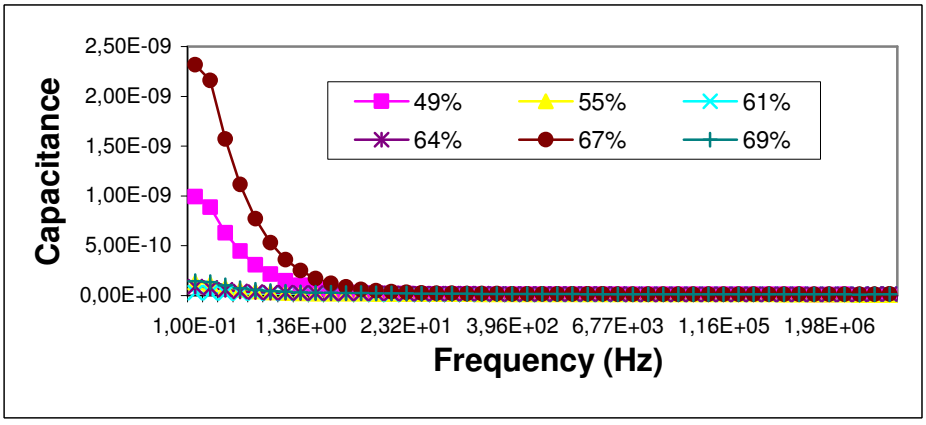
5.2.6.3 Capacitance

As known very well capacitance is a measure of the amount of electric charge stored (or separated) for a given electric potential. The most common form of charge

storage device is a two-plate capacitor. In these experiments, a relationship between capacitance and huntite/hydromagnesite reinforced plastic composite materials as a function of particle size and content can be evaluated as demonstrated in Figure 5.17. It can be suggested that capacitance decreases with increasing particle size and content of huntite/hydromagnesite particle in the polymeric composites as explained in electrical impedance.



(a)



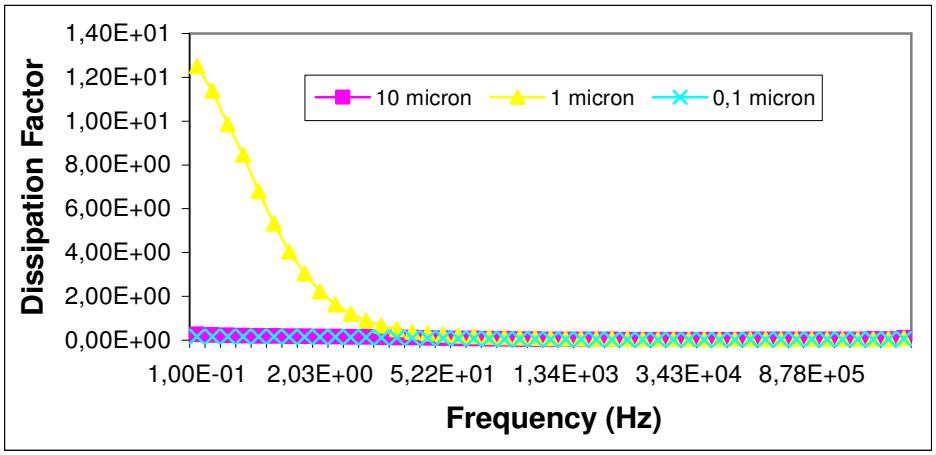
(b)

Figure 5.17 Capacitance values of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.

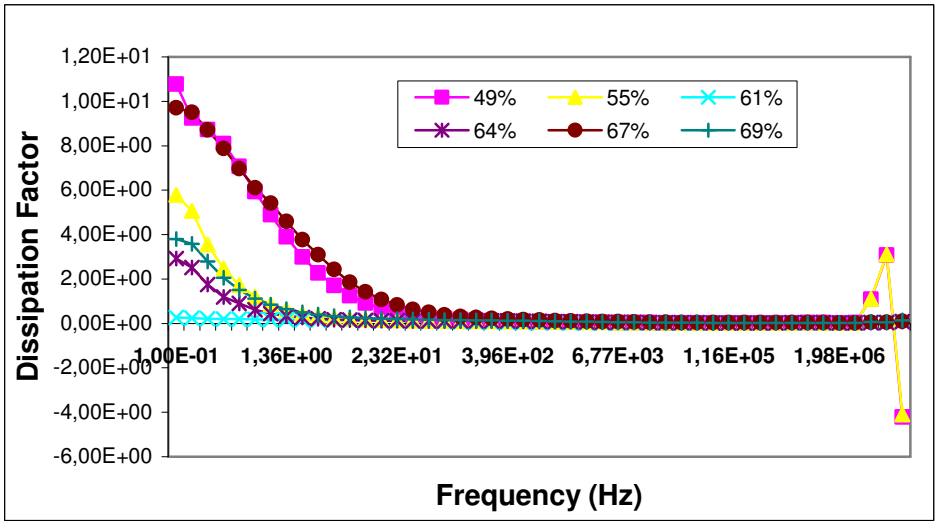
5.2.6.4 Tan Delta or Dissipation Factor

In the realm of electricity, dissipation factor is a measurement of the parasitic loss (as heat) that results from subjecting a dielectric to an alternating electric field. This

parasitic loss occurs because the polarization of the dielectric that results from the increasing electric field requires energy that is not recovered when the field collapses. Usually, dissipation factors are given as resulting power factor when an alternating current is run through a purely capacitive circuit (i.e. no inductance or resistance) in which the capacitor is using the dielectric in question. An ideal capacitive circuit with no dissipation factor would have a power factor of zero, but the parasitic losses cause the power factor to be very slightly over zero. Dissipation factor does increase somewhat with the frequency of the alternating field, so it is usually quoted at a certain frequency.



(a)



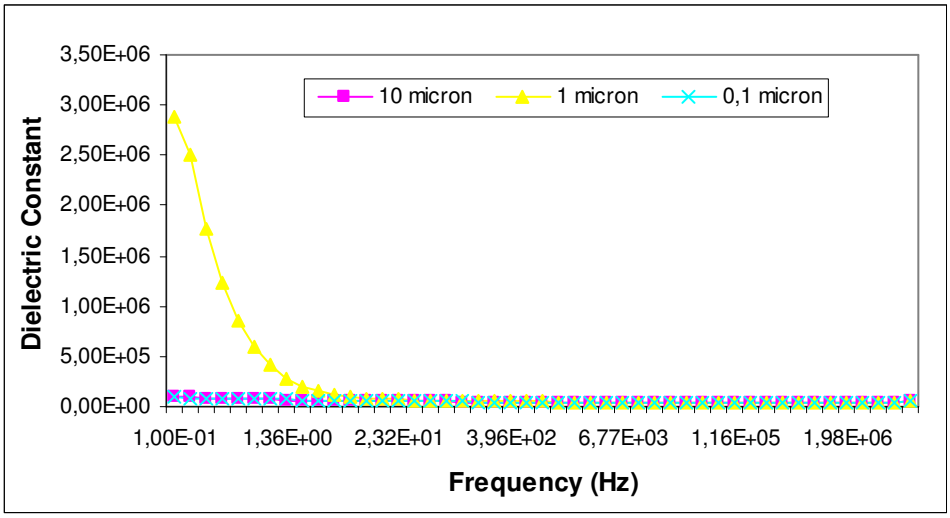
(b)

Figure 5.18 Dissipation factor curves of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.

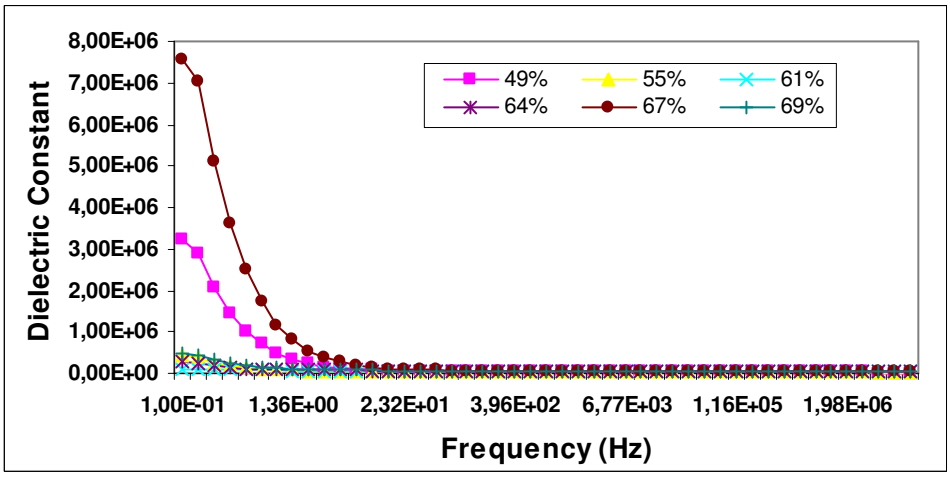
Figure 5.18 shows dissipation factor curves of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size and content. It was determined that dissipation factors of huntite/hydromagnesite reinforced plastic composite materials were high at low frequencies.

5.2.6.5 Dielectric Constant

Dielectric is a physical model commonly used to describe how an electric field behaves inside a material. It is characterised by how an electric field interacts with an



(a)



(b)

Figure 5.19 Dielectric constant curves of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.

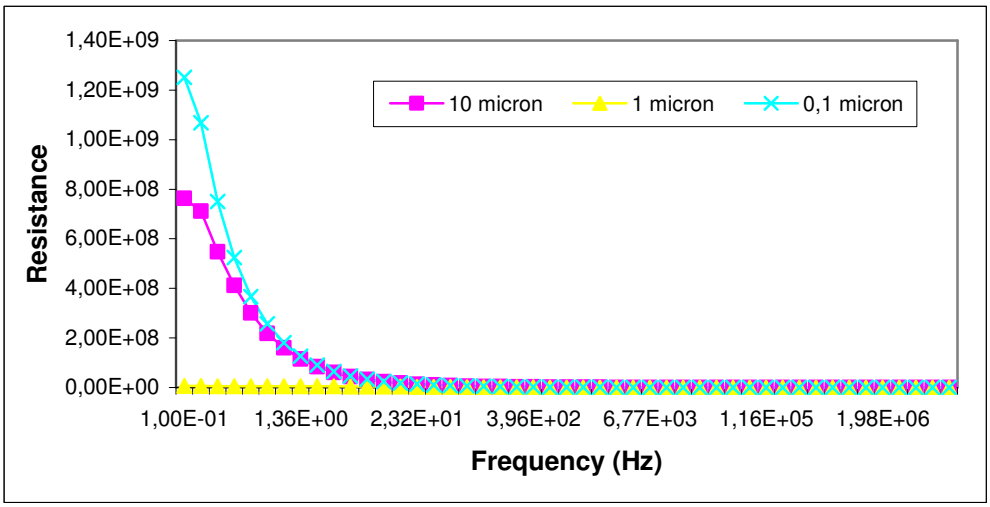
atom. It is possible to approach dielectrics from either a classical interpretation or a quantum one. How effective a dielectric is at allowing a capacitor to store more charge depends on the material the dielectric is made from. Every material has a dielectric constant. The larger the dielectric constant, the more charge can be stored. If a metal was used for the dielectric instead of an insulator the field inside the metal would be zero, corresponding to an infinite dielectric constant. The dielectric usually fills the entire space between the capacitor plates, however, and if a metal did that it would short out the capacitor - that's why insulators are used instead. In this case, dielectric properties of huntite/hydromagnesite reinforced plastic composite materials were investigated depending on mineral particle content and size. Figure 5.19 demonstrates dielectric constant curves of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content and size.

5.2.6.6 Specific Resistance

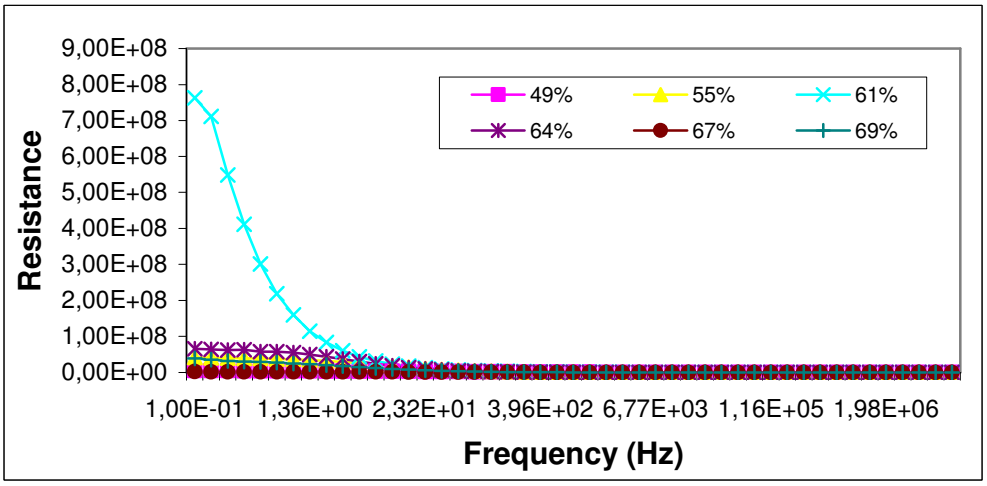
Figure 5.20 presents specific resistance curves of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content and size. Due the fact that electrical resistance is a measure of the degree to which an object opposes an electric current through it, it was found that spesific resistance values of huntite/hydromagnesite reinforced plastic composite materials are high.

5.2.6.7 Ag-Coated and uncoated polymer's measuremets

Figure 5.21 shows conductivity, empedance, capacitance, dissipation factor, dielectric constant and specific resistance curves of Ag-coated and uncoated huntite/hydromagnesite reinforced plastic composite materials. Besides different sizes and different loading level measurements, all electrical tests are performed for Ag-coated polymeric composite to see if any pores or dispalcements in the body of huntite/hydromagnesite reinforced plastic composite materials.

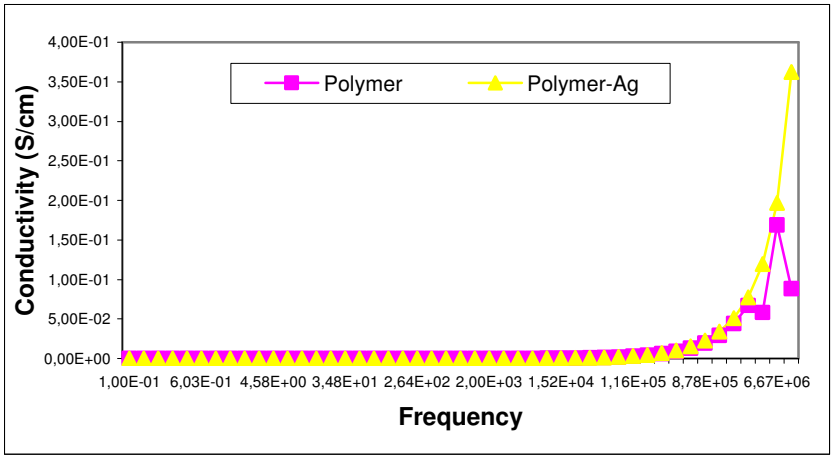


(a)

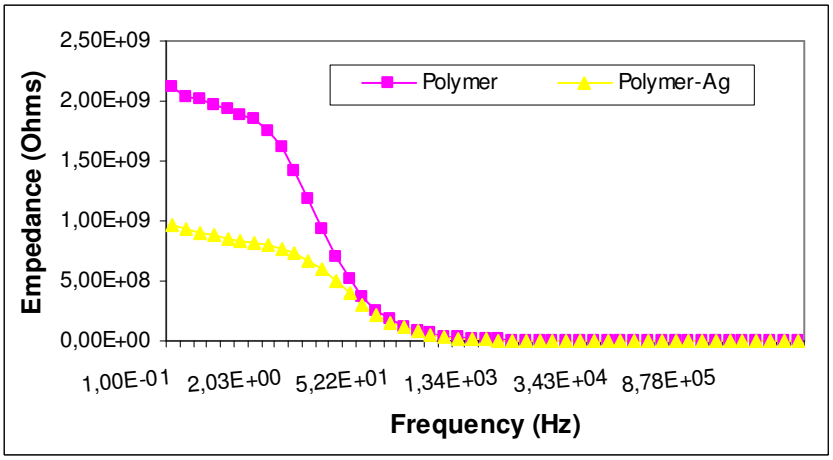


(b)

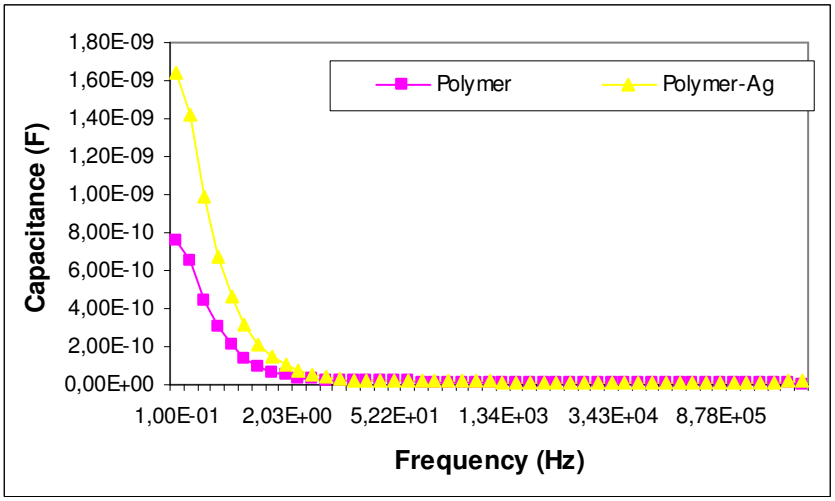
Figure 5.20 Specific resistance curves of huntite/hydromagnesite reinforced plastic composite materials as a function of (a) particle size and (b) particle content.


Conductivity (S/cm)
4,00E-01
3,50E-01
3,00E-01
2,50E-01
2,00E-01
1,50E-01
1,00E-01
5,00E-02
0,00E+00
Polymer
Polymer-Ag
1,00E-01 6,03E-01 4,58E+00 3,48E+01 2,64E+02 2,00E+03 1,52E+04 1,16E+05 8,78E+05 6,67E+06
Frequency

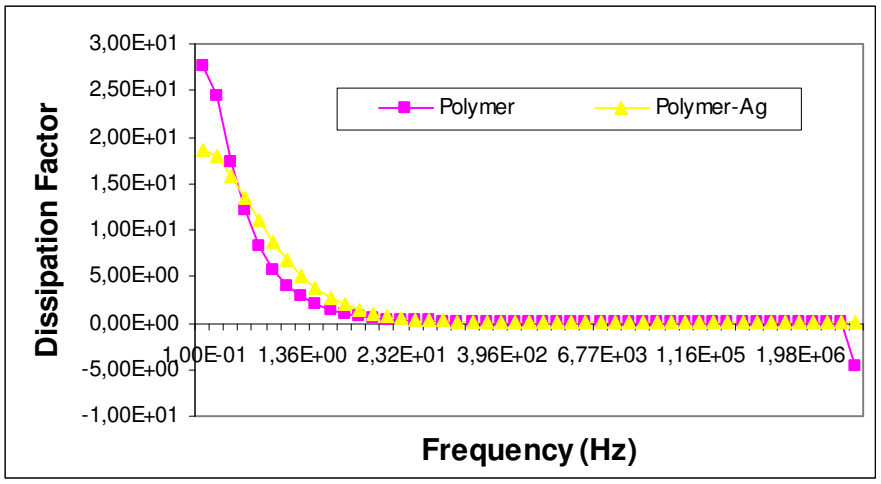
(a)


Empedance (Ohms)
2,50E+09
2,00E+09
1,50E+09
1,00E+09
5,00E+08
0,00E+00
Polymer
Polymer-Ag
1,00E-01 2,03E+00 5,22E+01 1,34E+03 3,43E+04 8,78E+05
Frequency (Hz)

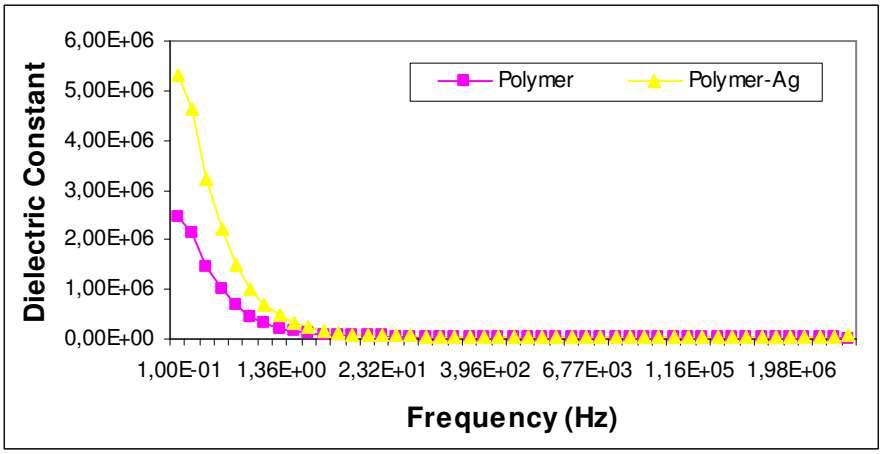
(b)


Capacitance (F)
1,80E-09
1,60E-09
1,40E-09
1,20E-09
1,00E-09
8,00E-10
6,00E-10
4,00E-10
2,00E-10
0,00E+00
Polymer
Polymer-Ag
1,00E-01 2,03E+00 5,22E+01 1,34E+03 3,43E+04 8,78E+05
Frequency (Hz)

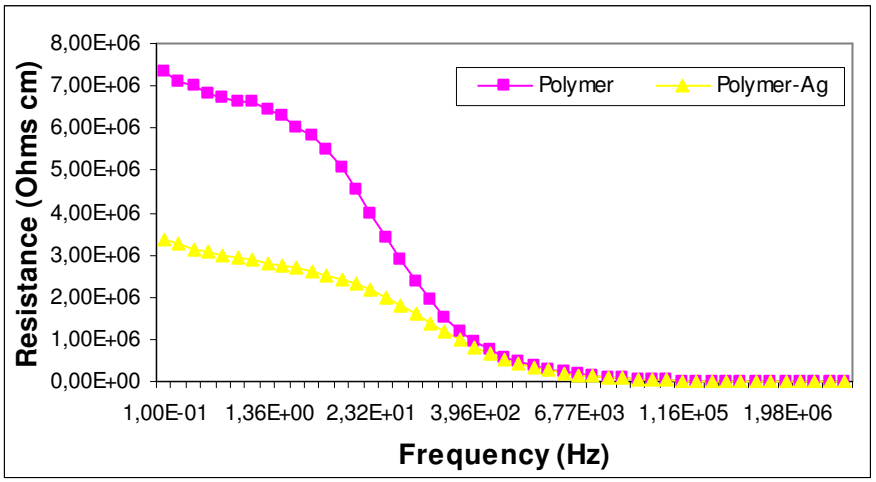
(c)



(d)



(e)



(f)

Figure 5.21 (a) Conductivity, (b) empedance, (c) capacitance, (d) dissipation factor, (e) dielectric constant and (f) specific resistance curves of Ag-coated and uncoated huntite/hydromagnesite reinforced plastic composite materials.

5.2.7 Flame Retardancy

Figure 5.22 denotes oxygen index of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content in the plastic. It can be easily seen that increasing the filler amount increases the flame retardancy of the polymer. Rothon (1994) coMPared the oxygen index values of polyethylene with different particle contents of $Al(OH_3)$ and $CaCO_3$ and he found that in the oxygen index of $Al(OH_3)$ is 35 % and $CaCo_3$ is 20% at 60% filler loading point. However, in huntite/hydromagnesite added polymers at the 60% filler loading level, the oxygen index is 40%. Thus it can be indicated from Figure 5.21 that huntite/hydromagnesite is more effective than the other flame retardants.

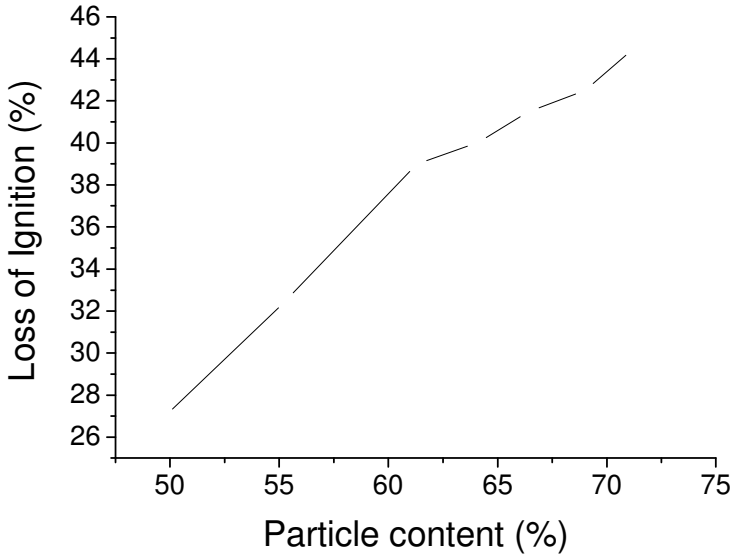


Figure 5.22 Oxygen index of huntite/hydromagnesite reinforced plastic composite materials as a function of particle content.

Flame retardancy test results according to different sizes are shown in Figure 5.23. It can be easily seen that decreasing the size of the additive increases the flame retardancy of the polymer. That is because of that surface area of the additive increases. At the same study of Rothon (1994), it is also coMPared the oxygen index values of polyethylene with different grades of $Al(OH_3)$, and it is found that in the

oxygen index of $Al(OH_3)$ increases to 35 from 25 when the size distribution decreases to 2 μm from 70 μm. Similarly, it can be seen in the present study in Figure 5.23 that increasing size distribution increases oxygen index. Therfore it is clearly stated that decreasing size distribution of the mineral additive can help us to achieve much more flame retardancy in the polymer products.

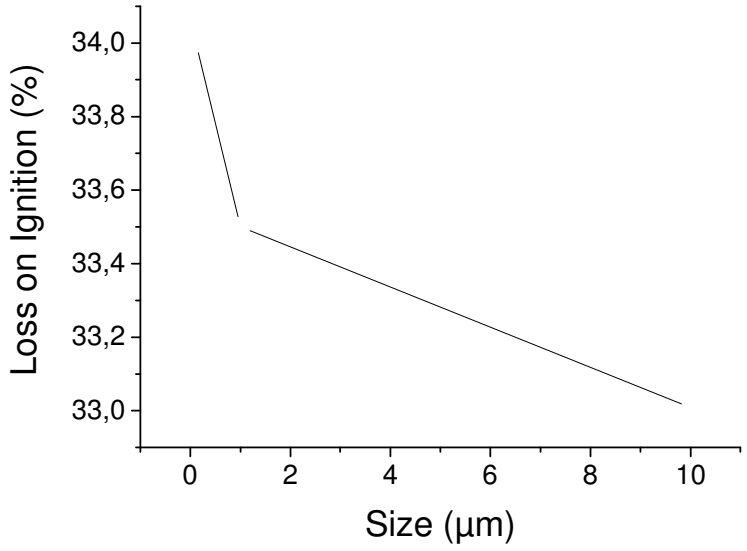


Figure 5.23 Oxygen index of huntite/hydromagnesite reinforced plastic composite materials as a function of particle size.

CHAPTER SIX
CONCLUSIONS

6.1 General Results

Fire retardant materials provides a comprehensive source of information on all aspects of fire retardancy, emphasizing the burning behavior and flame retarding properties of polymetric materials. It covers combustion, flame retardants, smoke and toxic products in general, and material-specific aspects of combustion in relation to textiles, composites, and bulk polymers. Flame retardant materials increase the initial resistance to ignition and are able to effectivelly slow down burning rates which in turn are proportioned to the rate of smoke and toxic gas built up. Therefore potential escape time increases.

In this study, use of huntite/hydromagnesite mineral particles in plastic materials as a flame retardant was investiagated. Huntite and hydromagnesite minerals were added to the polymer compounds with different grades and with different particle contents. The following successfull conclusions are obtained from the experimental works:

1) It was found that HM3 sample possessed in the range of 1 µm and 30 µm. In HM2 sample, huntite/hydromagnesite mineral has the medium grade including the range of 1 µm and 5 µm. In HM1 sample, particle size distribution is in the range of 0.1 µm and 1 µm. It can be roughly indicated that submicron or nanosize powders were produced using sedimentation process.

2) In the mineral sample there are three thermal reactions. Three composition occured in these minerals at temperatures between 25ºC and 600ºC. In the polymer sample, four thermal reactions were determined. It was found that huntite/hydromagnesite material has much more consistent than polymer sample. Total weight losses of huntite/hydromagnesite mineral and polymer sample were

found to be 56 wt. % and 72 wt. %, respectively due to the fact that combustion or decomposition of huntite/hydromagnesite is lesser than that of polymeric material.

3) FTIR spectrum of calcium magnesium carbonate is quite characteristic with a very intense broad band centring at 2750-4000 cm^{-1}. This band can be illustrated by frequency of tension of C-H bons. There is another sharp band at 3750 cm^{-1}. This could be happened due to O-H groups in the samples. In addition, lower intensity absorptions at 600-700 cm^{-1} can be observed from magnessium carbonate. As FTIR analysis is related with the molecular bondings, as the material becomes finer to nano sizes, the bond numbers decrease.

4) It is found from XRD pattern that the basic minerals are hydromagnesite ($Mg_4(OH)_2(CO_3)_3.3H_2O$), huntite ($Mg_3Ca(CO_3)_4$) and dolomite ($CaMg(CO_3)_2$) in the raw huntite/hydromagnesite mineral.

5) Huntite/hydromagnesite mineral particles with 20 μm possess irregular shape after grinding process. EDS analysis proved XRD result because Mg, Ca, C and O elements were found and there is any other element as impurities. When particle size of huntite/hydromagnesite is increased in the composite material, the particles are clearly seen from microstructure. In this case, very dense structure was obtained in small particle size. SEM micrographs reveal that when the huntite/hydromagnesite particle content increases, microstructure of the composite materials clearly changes.

6) As mechanical properties, until level of 65%, tensile strength decreases by increasing particle content. However, up to 65 % tensile strengh is impoved by increasing filler amount. Increasing size of the additive mineral powder leads to decrease the tensile strength. Therefore it can be expressed that finer size gives to the polymer more tensile strength effect. Increasing particle content of huntite/hydromagnesite decreases the tear strength. It is also found that increasing the size of the mineral powder decreases tear strengh. Therefore, decreasing the additive will be usefull to obtain better tear strength for flame retandancy application. As a paralel to these, increasing particle content decreases elongation at break. The best result is achieved at the size of 1 μm. Lower or higher than 1 μm elongation at break decreases. But when we compare the two lower values, it can said that finer grades of mineral additive can improve elongation to fracture.

7) In electrical properties, increasing huntite/hydromagnesite mineral additive filler amount makes the polymer more conductive. Conductivity values of huntite/hydromagnesite reinforced plastic materials increase with increasing particle content in the composites. Impedence decreases with increasing particle size and content of huntite/hydromagnesite particle in the polymeric composites. Capacitance decreases with increasing particle size and content of huntite/hydromagnesite particle in the polymeric composites. It was also determined that dissipation factors of huntite/hydromagnesite reinforced plastic composite materials were high at low frequencies. In addition, dielectric properties of huntite/hydromagnesite reinforced plastic composite materials change as a function of particle content and size. It was found that spesific resistance values of huntite/hydromagnesite reinforced plastic composite materials are high. Furthermore, different sizes and different loading level measurements, all electrical tests are performed for Ag-coated polymeric composite to see if any pores or dispalcements in the body of huntite/hydromagnesite reinforced plastic composite materials.

8) In the flame retardant behaviour, increasing the filler amount increases the flame retardancy of the polymer. Huntite/hydromagnesite is more effective than the other flame retardants. It was found that decreasing the size of the additive increases the flame retardancy of the polymer. That is due to the fact that surface area of the additive increases. Similarly, it was determined that increasing size distribution increases oxygen index. Therefore it is clearly stated that decreasing size distribution of the mineral additive can help us to achieve much more flame retardancy in the polymer products. The results showed that huntite and hydromagnesite minerals have flame retardancy property, increasing the loading levels in the polymer compound, the flame retardancy of plastic increases. In addition it is considered that by decreasing the size distribution of the mineral, the flame retardancy effect increased. As it is seemed the flame retardancy properties of hydromagnesite and huntite minerals in plastics in this work, it can be considered that flame retardants help to increase safety in virtually every area of human existence. From office furniture and computer equipment to building materials/insulation, from car upholstery to jet

airliners, hospital buildings and wards; wherever we are and whatever we are doing, flame retardants are nearby helping to protect us from the dangers of fire.

6.2 Future Plans

Besides loading level, also the size distribution of the mineral is also important by means of effectiveness of flame retardancy. It is achieved the grinding material to 0.1 µm but it is aimed that the nanosizes of the mineral can be obtained and this size can be used in the advanced investigations of the flame retardancy. Because the specific surface area will be higher it is expected to get higher flame retardancy effect. On the other hand, with using flame retardancy effect of hydromagnesite and huntite material, much more advance materials can be obtained. With combining other specicif property material multifunctional materials cen be produced.

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APPENDIX

Tables and Figures