

**MECHANICAL, THERMAL AND FLAMMABILITY PROPERTIES OF  
HUNTITE HYDROMAGNESITE REINFORCED POLYURETHANE  
ELASTOMER**

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Approval of the thesis;

**MECHANICAL, THERMAL AND FLAMMABILITY PROPERTIES OF  
HUNTITE HYDROMAGNESITE REINFORCED POLYURETHANE  
ELASTOMER**

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## **ABSTRACT**

# **MECHANICAL, THERMAL AND FLAMMABILITY PROPERTIES OF HUNTITE HYDROMAGNESITE REINFORCED POLYURETHANE ELASTOMER**

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Polyurethane elastomer (Thermoplastic Polyurethane-TPU) has desirable properties for many applications including footwear, packaging, protective coatings, cables, wires and tubes in the mainly automotive and construction industries. Huntite and Hydromagnesite are naturally occurring minerals that has been used as fire retardants commercially since the late 1980's. The World's largest reserve of this mineral has been found in Turkey.

The main purpose of present work is to investigate the combustion and thermal degradation characteristics of the flame retardant TPU based composites containing huntite and hydromagnesite with and without expandable graphite. The combustion

and the thermal degradation characteristics of composites are investigated by LOI, UL-94 standard, thermogravimetric analysis (TGA) and mass loss calorimeter. Char residues remained after mass loss calorimeter test are investigated by conducting attenuated total reflectance – Fourier-transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The mechanical properties of the composites are also investigated by tensile testing and dynamic mechanical analysis (DMA).

**Keywords:** huntite, hydromagnesite, thermoplastic polyurethane, flame retardancy, mechanical properties

## ÖZ

### **HUNTİT HİDROMAGNEZİT TAKVİYELİ POLİÜRETAN ELASTOMERİNİN MEKANİK, TERMAL VE YANMAZLIK ÖZELLİKLERİNİN İNCELENMESİ**

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Poliüretan elastomer (Termoplastik Poliüretan-TPU) sağladığı üstün özellikleri nedeni ile özellikle otomotiv ve inşaat endüstrisinde, ayakkabı, ambalaj, koruma kıyafetleri, kablolar, teller, borular gibi pek çok alanda kullanılmaktadır. Huntit ve hidromagnezit 1980 den bu yana alev geciktirici olarak kullanılan doğal minerallerdir. Bu mineralin dünyadaki en büyük rezervi Türkiye'dedir.

Mevcut çalışmanın temel amacı alev geciktirici huntit ve hidromanyezit içeren TPU esaslı kompozitlerin, genişleyen grafit ile ve genişleyen grafit kullanılmadan, yanma ve termal bozunma özelliklerinin araştırılmasıdır.

Kompozitlerin yanma ve termal bozunma özellikleri LOI, UL-94 standardı, termogravimetrik analiz (TGA) ve kütle kaybı kalorimetre ile incelenmiştir.

Kütle kaybı kalorimetre testinden sonra kalan kalıntılar, toplam yansıma geçirgenliği azlatılmış – Fourier dönüşümlü kızılötesi spektrometre (ATR-FTIR), X-ışını kırınımı (XRD) ve taramalı elektron mikroskobu (SEM) ile incelenmiştir. Kompozitlerin mekanik özellikleride, çekme testi ve dinamik mekanik analiz (DMA) ile incelenmiştir.

Anahtar Kelimeler: huntit, hidromagnezit, termoplastik poliüretan, yanmazlık, mekanik özellikler

*To my family*

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## ABBREVIATIONS

ASTM	: American Society for Testing and Materials
ATH	: Aluminium Tri Hydrate
ATR-FTIR	: conducting attenuated total reflectance-Fourier-transform infrared spectroscopy
BS	: British Standards
DMA	: Dynamic Mechanic Analysis
EG	: expandable graphite
EPA	: Environmental Protection Agency
EVA	: Ethylene vinyl acetate
HB	: Horizontal Burning
HH	: Huntite and hydromagnesite
IEC	: International Electrotechnical Commission
ISO	: International Organization for Standardization
LOI	: Limiting Oxygen Index
MH	: Magnesium Hydroxide
MPa	: Mega Pascal
OIT	: Oxidative Induction Time
PU	: Polyurethane
PP	: Polypropylene
SEM	: Scanning Electron Microscopy
TGA	: Thermogravimetric Analysis
TPU	: Thermoplastic Polyurethane
XRD	: X-ray diffraction
ZnB	: Zinc borate

## **CHAPTER 1**

### **INTRODUCTION**

A polymer is a high molar mass molecular compound made up of many repeating monomeric units, which are bonded together by covalent bonds along the polymeric chains [1]. Polymeric materials have been used to produce myriad materials in many applications in daily life since beginning of 20<sup>th</sup> century because of their lower cost, easy processibility and formability. Polymeric materials are categorized into groups as plastics, rubber, synthetic fibers, polymeric coatings and additives.

Thermoplastic polyurethane that is thermoplastic polymer is the most widely used in day to day life. TPU is popular in wide range of markets and applications because of having ability to resist solvents, grease, chemicals, and also having high elongation, tensile strength and elasticity. Global market of TPUs is rapidly expanding at 6-8% rate by growth of automobile, footwear, electronics and medical industries. TPU is used in many applications such as footwear, food processing equipment, hoses, wire and cable coatings, medical tubings, biomedical apparatus, drive belts, film and sheet, caster wheels and hydraulic seals. Therefore flame retardancy properties of TPU have become important to increase safety and save lives since various TPU was used in applications such as consumer appliances and products [2-5].

One of the destructive forces of nature is fire which is known as material's rapid oxidation in the exothermic chemical process. Fire has effects on ecological systems both positively and negatively. Positive effects are colony-stimulating growth and

conservation different ecological systems, in addition cooking, heating and lighting purposes for humans. Negative effects are atmospheric pollution and water pollution. Every day in Europe there is about 12 fire victims and 120 people severely injured and the World Health Organization reports that there are approximately 300,000 deaths per year, globally from fire related burns [6].

In 2014, there were 1,298,000 fires reported in the United States. These fires caused 3,275 civilian deaths, 15,775 civilian injuries, and \$11.6 billion in property damage [7]. As indicated in fire statistics, there were 350 civilian deaths in Turkey.

Fire safety of plastic products has been a matter of great concern to legislators, authorities, and manufacturers since the advent of building fire regulations. Most such products are found in buildings, transport vehicles, or enclosures of some kind, and considerable effort is dedicated to minimizing the material reaction-to-fire and the resulting hazard to humans [8].

Flame retardants should reduce rate of burning or flame spread or smoke generation and increase ignition temperature during fire. There is various type flame retardants which are organic, inorganic, mineral, halogen containing or phosphorus containing are widely used in polymeric materials. Inorganics flame retardants are generally aluminum trihydroxide, ammonium polyphosphate, antimony trioxide. Brominated and chlorinated flame retardants are usually including chlorinated paraffins, tetrabromobisphenol-A, decabromodiphenyl ether. Organic phosphorous flame retardants are usually phosphate esters such as triphenyl phosphate, others combined with halogen compounds. Nitrogen based flame retardants are generally melamine. Halogen containing flame retardants emit toxic gases, smoke and corrosive products. Mineral flame retardants release only harmless metal oxide, carbondioxide and water.

The role of the flame retardant is not to prevent material from ignition. It should keep the rate of the spread of the flame minimum and prevent the sustained burning. For this reason, flame retardants tend to prevent the spread of flame by increasing the resistance of the polymer to ignition.

Therefore, an ideal flame retardant should have properties like below [8]

- It should have low toxicity free and do not cause any health hazard
- Small particle size
- It should be colorless
- It should be thermally stable at processing temperatures
- It should be compatible with the polymer binder
- It should at least maintain or improve the mechanical properties of the polymer
- It should be available and cost effective

Huntite and hydromagnesite minerals which are naturally occurring minerals can be used as filler for various applications. Huntite is magnesium calcium carbonate, Hydromagnesite is hydrated magnesium carbonate. Mixtures of the minerals have a use in industry. Their endothermic decomposition of mineral mixture is similar with the flame retardants that mostly used. A huntite and hidromagnesite mixture emits water and carbon dioxide. In many applications we can see the use of Huntite and Hidromagnesite as a flame retardant instead of aluminum hydroxide and magnesium hydroxide. They are similar to brucite based flame retardant which is introduced to the market in 1980s.

The hydromagnesite is probably a more effective flame retardant than the huntite and grades richest in this phase would be expected to be most effective in this respect [9]. There are various mixtures that include different proportions of huntite and

hydromagnesite that are prepared by Likya Minelco Mining company which has mining capacity over 25,000 tons in a year is increasing up to 40,000 tons for huntite.

Huntite and hydromagnesite's endothermic decomposition which releases water, carbon dioxide, calcium oxide and magnesium oxide as result, starts at approximately 250 °C. Huntite and hydromagnesite reserves which are economically important are found in Turkey.

In this study, flame retardancy capacity of TPU was examined with using huntite and hydromagnesite, expandable graphite mixtures as flame retardant additive with varying proportions of TPU. The main aim of this thesis is to investigate the combustion and thermal degradation characteristics of the flame retardant TPU based composites containing huntite and hydromagnesite with and without expandable graphite. The combustion and the thermal degradation characteristics of composites are investigated by LOI, UL-94 standard, thermogravimetric analysis (TGA) and mass loss calorimeter. Char residues remained after mass loss calorimeter test are investigated by conducting attenuated total reflectance – Fourier-transform infrared spectroscopy (ATR - FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. The mechanical properties of the composites are also investigated by tensile testing and dynamic mechanical analysis (DMA).

## **CHAPTER 2**

### **BACKGROUND INFORMATION**

#### **2.1 Polyurethane**

Polyurethanes are the most well known polymers used to make foams. It also exists in a variety of forms, including flexible foams, rigid foams, chemical-resistant coatings, paints, rigid insulation pannels, elastic fiber, adhesives and sealants. Prof. Dr.Otto Bayer is inventor of polyurethane and known as a father in polyurethane industry. Polyurethane is invented at the I.G. Farbenindustrie, Germany in 1937, but industrial production started in 1940 with DuPont and ICI [10-13].

It was first developed to replace rubber. In World War II, polyurethane is used for the airplane finishes, chemical and corrosion-resistant coatings to protect metal. By the mid-50's, polyurethanes produced as elastomer and rigid foams for cushioning. After the development of polyether polyol, flexible foams opened the door to the furniture and automotive industry [13].

Today, polyurethanes used in chairs, desks, automobiles, telephones, clothes, footwear, appliances, beds also insulation of walls and roof and moldings. Polyurethanes can be classified into various categories depending on their properties and applications as decribed below;

- Flexible Polyurethane Foam: is used in furniture, carpet underlay, otomotive interior, bedding and packaging. Foam is flexible to create most of the shapes and firmness. It is light, and durable.
- Rigid Polyurethane Foam: These foams are used for insulation and reduce the enegy cost energy significantly in roofs and walls also in windows and doors.
- Coatings, Adhesives, Sealants and Elastomers: Polyurethane coatings make the product apperiance better and make it more durable upon its lifetime. Polyurethane adhesives have strong bonding capability. They can be molded into most of the wanted shapes. They are light and offer good mechanical properties and have resistance to the environmental factors.
- Reaction Injection Molding (RIM) : Reaction injection molding (RIM) is a production technique to produce electrical housing panels, car bumpers, and computer. Polyurethane RIM parts can exhibit heat resistance and also have to high strength. Thye have high stability and high dynamic properties.
- Binders: Polyurethane binders are used to accrete particles and fibers. They used in wood panel manufacturing, elastomeric of rubber surfaces, industrial sand cating etc.
- Thermoplastic polyurethane (TPU): Thermoplastic polyurethane is a thermoplastic elastomer. It is elastic and melt-processable and has many physical property combinations and processing applications. Extrusion, injection molding, blow molding and compression molding equipments can be used to process TPU. Vacuum forming or solution coating is also used process to form TPU. It is resistant to abrasion, impact and weather. It is mostly used in construction, automotive and footwear industry [10, 13].

With its higher mechanical strength, abrasion resistance, easiliy process capability and bio-compatibility TPU is the widely used material amongst all the grades of polyurethanes.

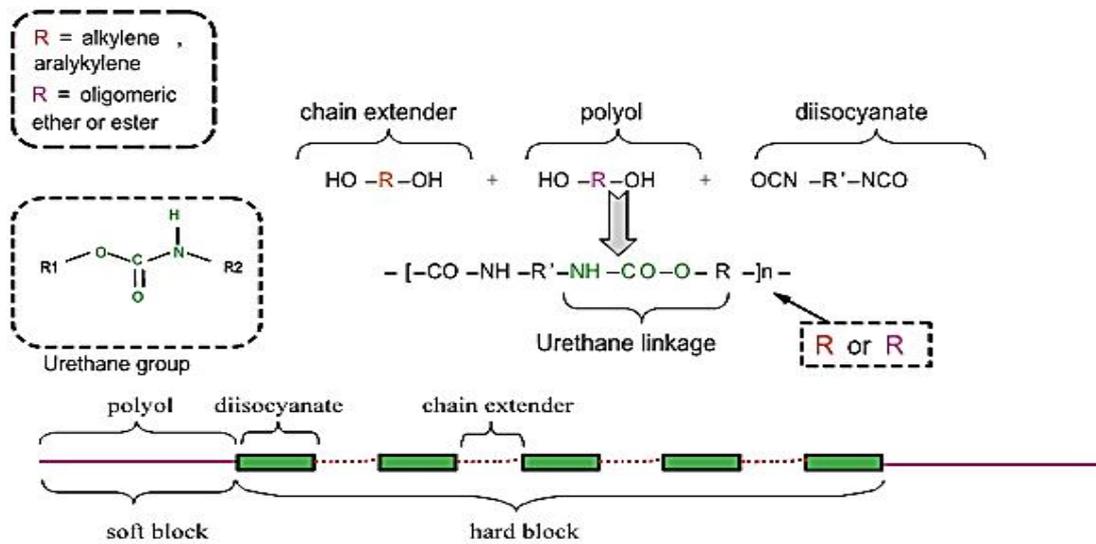
### **2.1.1 Thermoplastic Polyurethane**

Thermoplastic polyurethane: (TPE-U or TPU) is a class of polyurethane plastics. TPU is a multi phase block copolymer. It can be created with three basic raw materials. These materials must be combined together in a specific way. The components that require producing a TPU are [14]:

- A long chain diol or polyol
- A chain extender
- A di-isocyanate

TPU is formed by the reaction of di-isocyanates with short chain or long chain diols. The soft segment is prepared by the reaction between the polyol and the diisocyanate, hard segment is formed by the reaction between the diisocyanate and the chain extender. They form block copolymers by the help of covalent links at the both types of the segments [15].

As illustrated in Figure 2.1 TPU is consisting of linear hard and soft segments of block copolymers. The soft block is gives TPU the flexibility character. The hard block gives a TPU its toughness and physical performance properties. By varying the structure and/or molecular weight of the basic three reaction compounds, many variety of TPU can be possibly created.



**Figure 2.1** Components required to produce a TPU [16]

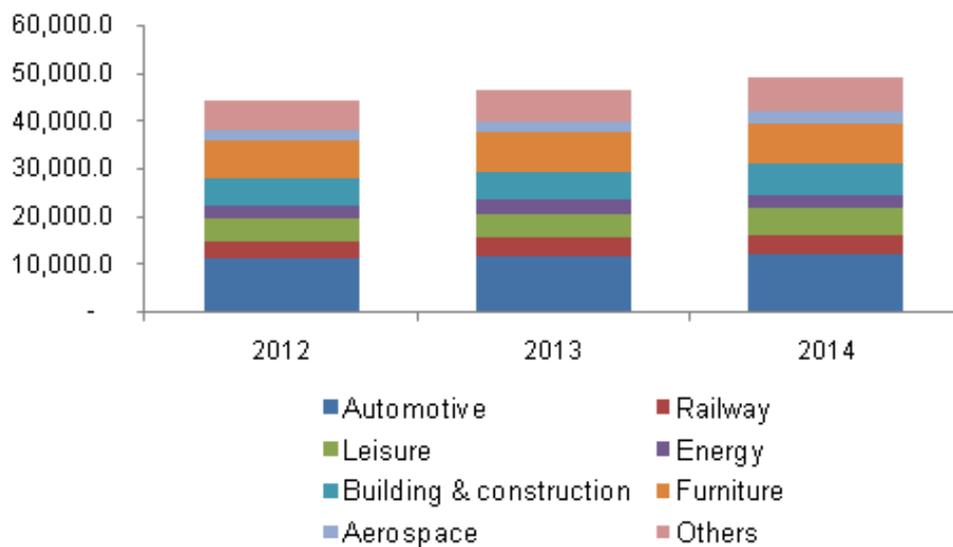
Polyesters and polyethers are used as the polyol component. If the polyol is produced from renewable resources, produced TPU is called bio-based. The urethane group is formed usually by the reaction between hydroxyl groups and isocyanate. 4,4'-methylene bis (phenyl isocyanate) (MDI), 2,4-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI), isophoron diisocyanate (IPDI) are the most commonly used diisocyanates [17].

TPU also have some advantages from other materials like below:

- Higher reproducibility and so lower quality control costs.
- Good flexibility in a wider temperature range so it can be extruded or injection molded.
- Good impact strength so it is desirable for sturdy products.

- High elasticity and flexibility to create solid components typically for shoes, cables, wires, films, etc.
- It can easily be compounded with additives, oils, greases and numerous solvents to create, plastic moldings, laminated textiles, protective coatings or adhesives.
- High resistance to weather and UV radiation makes TPU useful in automotive industry, foot wear, mobile phones and medical devices.
- Recyclability
- Ease of coloring [13, 18]

TPU have a broad range of useage area applications such as insulation of refrigerators and freezers, producing cushioning for furniture, car parts, foot wear, sportswear, mobile phones, building insulation, coatings, adhesives, medical devices, mattresses, rollers and tyres, composite wood panels [19, 20]. Application areas of global TPU market from 2012 to 2014 have shown in Figure 2.2.



**Figure 2.2** Global TPU films market volume growth by application, 2012-2014 (Tons) [21]

Most of the material produced from thermoplastic polyurethane is used everyday in homes with close contact with humans. It requires some more property when human contact is in process. One of them is flame retardancy. Especially for the building isolation flame retardancy have a key role. However, its wider application is restricted due to the easily combustible character with melt dripping. The flame retardant properties of TPU can be improved using various kinds of flame retardant additives like below:

- Halogen containing retardants: aliphatic bromine, aliphatic chlorine
- Boron-containing retardants: Boric acid with 1,2-propanediol
- Mineral fillers
- Intumescent systems: Ammonium polyphosphate (PPP), iron graphene, melamine expandable graphite
- Phosphorus containing retardants: Aromatic poly phosphonate and bisphenol-A poly carbonate, poly bispropoxy phosphazene, poly dimethylsiloxane [13, 22-34]

## **2.2 Composites**

Composites consists at least two ingredients which have different physical or chemical properties. These different ingredients produce a material which has different properties than these two components. Composites are stronger, lighter and less expensive materials, because of that, they preferred. Mainly composite materials are composite cements, concrete, reinforced polymers, metal composites and ceramic composites.

### **2.2.1 Production Methods of Polymer Composites**

Melt blending is the most practical and suitable method for large scale polymeric composite production applications. Usually the additives, mix with the polymer using twin screw extruder to manufacture of polymer composites as melt mixing

method preferred. After extrusion the polymer composites are shaped using injection and compression molding processes to use in mechanical and flammability tests.

#### **2.2.1.1 Extrusion**

In plastic industry extrusion is widely used to melt the polymer and mix it with the other ingredients like colorants, anti-oxidants, fillers and other types of additives. Thermoplastics and some thermosets can be extruded and produced in required shapes such as sheets, cables fibers, profiles, films, fibers and pellets [35, 36]. In extrusion process the ingredients of the composite material are fed in the hopper of the extrusion machine and passes to screw part of the extruder. Screw part of the extruder is heated externally and also rolling screws produce heat with friction of polymers. Melted plastic shaped with a die at the screw and cools instantaneously and becomes solid when it is comes out from the die. [35].

#### **2.2.1.2 Compression molding**

Compression molding is used to shape the polymeric materials. Firstly material will be heated in open mold cavity, and then, mold is closed. After that pressure will be applied to the mold. Heat and pressure is hold until the molding process finished. Molded material is cooled and then removed from the mold.

#### **2.2.1.3 Injection molding**

Polymeric materials (generally thermoplastics and thermosets) are shaped also with injection molding process. In this process the material is melted in a barrel then with a high pressure injected into cavity of the mold. Material cools in the mold and gets the mold's shape. Tensile test samples which have the dog bone shape have prepared with using injection molding technique [37].

## **2.3. Flammability of Polymers and Flame Retardants**

### **2.3.1 Polymers and Classification**

Polymers are used in a wide range of applications, as coatings, as adhesives, as engineering and structural materials, for packaging, and for clothing to name a few [38].

Nowadays it is possible to compose polymer from different elements with any quality desired. Polymers which can be created in the form of solid plastics, elastomers, foams or fibers, can be hard or soft, flexible, transparent, coating or adhesives, also they can be vugular or smooth. There are almost infinitive possibilities in the end product.

Polymers are divided into two main classes such as, natural and synthetic. For instance, cotton, cellulose, wool and protein fiber are familiar natural polymers. There are different classes which are branch of synthetic polymers are based on structure, property, polymerization, processing characteristics and applications. Polymers are classified into plastics, fibers and elastomers depending on their physical properties. Elastomers have high extensibility which gives ability for returning to their original shapes or sizes, however, plastics have only partially elastic ability and fibers have high tensile strength.

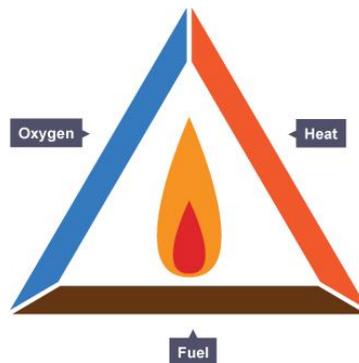
Polymer is large molecule which is constituted by smaller molecules. These small molecules are termed as monomers are repeating units. Linking of monomers is named polymerization. Different monomer types, build different polymer. Also polymers can be characterized by how they are made as addition or condensation polymers. Polymer has same formula as its monomer but superior molecular mass in addition polymerization. Most known ones are polyethylene, polypropylene,

polystyrene and polyvinyl chloride. In condensation polymerization, there are chemical condensation reactions between molecules which are releasing small molecules such as water, methanol or ammonia while polymers are being created. Most known ones are polyesters, polyamides and polyurethanes.

## 2.3.2 Burning Behaviour of Polymers

### 2.3.2.1 Combustion and fire

Combustion is a chemical process in which a material reacts rapidly with oxygen and emits heat. Combustion is often a complicated sequence of elementary radical reactions. Fire is simple definition of combustion and it is represented as a triangle.



**Figure 2.3** Fire triangle

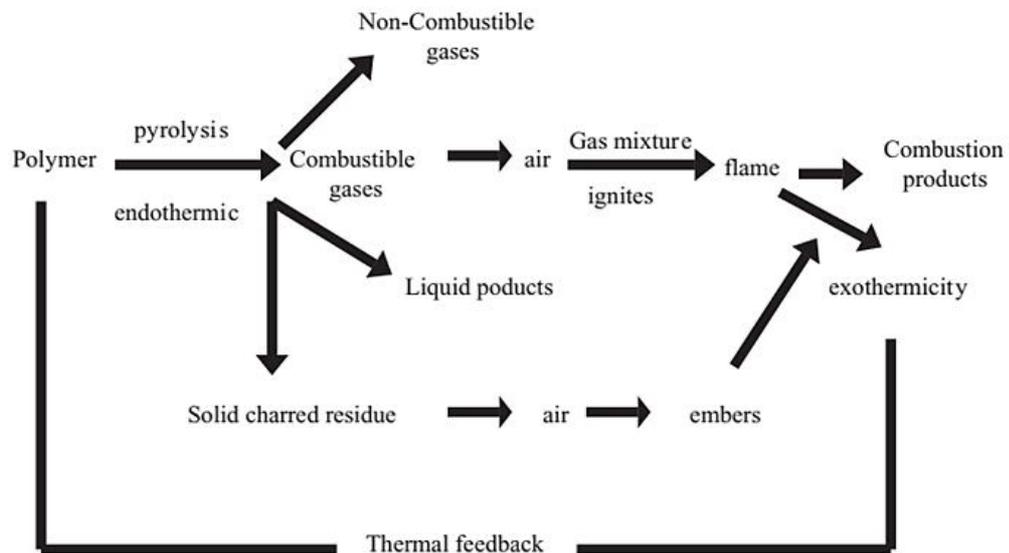
This combustion cycle should be enclosed for existing fire event. Also, oxygen, heat and fuel are the three sides of fire triangle. If one of the three elements of the fire triangle is removed, combustion reaction stops. The fuel should be available in appropriate amount. Also ignition temperature is important factor at fire triangle. The fuel's temperature should be raised to ignition temperature for combustion and to spontaneous combustion. There are three main stages which are firstly, heating of the fuel source (Polymers, Plasticizers, Process oils, Resins). Secondly decomposition of

the fuel source into combustible and non-combustible materials and thirdly ignition of the combustible fuel and air mixture to produce a flame. After ignition, proper conditions may allow flame spread and solid burning which, among others, determine the heat release rate. Also heated zone should be appropriately large to overcome heat loss.

### **2.3.2.2 Burning Behavior and Thermal Decomposition of Polymers**

Combustion is defined as rapid, exothermic chemical reduction-oxidation reaction which may be spontaneous or continuous due to ignition and heat loss. Process of combustion for polymeric materials can be separated into stages such as heating, decomposition, ignition, and combustion and flame propagation.

With heating polymer's temperature is raised to specific point which decomposition starts in heating stage at and mostly polymers release flammable gas that diffusing in flame zone. Following decomposition, if ignition source energy is available, combustion will begin in gas phase and release more heat for self-sustaining also this gas phase reaction produces combustion near solid surface polymeric material. Flames may occur due to polymeric material's chemical properties and fire performance.



**Figure 2.4** Combustion decomposition process of polymers [39]

In Figure 2.4 it can be seen that at first polymers go pyrolysis stage then by the help of heat produced in pyrolysis, hot radicals react with air and volatile radicals, the ignition occurs. Flames may spread horizontally or vertically depending on pyrolysis zone and polymeric materials' alignment. Horizontal flame spreads slower than vertical because flame is heated only by downward gas phase heat transfer. Vertical flame spreads faster, because heat transfer will be consist of conductive, convective and gas phase.

Polymers can be classified depending on their chemical composition with varying thermal decomposition and fire performance. Decomposition of many polymer materials accelerated through oxidants, such as oxygen or air.

The thermal degradation of polymers refers to the case where polymers at elevated temperatures start to undergo chemical changes without the simultaneous involvement of another compound. Thermal degradation of polymers has an importance to develop a technology in polymer processing for using polymers at higher temperature, and understanding thermal decomposition mechanisms for the synthesis of fire-safe polymeric materials [40].

It has two main mechanisms which are depolymerization and fragmentation of chains. Polymers have different and various types of bonds. Random chain scission, chain-end scission, depolymerization and elimination of pendant groups are the three main types of thermal degradation of polymers. [41]

### **2.3.2.3 Decomposition and Properties of Thermoplastic Polyurethane**

Thermoplastic polyurethanes constitute an important group of polymers that have found wide applications due to their fundamental physical properties that make them a polymer of choice [40].

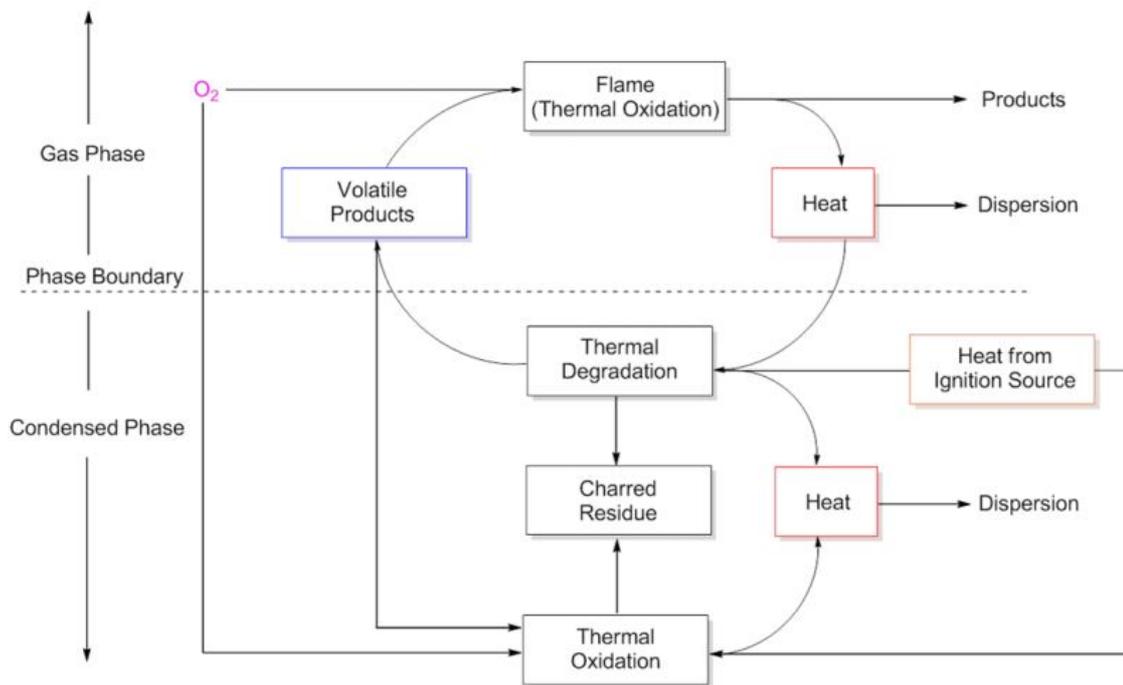
TPU can be used in various applications in day to day life. They have trade names such as Elastollan (BASF), Desmopan (Covestro), Irogran (Huntsman), Estane (Lubrizol), Pearlthane (Marquinsa), Ravathane (Ravago) and Roylar (Uniroyal). Global market of TPUs is one of the fastest growing thermoplastic polymers that have 6-8% growth rate each year. Polyurethanes are produced by the exothermic chemical reaction with alcohols and more than one hydroxyl (OH) and isocyanate (NCO) groups. Diols, triols and polyols are reactive hydroxyl groups and diisocyanates, polyisocyanates are reactive isocyanate groups.

Polyurethanes chains don't break down until 200°C and air causes, slow decomposition. With pyrolysis temperature, hydrogen cyanide and carbon monoxide are formed. Main mechanism in urethanes while decomposition, is the scission of polyol-isocyanate bond that is formed while polymerization. Isocyanate vaporizes as a smoke and polyol melts as a liquid for next decompose. Several studies indicate that the thermal decomposition of ether based TPUs is predominantly and oxidative process. The ester based TPUs normally exhibit considerably better thermal and oxidative stability than ether based ones [42].

### **2.3.3 The Flame Retardancy Mechanisms of Polymers**

Flame retardants should block or restrain the combustion. Flame retardants can act in during heating, decomposition, ignition, or flame spread of polymer. There are varieties of flame retardants that have different specifications. Some of them can act in combustion process in the solid phase, (condensed phase) and some of them can act in the flame zone (vapor phase). They can act through physically, chemically or combination of, these two mechanisms.

- Condensed-phase: Some of the flame retardants can form a carbon layer on surface of polymer. This layer insulates the material as a physical barrier and reduces the heat transfer, slows down heat and mass transfer from the flame [43, 44]. Boron based flame retardants, phosphorous based flame retardants act in condensed phase generally.
- Gas phase: With a flame retardant radical mechanism of the combustion process is stopped in the gas phase. System starts to cool down due to reduced exothermic process occurred in the flame and also with reduced concentration of flammable gases. Halogenated flame retardants usually act in gas phase. [43, 14].



**Figure 2.5** Two phases of combustion of a polymeric material [45]

### 2.3.3.1 Physical Interaction Mechanisms

Physical methods is used to lower temperatures by endothermic reactions and cool the combustion environment and slow down reaction pathways and also to slow down the spread of flame by diluting oxygen with non-combustible gases. Physical methods are described as below. [46]

- By cooling: The flame retardant additives degrades endothermically and cools the substrate to a temperature below the combustion, pyrolysis and thermal decomposition temperature. Metal hydroxides such as aluminum hydroxide and magnesium hydroxide works by cooling method as a flame retardant.

- By inert gas dilution: The flame retardant additives decompose with combustion and produce large volumes of noncombustible inert gases. These gases dilute the oxygen supply for the flame or dilute fuel concentration below the flammability limit. Retardants which release H<sub>2</sub>O, CO<sub>2</sub>, talc, chalk, aluminum hydroxide work by dilution method as a flame retardant.
- By dilution: heat capacity of the product can be increased by addition of the flame retardant. Also the flame retardant can reduce the fuel content of product to a level below the lower limit of its flammability. Inert fillers like glass fibers minerals usually act by dilution.
- By forming char formation (barrier): The flame retardant can act by forming protective barrier layer. The heat transfer is reduced by the help of the char layer. Char also blocks the flammable radical and flammable gas flow to the atmosphere. Most popular char forming flame retardants are phosphorus and intumescent compounds.
- By thermal quenching: Flame retardant degrades endothermically. Increases thermal conductivity. Physical or chemical change that results in the heat being absorbed by the additive thereby prevents combustion. Metal hydroxides and carbonates act in this way.

### **2.3.3.2 Chemical Interaction Mechanisms**

Chemical interaction mechanisms are used to interfere with free radical reactions which occur during combustion and also to insulate the underlying material from temperature rises by char formation. This is a general flame-retarding mechanism of brominated flame retardants. Reaction occurs in gas phase or solid phase. Reaction

in gas phase occurs by the free radical mechanism of combustion and this stop or suppresses the exothermic reactions and as a result it cools down the system. Reaction in solid phase occurs by forming carbonaceous layer on the polymer surface (e.g. phosphorus compounds) [47]

Polymers are considered as more flammable if they are susceptible to random chain breaks that dissociate into smaller fragments like Polyethylene and Polypropylene and depolymerization like Polystyrene. Like Polyvinyl chloride and crosslinking Polyacrylonitrile are less flammable because of the susceptible elimination of pendant groups [41].

#### **2.4. Flame-Retardant Additives**

Flame retardants are a group of chemicals. They can be added to materials, like plastics, textiles, coatings etc. A flame retardant should restrain or retard the combustion process. By the nature of the flame retardant additive, they can act chemically and/or physically in the solid, liquid, or gas phase.

When they mixed with the base material we call them additive flame retardants and if they are chemically bonded to material we call them reactive flame retardants. Mineral flame retardants are typically additives while halogenated and phosphorus compounds can be either reactives or additives.

### **2.4.1 Halogenated Flame Retardants**

Although the regulations from Europe and USA, that about the health issues, halogenated flame retardants are still commonly used with polymers. Halogenated flame retardants cause reproductive, thyroid, endocrine, developmental and neurological disorders including decreased fertility, birth defects, learning disorders. Four classes of chemical compounds can be used as halogenated flame retardants those containing fluorine, chlorine, bromine, or iodine. Fluorinated retardants are normally more stable than any other polymers and do not release fluorine radicals or hydrogen fluoride. Iodinated retardants have very low thermal stability and cannot be processed with most commercial polymers. Brominated retardants are more expensive than others [41].

### **2.4.2 Phosphorus Containing Flame Retardants**

Phosphorus based flame retardants are second most widely used flame retardants. There are four types of phosphorus based flame retardants like elemental red phosphorus, inorganic phosphates, numerous organic phosphorus based products and chloroorgano phosphates. These phosphorated flame retardants can be used as additives or incorporated into the polymer chain during its synthesis. Both inorganic and organic phosphorus compounds are useful to improve flame retardance of polymers. A phosphorus containing flame retardant can function in the condensed phase, the gas phase, or concurrently in both phases [48]. Typically, phosphorus based flame retardants shows its activity in combination with the starting decomposition of polymer. It can produce a partial gas phase for the flame extinguishing effect. The main feature is char forming activity sometimes combined with foaming which forms a protective top layer on the surface [41].

### **2.4.3 Mineral Flame Retardants**

Metal hydroxides (of aluminum and magnesium) are the mostly used mineral flame retardants. They have an action as direct physical flame retardant. By endothermic decomposition metal hydroxides releases water vapor and an inorganic residue. Mineral flame retardants are used mostly as mineral fillers in polymer composites. Mineral fillers help to dilute the combustible products by releasing water and cooling the environment in condensed phase with endothermic dehydration.

#### **2.4.3.1 Huntite and Hydromagnesite**

Huntite and Hydromagnesite are special magnesium carbonate containing minerals. Huntite is magnesium calcium carbonate  $Mg_3Ca(CO_3)_4$ , Hydromagnesite is hydrated magnesium carbonate  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ . Huntite and hydromagnesite mixtures are mostly used in industry.

They have a decomposition endothermically. This decomposition is similar to mostly used flame retardants. The mixture of huntite and hydromagnesite replaced the use of aluminum hydroxide and magnesium hydroxide.

Physical properties of potential fire retardant mineral fillers.

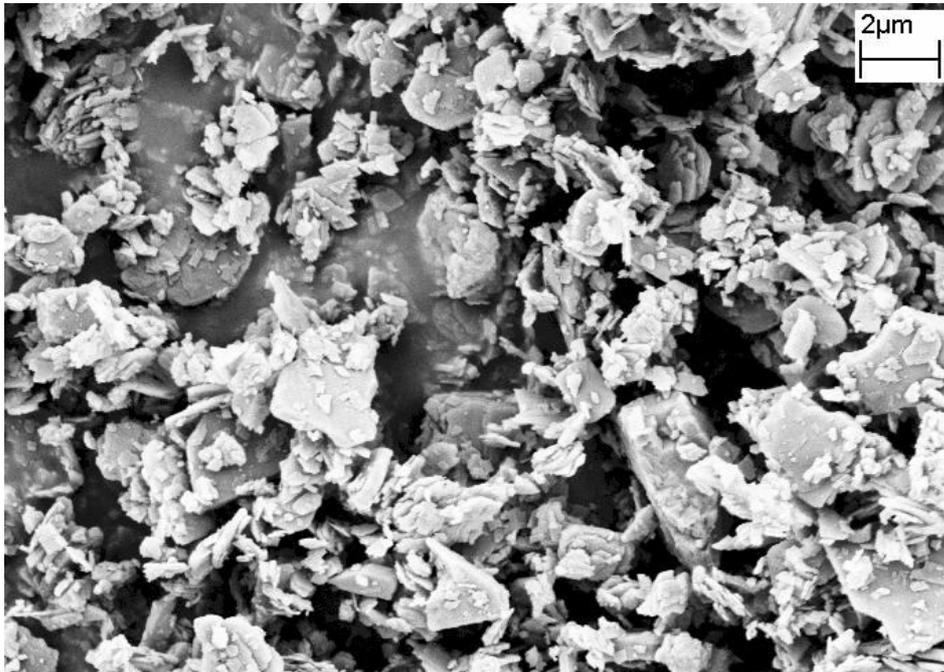
Filler	Formula	T <sub>decomp</sub> /°C	ΔH <sub>decomp</sub> /kJ g <sup>-1</sup>
Aluminium hydroxide	Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O	180–200	1300
Magnesium hydroxide	Mg(OH) <sub>2</sub>	300–320	1450
Calcium hydroxide	Ca(OH) <sub>2</sub>	430–450	1150
Nesquehonite	MgCO <sub>3</sub> ·3H <sub>2</sub> O	70–100	1750
Hydromagnesite	Mg <sub>5</sub> (CO <sub>3</sub> ) <sub>4</sub> (OH) <sub>2</sub> ·4H <sub>2</sub> O	220–240	1300
Huntite	Mg <sub>3</sub> Ca(CO <sub>3</sub> ) <sub>4</sub>	400	980
Ultracarb	Hydromagnesite/ Huntite 60/40	220–400	1172
Boehmite	AlO(OH)	340–350	560

Figure 2.6 Physical properties of potential flame retardant mineral fillers [49]

In lakes region that include Afyon-Denizli-Isparta there are some mining companies that produces huntite. For hydromagnesite the world's largest known reserves are in Turkey. An average mineralogical composition based on XRD analysis is like huntite (46%), hydromagnesite (46%), magnesite (4%), aragonite (3%) and calcite (1%) [49].

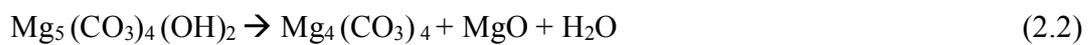
With reasonable costs, fine particle size naturally and high purity, Huntite and hydromagnesite minerals have a similar history in terms of flame retardant applications as magnesium hydroxides. To create synergism they can be used either alone or in combination with other mineral flame retardants. Huntite particles have platy morphology and hydromagnesite particles have a blocky morphology.

Figure 2.7 shows the scanning electron microscope (SEM) graph of huntite-hydromagnesite sample. The bigger, blocky particles represent hydromagnesite while the smaller, platy particles represent the huntite.



**Figure 2.7** Scanning electron microscope (SEM) graph of huntite-hydromagnesite [50]

Hydromagnesite has three decomposition steps about 220°C to 550°C, which are the releasing water and carbon dioxide, then the hydroxide ion decomposes and leaving magnesium oxide as a residue [50].



Huntite decomposes in two step process. It releases carbon dioxide at temperatures 450°C to 800°C. Huntite decomposes firstly to magnesium oxide, then decomposes to carbon dioxide and calcium carbonate, after that decomposition of calcium carbonate to carbon dioxide and calcium oxide occurs [51].



Mixture of huntite and hydromagnesite has advantages with the decomposition mechanism and morphology, in comparison to the well-known metal hydrate flame retardants. Aluminium hydroxide decomposes less temperature than Hydromagnesite. This means hydromagnesite can be used with polymers which require higher temperatures at processing. And also it has a broad decomposition range which starts about 220°C and finishes about 740°C. That means that aluminium hydroxide and magnesium hydroxide has limited temperature range for cooling than huntite and hydromagnesite mixture [50, 51].

#### **2.4.4 Inorganic Flame Retardants**

Inorganic flame retardants are mostly has an effect in condensed phase. They are important because of their relatively low toxicity, easy of handling and low cost and are typically synergists for other flame retardant additives. The two most commonly used are aluminum oxide trihydrate (ATH) and magnesium hydroxide (MH). Zinc borate is also used as an inorganic flame retardant. Inorganic flame retardants can release water above 200°C endothermiccally. With this endotermic effect the heat removes from substrate.

The decomposition of substrate is slow and substrate cannot reach its ignition temperature. Another advantage is they can reduce the amount of smoke generated on combustion [52]. Polymers mixed with in large quantities (>50% by weight) with flame retardants to get a significant effect for flame retardancy.

#### **2.4.5 Intumescent Flame Retardants**

The word intumescence comes from the Latin, and means “to swell up.” It describes intumescent material. When intumescent material heated beyond a critical temperature, it begins to swell and then to expand. The result of this process is a foamed cellular charred layer on the surface protects, underlying material from the heat flux [53].

Intumescent flame retardants mostly include a carbon source, polymer or polyol, acid source, ammonium polyphosphate, gas blowing additive or melamine. Charred layer acts as a physical barrier and slows heat and mass transfer between the gas and condensed phases [54].

Intumescent flame retardants have some benefits. They are very robust fire safety and flame resistance performance. Intumescent materials are mostly used in most of the building, construction, fire door barriers, military, wire and cable and also in aerospace products.

##### **2.4.5.1 Expandable Graphite**

Expandable graphite is also known as intumescent flake graphite. Graphite has a structure consisting of carbon atoms bonded in hexagonal rings joined at their corners to form large planar arrays. These carbon layers are held together by weak interlayer bonds which can crack easily.

A layered structure combined with weak bonding make graphite an ideal material for intercalation, which is the introduction of atoms or molecules between the layers. Common intercalants include sulfuric acid, nitric acid and acetic acid. Other strong oxidizers, such as hydrogen peroxide, nitric acid or potassium permanganate, are used as catalysts to drive the intercalation process. When the intercalated graphite is exposed to heat or flame, the inserted molecules decompose to generate gas. The graphite layer planes are forced apart by the gas and the graphite expands.

Expandable graphite has the expansion behavior. This expansion behavior makes it an ideal additive in flame retardancy studies. It increases in the volume of the graphite of up to 300 times, a lowering of bulk density, and approximately a 10-fold increase in surface area.

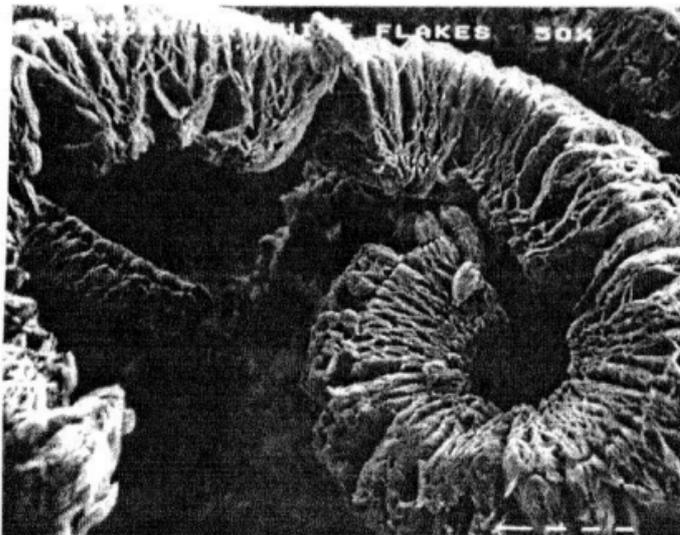
It is often combined with other flame retardants such as phosphorus-based additives (red phosphorus), boron compounds (zinc borates), antimony trioxide, or magnesium hydroxide [55–57].

The expanded, graphite has low-density. It is nonburnable, and used as thermal insulation material. It can reflect up to, 50 % of radiant heat. Because of the long twisting shape it is often referred to as a worm. Typical expanded graphite that has a worm shape is shown in Figure 2.9.

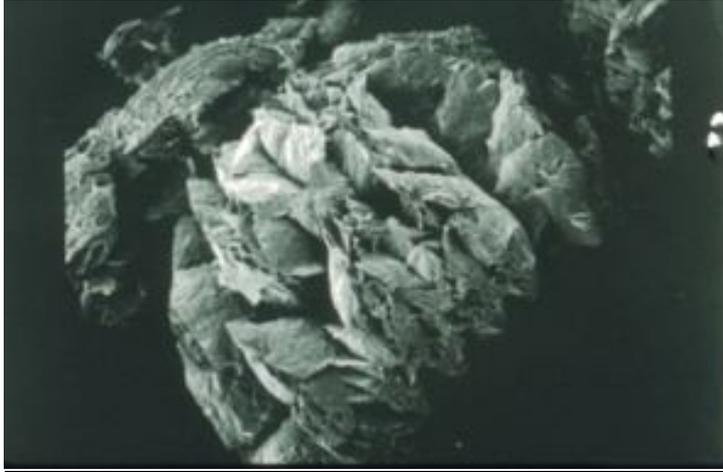
Expandable graphite is mainly used as a fire retardant in conductive fillers, electromagnetic pulse and radiation shielding, roofing, insulation materials, foundry products, etc.[58].



**Figure 2.8** Flake Graphite, Unexpanded [59]



**Figure 2.9** Scanning Electron Micrograph of Expanded Graphite Flake [58]



**Figure 2.10** Expanded intercalated flake graphite [60]

## **2.6. Characterization Tests**

### **2.6.1 Tensile Test**

Tensile tests used to measure the force needed to deform a sample permanently and also the % elongation at point of fracture. For dog bone shaped samples ASTM D638 test method can be used.

Dog boned sample that is clamped at the two ends, pulled in z direction with a constant force until the sample ruptures. For determining engineering stress ( $\sigma$ ) (Eq. 2.6) and strain ( $\epsilon$ ) (Eq. 2.7) cross-sectional area ( $A_0$ ) and length ( $l_0$ ) of the sample is must be known.

$$\sigma = F/A_0 \quad (2.6)$$

$$\epsilon = (l_i - l_0) / l_0 \quad (2.7)$$

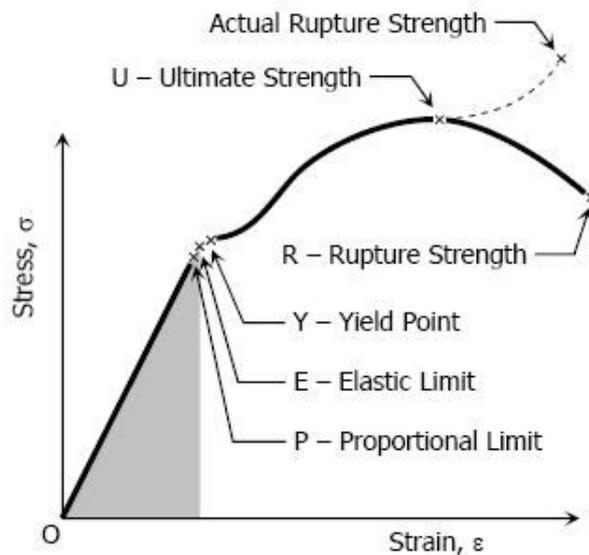
F: applied force

$A_0$  : initial crosssectional area

$l_i$  : final length of specimen

$l_0$ : original length of specimen

By the help of stress vs. strain graph, ultimate tensile strength, Young's modulus, elongation at break (rupture point) can be determined..In Figure 2.11. engineering stress vs. engineering strain graph can be seen.



**Figure 2.11** Engineering stress vs. strain graph of a typical polymer during a tensile test [61]

Modulus of elasticity is the measure of stiffness of an elastic material. The ratio of stress to strain is  $E$  and expressed in force per unit area. It is also named as elastic modulus (Eq. 2.8).

$$E = \sigma/\epsilon$$

(2.8)

### 2.6.2 FTIR

FTIR stands for Fourier Transform Infrared, which is the preferred method of infrared spectroscopy. In infrared spectroscopy IR radiation is passes through the sample. Sample absorbs some of the infrared radiation. And also sample transmits

some of the infrared radiation molecular fingerprint of the sample is created with this absorbing and transmitting data. This data is a spectrum of molecular absorption and transmission. This makes infrared spectroscopy useful for several types of analysis.

FTIR provides the informations below;

- It can identify unknown materials
- It can determine the quality or consistency of a sample
- It can determine the amount of components in a mixture

ATR FTIR imaging is useful for difficult samples which are hard to image in transmission or reflection, and also for the samples which have confusing depth structure. It is a contact technique. In this technique the sample is pressed against an ATR crystal and illuminated by an infrared beam from spectrometer. ATR is ideal for solid strongly absorbing or thick samples. In addition, ATR is often used for liquid analysis. It simply requires a drop of liquid to be placed on the crystal. [62, 63]

### **2.6.3 X-Ray Diffraction (XRD)**

The structure or morphology of composites is mostly characterized with X ray diffraction. It gives information like crystalline and amorphous states. To investigate small scale structures usually Wide angle X-Ray scattering (WAXS) technique is used. To investigate large scale morphological structures, Small angle X-Ray scattering (SAXS) technique is used [64, 65].

#### **2.6.4 Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis is a technique that measures the mass of the sample as a function of time or temperature. The sample is in a controlled atmosphere and subjected to a controlled temperature program. Mostly nitrogen atmosphere is used but also air or other atmospheres can be used. The different atmospheres can have different effect on decomposition mechanism. To study the thermal decomposition with mass loss of the materials thermogravimetric analysis is the commonly used.

A TGA consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. In commercial instruments usually 0.1 mg to 2 gr sample sizes are used. Also for these instruments the heating rates varies from 0.1 to 150°C/min, but usually 10, 15, 20, 25, and 30°C/min heating rates are used. The mass of the sample is monitored during the experiment. The balances of the instruments are highly sensitive that have resolutions down to 1 µg and detects when the sample gains or loses weight. With using TGA instrument loss of water, solvent plasticizer and also oxidation, pyrolysis, decomposition, % filler weight, and % ash weight can be determined.

TGA instrument gives data as a graph that shows the percentage mass loss against temperature. By the help of the graph we can determine the decomposition of materials. Materials can lose all of their mass at one temperature and also they can lose the mass at several stages at different temperatures.

When we differentiate the TGA curve we can get mass loss rate versus time (DTA curve). In addition to the rate of decomposition, the heat involved in the decomposition process is also of interest of DTA. TGA and DTA are used to determine the flame retardant mechanisms that will occur before the polymer degrades. They are also useful for characterizing mineral flame retardants [66-70].

### **2.6.5 Dynamic Mechanical Analysis**

DMA is useful instrument to study the viscoelastic behavior of polymers. A sinusoidal stress (stress  $\sigma$ ) is applied to the material and resulting displacement (strain  $\epsilon$ ) is measured and also the complex modulus is determined. Varied temperature or the frequency of the stress can be applied to the sample and variations in the complex modulus occurs with this approach glass transition temperature of the material can be identified [71, 72].

### **2.6.6 Scanning Electron Microscopy**

Unlike normal microscopes SEM scans the sample with help of focused beam of electrons instead of light. The electrons will be sending to the surface of the sample and then reflected or scattered electrons from the sample are analyzed. By the help of SEM, surface information like topography and with using energy dispersive x-ray (EDX) spectroscopy composition information of the sample will be investigated with magnification up to 100000. [67] The surface of the sample has to be electrically conductive. If it is not conductive like most of the polymeric composite materials, it has to be coated by applying a very thin layer of gold or silver coating before the measurement.

## **2.7. Test Methods of Flammability Test Standards**

### UL 94 Test:

ASTM D635-10 is a used method for plastics to determine rate of burning and time, in a horizontal position.

ASTM D3801-10 is a used method for solid plastics to determine the comparative burning characteristics, in a vertical position.

### Limiting Oxygen Index:

ASTM D2863-10 is the test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (Oxygen index)

### Cone Calorimeter Test:

ISO 5660-1 is the reaction-to-fire tests- heat release smoke production and mass loss rate- Part 1: heat release rate (cone calorimeter method)

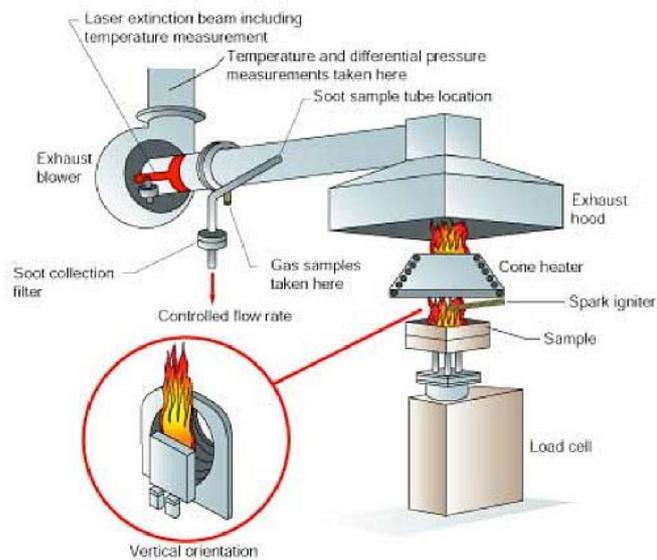
ISO 5660-2 is the reaction-to-fire tests- heat release smoke production and mass loss rate- Part 2: Smoke production rate.

ASTM E1354-11 is the test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter.

## **2.7.1 Cone Calorimeter Test**

To evaluate the flammability properties of polymeric materials the cone calorimeter is one of the most important and effective standardized (ISO 5660 or ASTM E1354.) bench scale fire test [73-75].

During the test the specimen is mounted horizontally on a insulating ceramic material. The orientation of the specimen can also be vertical, this position mainly used for the exploratory studies. The equipment that seen in Figure 2.12 have a horizontally and also a vertically sample stage to mount the samples. Sample stage has a connected load cell to measure the mass of the sample at combustion.



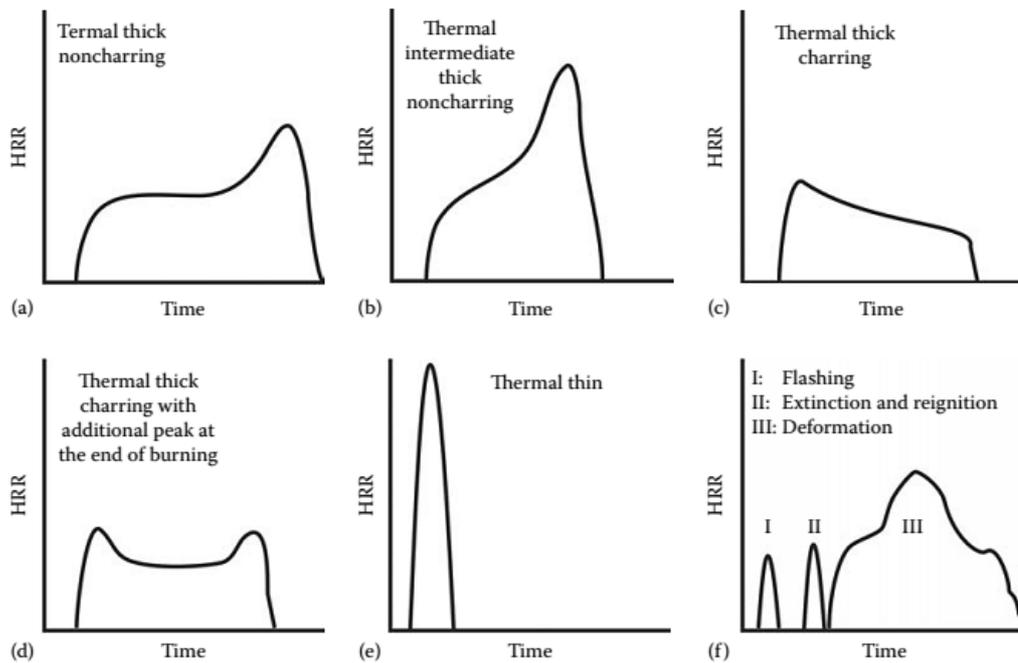
**Figure 2.12** Cone calorimeter test setup [76]

Sample plates 100x100 mm in size and has a thickness between 6 mm and 50 mm are investigated under forced flaming conditions with this method. The test apparatus consist basically of an electric heater, an ignition source and a gas collection system.

On sample surface there is a conical heater which has a capacity to produce external heat flux in the range 0–100 kW/m<sup>2</sup>. Specimen ignited by an electric spark source when the mixture of gases above the specimen is higher than the lower flammability limit. By using cone calorimeter we can obtain some of the most important material properties which are listed below.

- Peak heat release rate (PHRR): is known to be the most important criteria to describe flammability properties of natural and synthetic polymeric materials. Its unit is  $\text{kW/m}^2$ .
- Heat release rate (HRR): HRR represents the combustion process that has a unit  $\text{kW/m}^2$ .
- Total heat evolved (THE): is the total fire load of the material and has a unit  $\text{MJ/m}^2$ . It can be calculated from the area of the graph of heat release rate versus time.
- Time to ignition (TTI): it is the time until the material ignites and starts to burn. The unit of TTI is seconds.
- Total time of burning (TTB): it is the time passed until the beginning of the test to the flame is out of the material. The unit of it is seconds.
- Total mass loss (TML): the mass change of sample during combustion. The unit is grams. Percent fire residue by weight is calculated with using TML.
- Fire growth index (FGI): it is the  $\text{PHRR} / \text{TTI}$ . and have a unit  $\text{kW/m}^2\text{s}$ . Flame spread rate is described with using FGI
- Fire growth rate (FIGRA): it is  $\text{PHRR}/\text{time-to-PHRR}$ . Flame spread rate is described with using also FIGRA that have a unit  $\text{kW/m}^2\text{s}$ .

Different types of typical burning behavior give characteristic HRR curves. Some are illustrated schematically Figure 2.13.



**Figure 2.13** HRR in the cone calorimeter for typical burning behaviors: (a) thermally thick noncharring; (b) intermediate thermally thick noncharring; (c) thermally thick charring; (d) thermally thick charring with additional heat release maximum at the end of burning; (e) thermally thin samples; (f) samples that show flash-ing, extinction and reignition, and deformation [77].

### 2.7.2 UL 94 Test

This test method is used to measure linear burning rate of mounted sample vertically or horizontally. Figure 2.14 is illustration of the test. This test method is very easy and practical to test the flammability properties of the polymers. Similar tests also exists BS2782-1 Method 140A1992 (ISO 1210), ASTM D3801 [78, 79].

Sample size is like 12.5 cm long, 1.3 cm wide, and thickness is 0.3 cm. Sample is hold by the help of clamp. There is also a surgical cotton stands below the sample. In vertical burn test the sample holds vertically, and be ignited at the bottom. In horizontal burning test the sample is hold horizontally in this test. This test is easier than vertical burning and used when the vertical test cannot distinguish between materials. Burner flame is hold distance between burner flame and sample is 1 cm the burner flame is applied 10 seconds and removed. Then after flame removed, the sample is observed for flaming and its duration time recorded (flame time  $t_1$ ). As soon as the flame extinct the burner flame is reapplied for an additional 10 seconds and also duration time recorded (flame time  $t_2$ ).  $t_3$  is the afterglow time.  $t_3$  is the time passed until fire glow to went off.

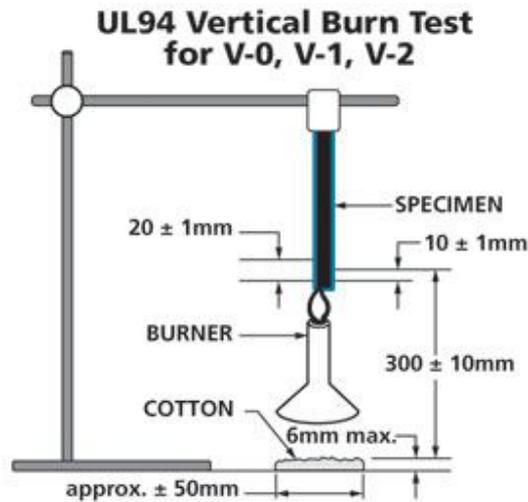
A piece of cotton stands under sample if there is any ignition of the cotton by dripping particles from the test specimen, is recorded. Five specimen tests like this, and after the test the material is categorized in to three parts with flammability ratings like V-0, V-1, or V-2 according to its burning time and the presence or absence of burning drips. The V-0 rating is the best flammability rating, which a material can receive.

UL-94 classification is given below.

- V-0 (Vertical Burn): Once flame is held 10 seconds to specimen then removed. After the flame removed burning stops in 10 seconds. Flame is held again to burned specimen in 10 seconds and removed. After the flame removed burning stops also in 10 seconds. Flaming drips are not allowed.
- V-1 (Vertical Burn): Once flame is held 10 seconds to specimen then removed. After the flame removed burning stops in 30 seconds. Flame is held again to burned specimen in 10 seconds and removed. After the flame removed burning stops also in 30 seconds. Flaming drips are not allowed.
- V-2 (Vertical Burn): Once flame is held 10 seconds to specimen then removed. After the flame removed burning stops in 30 seconds. Flame is held again to burned specimen in 10 seconds and removed. After the flame removed burning stops also in 30 seconds. Flaming drips are allowed.
- H-B (Horizontal Burn): 3mm thick specimen is used. burning rate must be less than 3 inch/min. Self extinguishing materials are usually H-B rated.

**Table 2.1** - Criteria for UL-94 classifications

	V0	V1	V2
t <sub>1</sub>	<10 sec	<30 sec	<30 sec
t <sub>2</sub>	<10sec	<30 sec	<30 sec
t <sub>1</sub> + t <sub>2</sub> (for five samples)	<50 sec	<250 sec	<250 sec
t <sub>2</sub> + t <sub>3</sub>	<30 sec	<60 sec	<60 sec
Cotton ignited by flaming drips	No	No	Yes
Afterglow or after flame up to the holding	No	No	No



**Figure 2.14** The Schematic view of UL-94 test design [80]

### 2.7.3 LOI (Limited Oxygen Index) Test

LOI is a laboratory scaled flammability test. In Figure 2.15 schematic representation of the LOI test can be seen. LOI test is done according to standard ASTM D2863 or ISO 4589. In the LOI test a sample is suspended vertically so inside a closed chamber (usually a glass or clear plastic enclosure). At room temperature, oxygen and nitrogen gas mixture which oxygen gas percentage is determined, send to the fired sample. Test sample used in test, is usually a bar in 100 x 65 x 3 mm size. The top of the test sample is ignited, and the atmosphere is adjusted to determine the minimum amount of oxygen to just sustain burning. The minimum oxygen concentration that keeps the burnout for more than 3 minutes is the LOI value [65].



**Figure 2.15** The view of LOI test design [81]

LOI value is calculated according to the equation given below:

$$\text{LOI} = [\text{O}_2 / (\text{O}_2 + \text{N}_2)] \times 100 \quad (2.9)$$

If the test sample does not ignite in 30 seconds, the concentration of oxygen is increased until the test sample represents stable combustion for more than 3 minutes after removing the ignition. By repeating of these steps, LOI is determined [82].

The oxygen concentration of atmosphere is 21 percent. Materials which have LOI values lower than 21% are classed as highly flammable and materials which have more than 27-28% LOI values are classed as retardant characteristic materials. Higher LOI values represent better flame retardancy and a smaller LOI represents a more flammable material.

## CHAPTER 3

### EXPERIMENTAL

#### 3.1 Materials Used

##### 3.1.1 TPU

Thermoplastic polyurethane (Pearlthane® ECO D12T85) was supplied from Merquinsa (Barcelona, Spain). It has a density of  $1.15 \text{ g/cm}^3$  and hardness 85 (Shore A). It is produced from renewably-sourced polyol (Cerenol) with a content of 46 wt%.

##### 3.1.2 Huntite and Hydromagnesite

Huntite-hydromagnesite (Minelco Ultracarb LH-15) was supplied from Likya Madencilik, Turkey. It has density and surface area of  $2.5 \text{ g/cm}^3$  and  $11\text{-}13 \text{ m}^2/\text{g}$ , respectively. In Table 3.1 and Table 3.2 the chemical composition of Huntite and hydromagnesite and also the properties of it is shown.

**Table 3.1** Chemical composition of huntite and hydromagnesite [83]

Chemical Analysis	% weight
MgO	36 - 39
CaO	6 - 9
SiO <sub>2</sub>	0.2 - 1
Loss on ignition at 1000°C	51 - 54

**Table 3.2** Properties of huntite and hydromagnesite [83]

<b>Properties</b>	<b>Values</b>
Specific gravity	2.5 g/cm <sup>3</sup>
Absorption of oil	20 - 40g/100g
Refractive index value	1.56
Surface area	11 – 13 m <sup>2</sup> /g
Hardness	2.5 Mohs
Loose bulk density	0.2 - 0.5 kg/L

### 3.1.3 Expandable Graphite

The commercial expandable graphite (LKAB - Firecarb TEG-315) with expansion coefficient of > 220 at 1000°C was supplied from Minelco Ltd, Italy. It is free flowing black flakes with a bulk density and pH value of 0.45-0.5 g/cm<sup>3</sup> and 5-7, respectively.

**Table 3.3** Properties of expendable graphite [84]

<b>Property</b>	<b>Value</b>
Appearance	free flowing black flakes with a metallic lustre
Moisture (105°C)	1% max
Volatiles	12% max
Expansion onset temperature	170°C
Loose bulk density	0.45 - 0.50 kg/l
Expansion at 1000°C	220+(ml/g)
Expansion at 250°C	100+ (ml/g)
pH value	5 - 7
Particle size	80% retained on 180 µm

### 3.2 Preparation of Composites

TPU and other filler agents were dried in an oven 2 hours at 100°C for prior to compounding. Composites prepared with various composition ratios shown in Table 3.5 with counter rotating twin screw micro extruder (15 ml micro compounder, DSM Xplore, Netherlands) with a screw speed of 100 rpm at 200°C for 5 minutes that can be seen in Figure 3.1. Also In Table 3.4.the extruder specifications can be seen.

**Table 3.4** Micro compounder properties

<b>Mixing control type</b>	Revolution per minute
<b>Range of the screw speed</b>	1-250 revolution per minute
<b>Max. Axial Force</b>	8000 Newton
<b>Volume of the hooper</b>	15 mililiter
<b>Max. torque value</b>	10 Newton/meter for per screw

Three different amounts of huntite and hydromagnesite containing TPU composites (40, 50 and 60 % by weight) were prepared and the flammability properties were found by LOI and UL-94 tests to understand which concentration is best to choose for synergistic effect studies with expandable graphite. Expandable graphite containing composites (10 and 20 % by weight) were also prepared and characterized. During the synergistic effect studies, the total amount of flame retardant additives kept constant at 50% by weight and the added amount of expandable graphite is deducted from the huntite and hydromagnesite content. The ratio of huntite and hydromagnesite to expandable graphite was adjusted as 9:1, 4:1, 3:2 and 1:1.

**Table 3.5** Compositions of composites

<b>SAMPLES</b>	<b>TPU (wt %)</b>	<b>HH (wt %)</b>	<b>EG (wt %)</b>
TPU/40 HH	60	40	0
TPU/50 HH	50	50	0
TPU/60 HH	40	60	0
TPU/45HH/5EG	50	45	5
TPU/40HH/10EG	50	40	10
TPU/30HH/20EG	50	30	20
TPU/25HH/25EG	50	25	25
TPU/20 EG	80	0	20
TPU/10 EG	90	0	10

Extrudate is pelletized and then dried in an oven at 60 °C for 24 hours for injection molding.



**Figure 3.1** The view of the twin screw extruder used for the composite production in this study [85]

Test samples prepared with cold injection with injection molding instrument (Microinjector, Daca Instruments) with a barrel temperature of 210°C Figure 3.2. The mold temperature is kept in room temperature. Filling and holding times were 30 seconds. Injection pressure was 5 bars. Dog-bone shaped specimens that have dimensions of  $7.4 \times 2.1 \times 80 \text{ mm}^3$  (length x depth x wide) were made by injection molding instrument. Specimens were used in tensile testing and DMA tests.



**Figure 3.2** The view of the laboratory scale injection-molding machine [86]

For measuring the LOI and cone calorimeter values of the composites the test samples extruded then dried in an oven at a temperature of 60 °C for 2 hours then pelletized and been put into laboratory scale hot press (Pneumo Hydraulic Press, Ats Faar, Italy) at 210 °C and 3 minutes at 10.000 psi pressure.

### **3.3 Characterization Methods**

#### **3.3.1 Scanning Electron Microscopy**

Surfaces of filler agents and freeze fractured surfaces of composites which were prepared in liquid nitrogen were examined by Field Emission Scanning Electron Microscope (FEI Quanta 400F). Also the microstructures of the residual chars remained after mass loss calorimeter test were examined with SEM (FEI Quanta 400F). All samples surfaces were coated with a thin layer of gold with a sputter-coater to provide the conductivity. The SEM photographs were taken in different varied magnifications from x200 x500 x1000 to x5000.

### 3.3.2 Tensile Test

Lloyd LR 5K universal tensile testing machine is used for the tensile measurements. The machine has 5 kN load cell, the measurements were done at room temperature. ASTM D 638 standard is used in these tests. In Figure 3.3 the photograph of the machine can be seen.

The specimens are waited in a desiccator until 2 days before the tests. Tensile measurements was held on with a speed of 5 mm/min on dog-bone shaped samples ( $7.4 \times 2.1 \times 80 \text{ mm}^3$ ) (length x depth x wide) which obtained from the micro compounder. Percentage elongation at break, modulus and tensile strength values was recorded. The results are known by calculating the average value of five samples with their standard deviations.



**Figure 3.3** The photograph of tensile test machine

### **3.3.3 Dynamic Mechanical Analysis**

DMA experiments was made by using Perkin Elmer DMA 8000 in dual cantilever bending mode at a frequency of 1 Hz to determine elastic modulus and  $\tan \delta$  of the composites. In the test heating rate was 5°C/min and samples was investigated in temperature sweep mode from room temperature to 100 °C. The samples used in the experiment with dimensions of  $50 \times 7.5 \times 2.5 \text{ mm}^3$  (length x depth x wide) was obtained from injection molding instrument.

### **3.3.4 UL-94 Test**

ASTM D3801 method was used in this test. According to this method V0 indicates the best flame retardancy results. V2 indicates worst flame retardancy results. Bar specimens have a dimension  $130 \times 13 \times 3.25 \text{ mm}^3$  (length x depth x wide) which were made with compression molding machine.

### **3.3.5 LOI - Limited Oxygen Index**

LOI value was examined with LOI instrument (Fire Testing Technology Limiting Oxygen Index Analyzer). Test bars which have the size of  $130 \times 6.5 \times 3.25 \text{ mm}^3$  (length x depth x wide) and made with compression molding machine. ASTM D2863 method is used for preparing the samples and test procedures.

### **3.3.6 Cone Calorimeter**

ISO 13927 method is used for the mass loss cone calorimeter test. Mass loss cone calorimeter instrument with thermopile attachment (Fire testing Technology) is used in this test.  $100 \times 100 \times 3 \text{ mm}^3$  square specimens are prepared by compression molding. Test samples were irradiated with heat flux of  $35 \text{ kW/m}^2$ .

### **3.3.7 Thermo Gravimetric Analysis (TGA)**

TGA tests were carried out with Hitachi-High Tech STA-7300 instrument. Heating rate was 10 °C/min. Test was carried out from room temperature up to 800 °C with a flow of nitrogen 50 ml/min.

### **3.3.8 XRD**

XRD data were collected on a Bruker AXS D8 diffractometer using Cu K<sub>α</sub> radiation ( $\lambda = 0.154595$  nm) with a 0.04  $2\theta$  step size and 3 second count time.

### **3.3.9 ATR-FTIR**

Attenuated total reflectance - Fourier transform infrared spectroscopy (ATR-FTIR) was used to analyze char residues remained after mass loss calorimeter test. FTIR measurements in attenuated total reflectance (ATR) mode were performed by using IR-spectrometer (Bruker VERTEX 70) at a resolution of 2 cm<sup>-1</sup> with 32 scans between 600-3800 cm<sup>-1</sup> wavenumbers.



## CHAPTER 4

### RESULTS AND DISCUSSION

Huntite and hydromagnesite, a naturally occurred mixed mineral, is mineral based flame retardant like aluminum hydroxide and magnesium hydroxide [50,51]. The flame retardant effect of huntite and hydromagnesite is studied in various polymers like ethylene vinyl acetate [87-93], polypropylene (PP) [91], polyethylene [94], ethylene propylene copolymer [95], vinyl ester resin [96] and poly vinylchloride [97]. The general flame retardant mechanism of huntite and hydromagnesite resembles to the aluminum hydroxide and magnesium hydroxide [51,98,118]. Huntite and hydromagnesite has higher onset decomposition temperature (220-240°C) than aluminum hydroxide (180-200°C) [98]. Thus, huntite and hydromagnesite becomes suitable for polymers which have higher processing temperatures. Whereas, the decomposition enthalpy of huntite and hydromagnesite (990 Jg<sup>-1</sup>) is, lower than that of aluminum hydroxide (1300 Jg<sup>-1</sup>) [98]. Accordingly, to increase the flame retardant effect of huntite and hydromagnesite with the synergistic effect studies causes the wide use of it in various polymers and applications. For this purpose, expandable graphite is chosen as synergistic additive in the current study.

In the previous studies, expandable graphite was used as synergistic agent with mineral based flame retardants in various polymers [99-103]. Chen et al. used two different expandable graphites with different particle size in combination with magnesium hydroxide in PP for their synergistic effect. They found that the addition

of expandable graphite improved the thermal stability of pure magnesium hydroxide containing PP composites. They also found that the limiting oxygen index (LOI) values of composites were increased as the added amount of expandable graphite increased. Although the pure magnesium hydroxide containing composites failed in UL-94 test, expandable graphite containing composites had the highest UL-94 rating of V0. The expandable graphite with large particle size was more effective for increasing the flammability properties of the composites [99-101]. Du et al. investigated the synergistic interaction between hydrotalcite and expandable graphite in ethylene vinyl acetate. They used two different expandable graphites with different expansion ratios. They found that the flame retardant property of ethylene vinyl acetate was increased when hydrotalcite and expandable graphite were used together. They also indicated that expandable graphite with high expansion factor was more effective than expandable graphite with low expansion factor [102]. Li and Qu investigated the synergistic interaction between magnesium hydroxide and different expandable graphites with different particle sizes and expansion ratios in ethylene vinyl acetate. The addition of expandable graphite with large particle size and high expansion ratio increased the flammability properties (LOI and UL-94) of composites. Wang et al. investigated the synergistic interaction between aluminum hydroxide and expandable graphite in polyisocyanurate polyurethane foams. They found that the LOI value increased when aluminum hydroxide and expandable graphite were used together. The LOI value of the composite increased as the added amount of expandable graphite was increased [103].

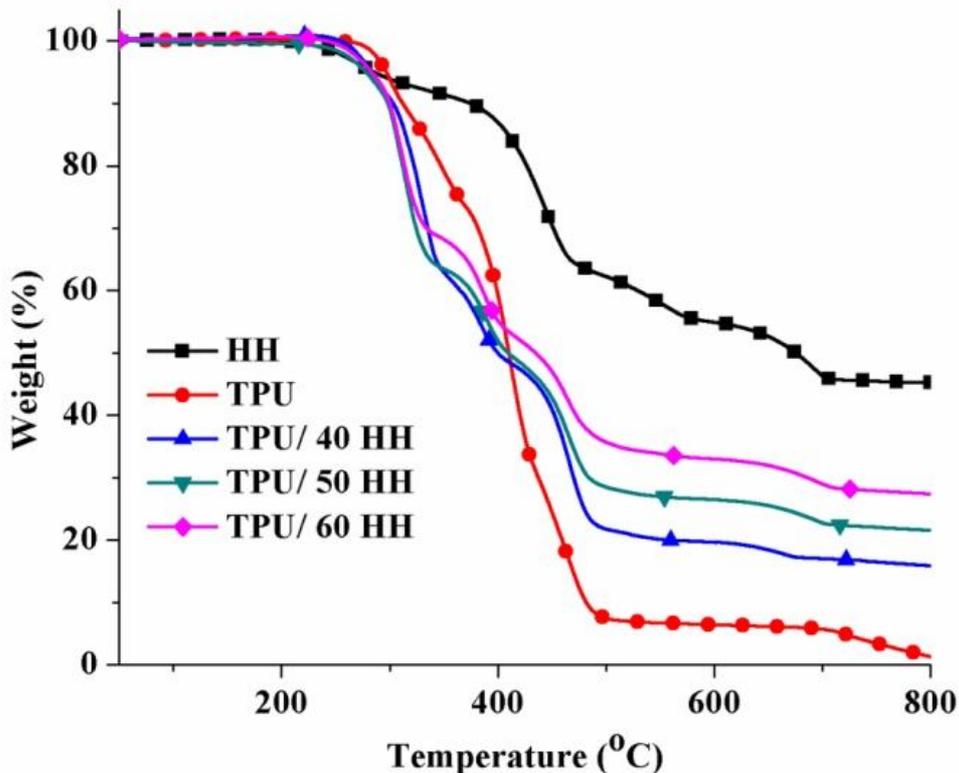
#### 4.1 Thermal Decomposition

Thermal properties of TPU, huntite and hydromagnesite, expandable graphite and their composites are investigated by TGA under nitrogen atmosphere. TGA data of TPU, huntite and hydromagnesite and all composites are given in Table 4.1. The related TGA curves are shown in Figure 4.1- 4.3.

**Table 4.1** TGA data of TPU, HH and all composites

<b>SAMPLE</b>	<b>T<sub>5%</sub></b> <b>(°C)<sup>a</sup></b>	<b>T<sub>max1</sub></b> <b>(°C)<sup>b</sup></b>	<b>T<sub>max2</sub></b> <b>(°C)<sup>b</sup></b>	<b>T<sub>max3</sub></b> <b>(°C)<sup>b</sup></b>	<b>T<sub>max4</sub></b> <b>(°C)<sup>b</sup></b>	<b>Residue</b> <b>(%)<sup>c</sup></b>
<b>TPU</b>	297	347	411	-	-	1.3
<b>HH</b>	285	267	445	556	694	45.2
<b>TPU/ 40 HH</b>	283	317	468	-	695	15.9
<b>TPU/ 50 HH</b>	281	312	466	-	695	21.6
<b>TPU/ 60 HH</b>	278	313	465	-	695	27.4
<b>TPU/ 10 EG</b>	315	358	411	-	-	15.2
<b>TPU/ 20 EG</b>	311	352	413	-	-	22.7
<b>TPU/45 HH/ 5 EG</b>	285	326	461	-	664	20.8
<b>TPU/40 HH /10 EG</b>	287	332	464	-	666	24.6
<b>TPU/30 HH /20 EG</b>	289	349	459	-	661	32.6
<b>TPU/25 HH /25EG</b>	294	348	460	-	661	32.8

**a:** Temperature at 5% weight loss **b:** The maximum degradation rate temperature **c:** Char Yield at 800 °C



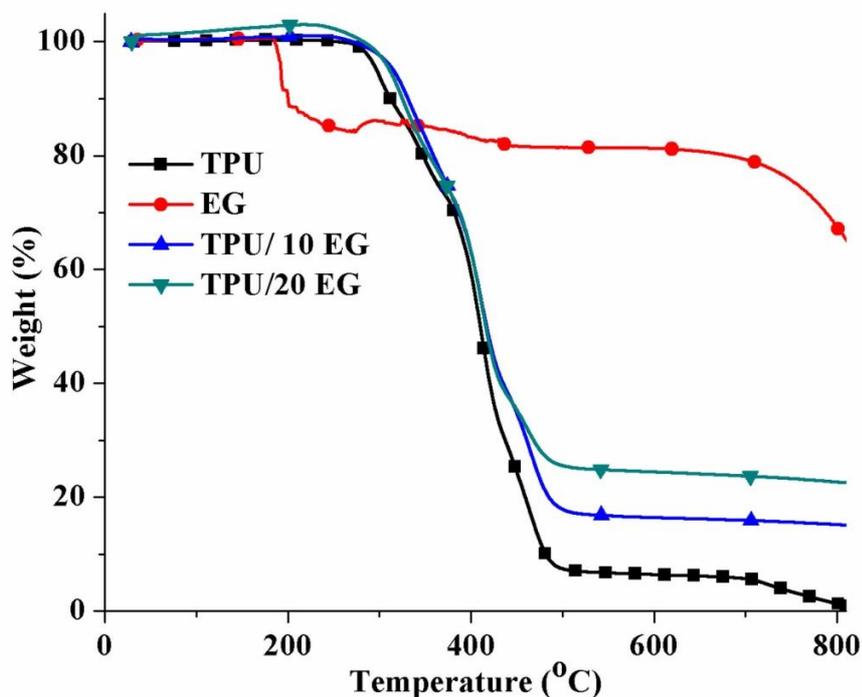
**Figure 4.1** TGA data of TPU, huntite and hydromagnesite

Thermal decomposition of TPU occurs through double step with maximum rates at 347 °C and 411 °C and two shoulders are seen at 300°C and 466 °C with leaving 1.3 wt% carbonaceous char. The first and second degradation stages are related with the urethane bond decomposition in the hard segments and the fragmentation of polyols in the soft segments, respectively [31,104,] huntite and hydromagnesite decomposes in four steps with maximum rates at 268°C, 445 °C, 556 °C and 693 °C with leaving 45.2 % inorganic residue mainly based on magnesium oxide and calcium oxide. The first and second decomposition steps of huntite and hydromagnesite are related to the

loss of water and CO<sub>2</sub> from hydromagnesite in huntite and hydromagnesite, respectively. The third and fourth degradation steps are related to the loss of CO<sub>2</sub> from huntite in huntite and hydromagnesite [50, 51, 88].

The huntite and hydromagnesite containing composites (TPU/x HH) degrade mainly into three steps. The peak related with the initial loss of CO<sub>2</sub> from huntite at around 555 °C is not shown in the DTG curves of TPU/x HH (given as supplementary material). It is thought that this observed trend arises from the early decomposition of huntite which is masked with T<sub>max2</sub>. The similar trend is also observed in huntite and hydromagnesite containing ethylene vinyl acetate based composites in the literature [50]. The initial thermal stabilities of composites are characterized by the temperature at which 5 wt% weight loss occurs (T<sub>5%</sub>). The addition of huntite and hydromagnesite into TPU reduces the T<sub>5%</sub> and T<sub>max1</sub> values at about 15 °C and 30 °C, respectively. It is thought that the reductions in T<sub>5%</sub> and T<sub>max1</sub> values stem from the lower dehydration temperature of the hydromagnesite than the first step degradation temperature of TPU. Whereas, the addition of huntite and hydromagnesite increases the T<sub>max2</sub> of TPU due to dilution effect of huntite and hydromagnesite. It is noted that the similar trend is observed when the dehydrated flame retardant additives are used in the previous studies [105-107]. The residue increases as the added amount of huntite and hydromagnesite increases due to the formation of inorganic materials mainly based on magnesium oxide and calcium oxide, as stated earlier.

The expandable graphite containing composites (TPU/x EG) degrade into two steps like pristine TPU.



**Figure 4.2** TGA data of TPU and expendable graphite

The addition of expendable graphite increases  $T_{5\%}$  and  $T_{max1}$  values at about 15 °C and 7 °C, respectively. This indicates that the expendable graphite improves the initial thermal stability of TPU. It is thought that the increase in the initial thermal stability of TPU arises from the high heat conductivity of expendable graphite. Whereas, the addition of expendable graphite does not have remarkable effect on  $T_{max2}$  value. The addition of expendable graphite greatly improves the char yield. Similar observations are seen in the literature when TPU and graphene based fillers are used together [33, 108]. It is thought that two possible effects, namely cage and catalytic effects may increase the char yield of TPU by undergoing additional pathways for increasing char yield. The catalytic effect may stem from acidic species

(sulphuric acid) which does not deeply penetrate into graphite layers. The cage effect arises from plate like structure of graphite sheets which forms a confined, superheated environment. The aforementioned effects are also observed with the use of organoclay, which has plate like structure bearing acidic sites on its surface, in various matrix materials [109].

All TPU/HH/EG composites show three steps weight loss as that of TPU/x HH composites.

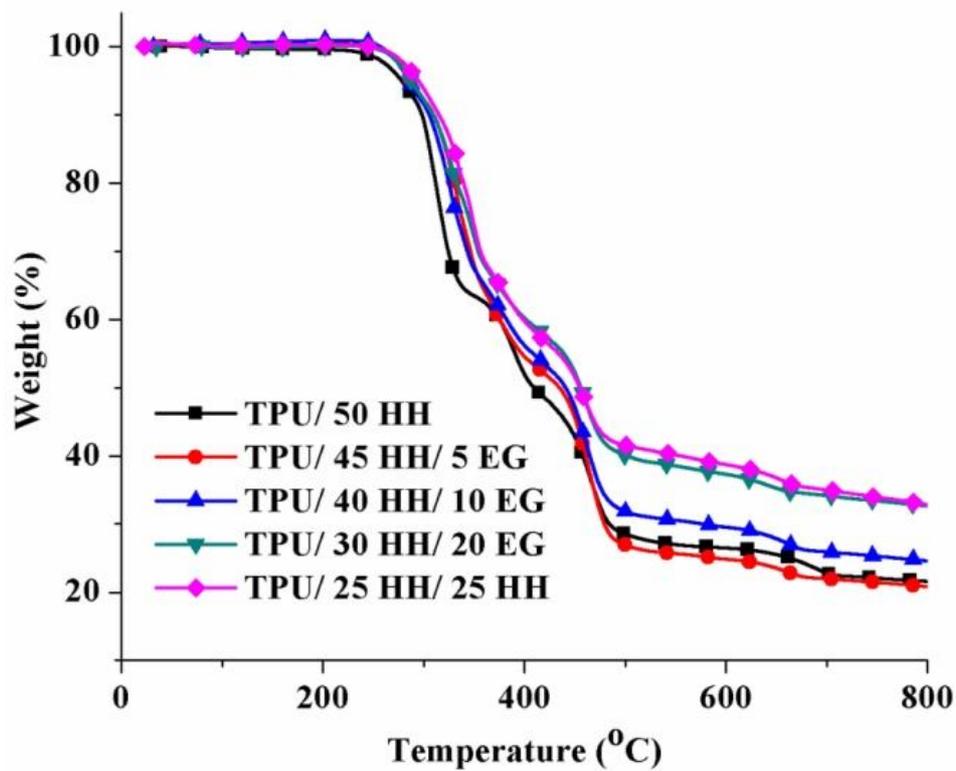


Figure 4.3 TGA data of TPU, expendable graphite, huntite and hydromagnesite

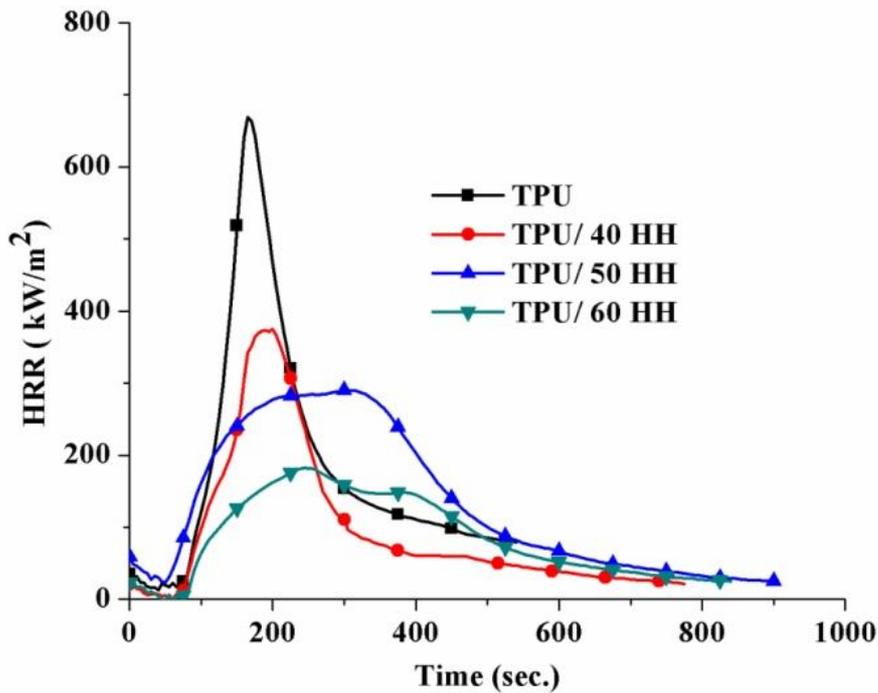
$T_{5\%}$  and  $T_{max1}$  values increase as the added amount of expandable graphite increases with respect to TPU/50 HH composite. The negligible decrease is observed in  $T_{max2}$  with the addition of expandable graphite. An interesting finding is observed with the inclusion of expandable graphite. Although the secondary loss of  $CO_2$  from huntite occurs at 695 °C in TPU/xHH composites, it occurs at about 30 °C below with the addition of expandable graphite. It is thought that the reaction between sulphuric acid and basic carbonate (huntite ( $Mg_3Ca(CO_3)_4$ )) reduces the decomposition temperature. The char yield increases as the added amount of expandable graphite increases which arises from the aforementioned reasons as stated before.

#### **4.2 Mass Loss Calorimeter Study**

Mass loss calorimeter investigations can be used as universal approach to compare and to evaluate the fire performances of polymeric materials. The fire performances of composites can be evaluated using peak heat release rate (pHRR), total heat evolved (THE), time to ignition (TTI), peak mass loss rate (pMLR) and fire performance index (pHRR/ TTI) (FPI) data. The reductions in these data except for FPI normally indicate the improved fire performance of composite. The higher FPI value is the higher fire safety rank. The HRR curves and the mass loss calorimeter data of pristine TPU and relevant composites are shown in Figure 4.4 - 4.6 and Table 4.2, respectively. The digital and SEM photographs of selected char residues remained from cone calorimeter test are shown in Figure 4.6 and Figure 4.7, respectively.

**Table 4.2** Mass loss calorimeter data of pristine TPU and relevant composites

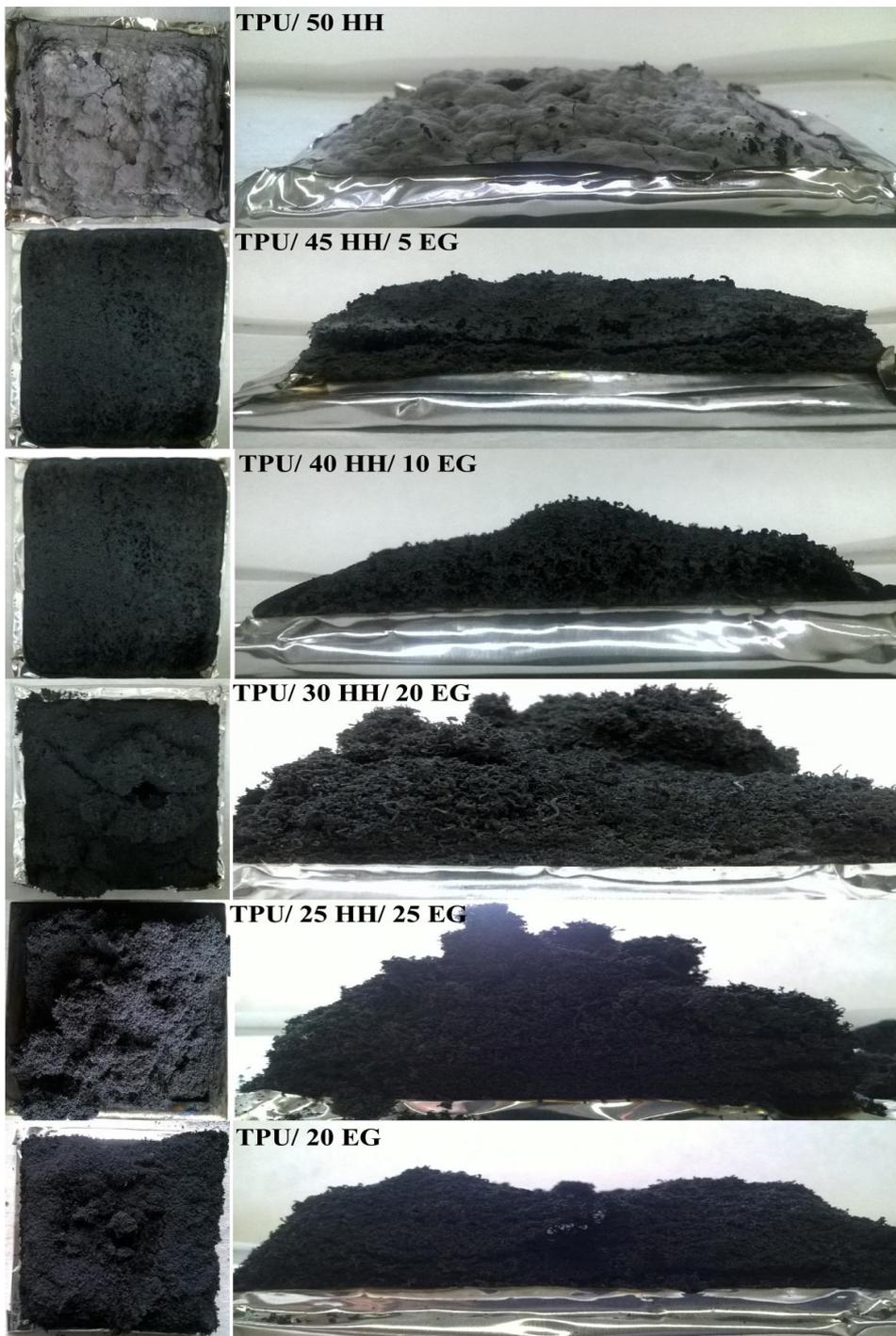
<b>SAMPLE</b>	<b>pHRR (kW/m<sup>2</sup>)</b>	<b>THE (MJ/m<sup>2</sup>)</b>	<b>pMLR (g/s)</b>	<b>FPI (kW/m<sup>2</sup>s)</b>	<b>Av. HRR (kW/m<sup>2</sup>)</b>	<b>TTI (sec.)</b>
<b>TPU</b>	668	89	0.43	0.11	242	76
<b>TPU/ 40 HH</b>	370	68	0.16	0.20	226	75
<b>TPU/ 50 HH</b>	290	64	0.14	0.27	204	77
<b>TPU/ 60 HH</b>	182	59	0.09	0.41	143	74
<b>TPU/ 10 EG</b>	189	79	0.10	0.18	152	34
<b>TPU/ 20 EG</b>	134	51	0.07	0.23	103	31
<b>TPU/45 HH/ 5 EG</b>	168	63	0.15	0.20	135	34
<b>TPU/40 HH /10 EG</b>	167	59	0.09	0.22	127	36
<b>TPU/30 HH /20 EG</b>	155	57	0.09	0.22	94	34
<b>TPU/25 HH /25EG</b>	133	55	0.08	0.26	107	35



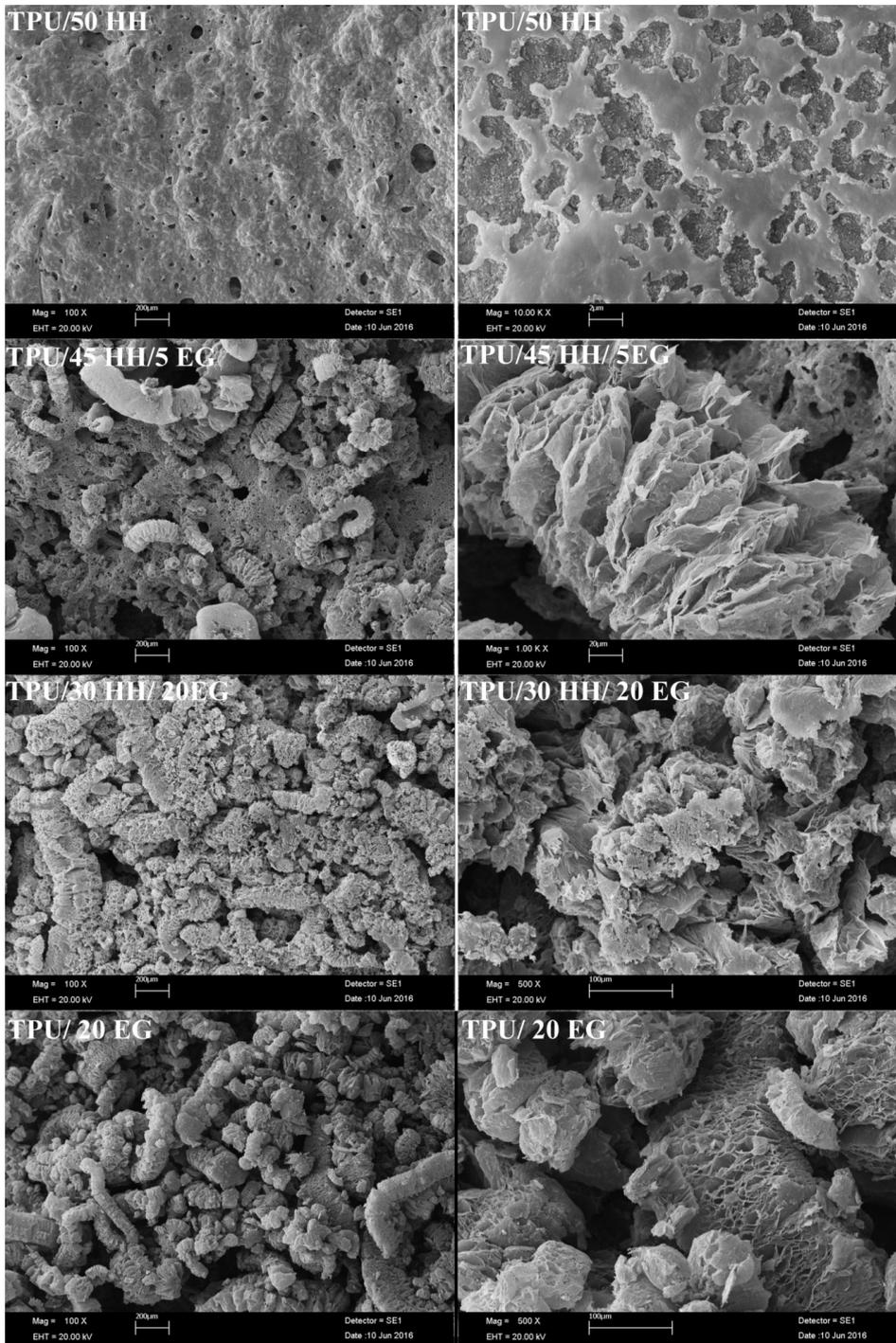
**Figure 4.4** Mass loss calorimeter graphs of pristine TPU and huntite and hydromagnesite.

According to Figure 4.4, TPU burns very fast after ignition and one sharp HRR peak appears with peak heat release and average heat release of 668 and 242  $\text{kWm}^{-2}$ , respectively. With the addition of huntite and hydromagnesite, HRR curves become more plateau like with the extended burning time due to the barrier effect of inorganic decomposition products of huntite and hydromagnesite based mainly on magnesium oxide and calcium oxide.

As seen from Figure 4.5 and 4.6, the residue remained after the combustion of TPU/50 HH has continuous structure with some cracks and small holes. The peak HRR reduces at about 45, 57 and 73% with the addition of 40, 50 and 60 wt% HH, respectively.



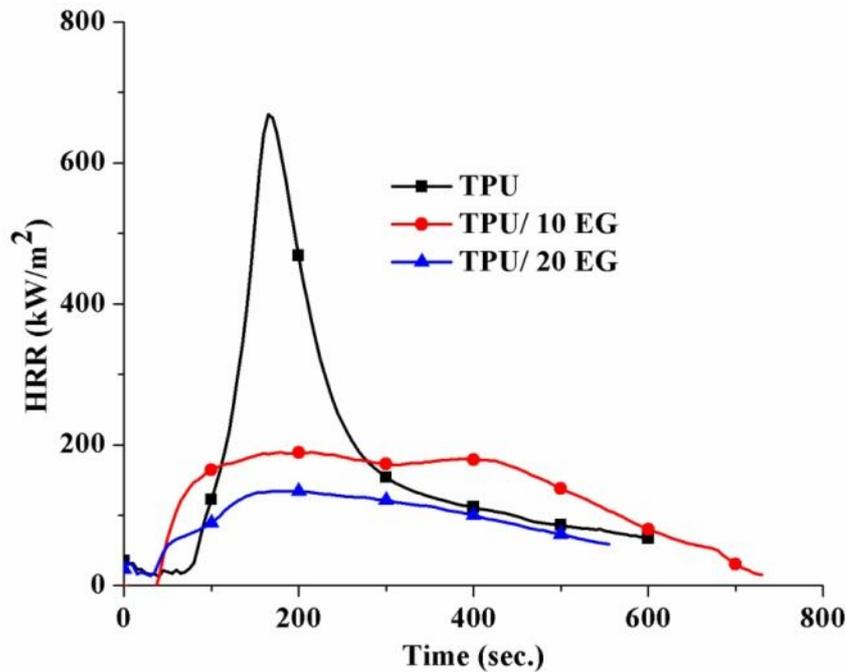
**Figure 4.5** Images of selected char residues remained from cone calorimeter



**Figure 4.6** SEM images of selected char residues remained from cone calorimeter

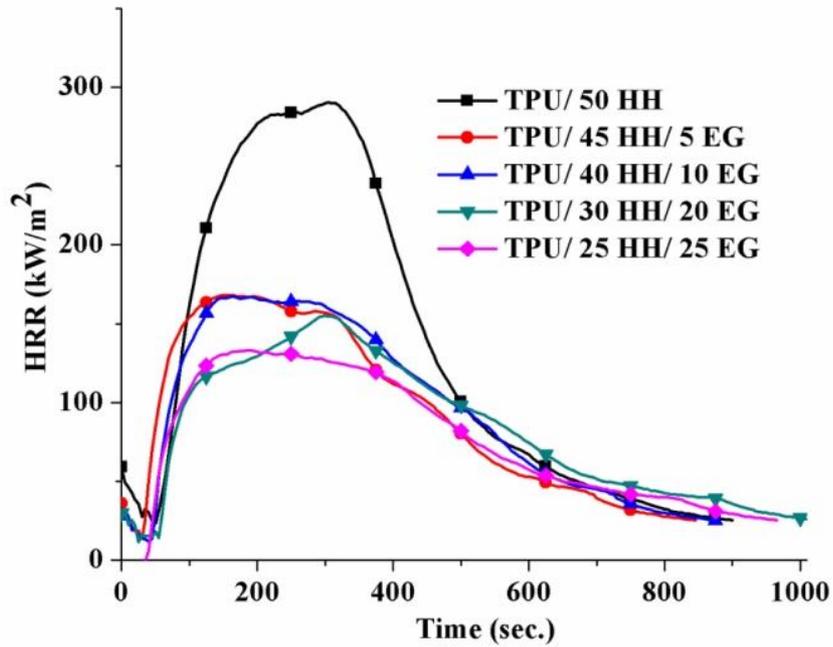
The THE decreases at about 24, 28 and 38 %, with the addition of 40, 50 and 60 wt% HH, respectively. pMLR values decrease and FPI values increase as the amount of huntite and hydromagnesite increases. These findings clearly show that the addition of huntite and hydromagnesite improves the fire performance of TPU. In the literature, numerous studies showed that the TTI value increases with the addition of hydrated mineral fillers into polymer due to the dilution of combustible gases in the gas phase [88, 110, 111]. On contrary to these findings, negligible change is observed in TTI values with the addition of huntite and hydromagnesite into TPU.

With the addition of expandable graphite into TPU, the shape of HRR curve totally changes and shows the typical HRR curve of typical insulating protective layer which stays relatively constant during the combustion with very low pHRR [112]. During the cone calorimeter test, expandable graphite expands via redox process between intercalant  $H_2SO_4$  and graphite and worm like structure is formed on the surface of material. This expanded graphite based fluffy char structure behaves as thermal insulation material limiting heat and mass transfer from polymer to the heat source [113, 114]. The formation of fluffy char structure on burning surface causes lower pHRR, THE, pMLR and higher FPI with respect to pristine TPU.



**Figure 4.7** Mass loss calorimeter graph of pristine TPU and expandable graphite

The fluffy char structure is easily seen on the photographs of expandable graphite containing composites (see Figure 4.5 and 4.6). The addition of expandable graphite causes the earlier ignition with respect to pure TPU. TTI reduces at about 45 seconds. The reduction in TTI arises from the black color of expandable graphite which causes the increased radiant heat absorption within the top layer of the material [115, 116]. The higher heat absorption causes the earlier initiation of thermal degradation of TPU. When the fire performances of TPU/60 HH and TPU/20 EG are compared, TPU/20 EG has lower pHRR, THE, pMLR, average HRR values than those of TPU/60 HH. Whereas, the FPI of TPU/60 HH is higher than that of TPU/20 EG due to the sharp reduction in TTI value.



**Figure 4.8** Mass loss calorimeter graph of pristine TPU, huntite and hydromagnesite and expendable graphite

When huntite and hydromagnesite and expandable graphite are used together, the pHRR, THE and pMLR values further reduce with respect to solely huntite and hydromagnesite containing TPU composite (TPU/50HH) as the added amount of expandable graphite increases. The lowest the pHRR, THE and pMLR values are observed when huntite and hydromagnesite and expandable graphite are used at a ratio of 1:1.

In order to understand whether a chemical interaction occurs between huntite and hydromagnesite and expandable graphite, the char residues remained after cone calorimeter is analyzed via XRD and ATR-FTIR. XRD patterns and ATR-FTIR spectrum of char residues are shown in Figure 4.9 and 4.10, respectively. According to Figure 4.9, the char residue remained from TPU/20 EG shows a very intense and narrow peak at  $2\theta=26.6^\circ$  which corresponds to the planes of well-ordered graphenes [108]. TPU/50 HH shows characteristics peaks of magnesium oxide at  $2\theta=29.4^\circ$ ,  $42.9^\circ$  and  $62.4^\circ$  and calcium oxide at  $2\theta=31.2^\circ$  [117,118]. XRD pattern of TPU/ 40 HH/ 10 EG does not contain any additional peaks existing in TPU/10 EG and TPU/ 50 HH.

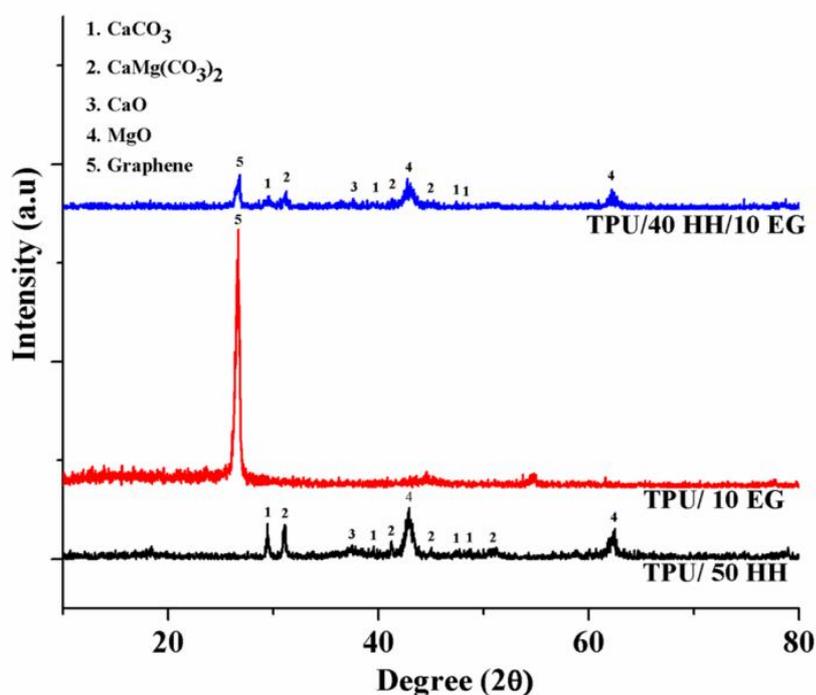
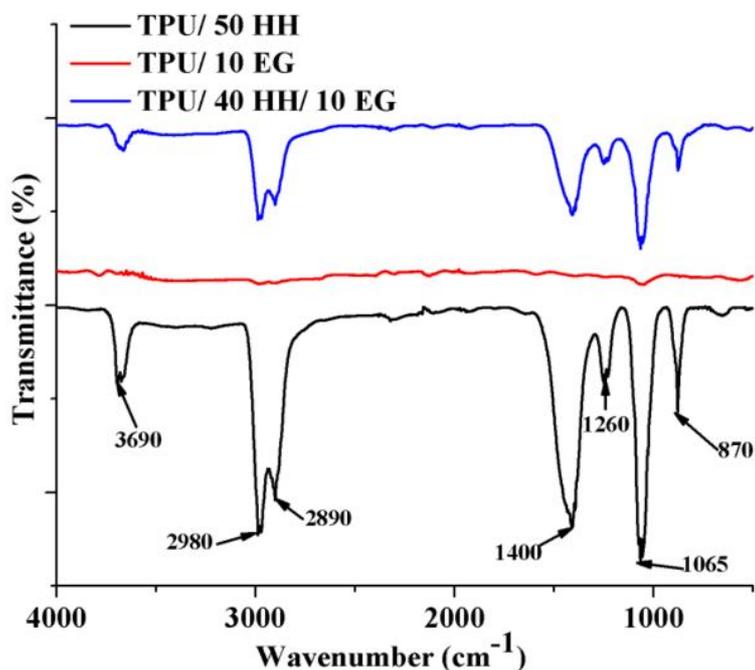


Figure 4.9 XRD spectrum of char residues

ATR-FTIR spectra of TPU/40 HH/10 EG and TPU/50 HH completely resembles each other. According to Figure 4.10, pristine HH containing composite shows the characteristic peaks at 3690, 2980, 2890, 1400, 1260, 1065 and 870  $\text{cm}^{-1}$ . The peak seen at 3690  $\text{cm}^{-1}$  stems from the asymmetric stretching vibration of OH bond. The peaks seen at 2980 and 2890  $\text{cm}^{-1}$  arises from asymmetric and symmetric vibrations of  $-\text{CH}_2$  and  $-\text{CH}_3$  groups in thermal degradation products of TPU. The peaks seen at 1400, 1260, 1065 and 870  $\text{cm}^{-1}$  are related with  $\text{CO}_3$  vibrations in carbonate minerals including huntite ( $\text{CaMg}_3(\text{CO}_3)_4$ ), calcium carbonate ( $\text{CaCO}_3$ ) and dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) in HH natural mineral mixture. These findings clearly show that no chemical interaction is occurred between expandable graphite and huntite and hydromagnesite.[114-116]



**Figure 4.10** ATR-FTIR spectrum of char residues

Thus, only physical interaction affects the fire performance of composites when expandable graphite and huntite and hydromagnesite are used together. As seen from SEM images of TPU/45 HH/5 EG, expanded expandable graphite particles are found locally on the surface of inorganic residue. As the added amount of expandable graphite increased to 20% (TPU/30 HH/20 EG), expanded expandable graphite particles fully covers the surface of inorganic residue and the surface of char residue looks like solely expandable graphite containing composite (TPU/ 20 EG). The formation of graphite based fluffy char structure over inorganic residue increases the barrier effect of the char. Thus, the higher fire performance is observed when huntite and hydromagnesite and expandable graphite are used together.

Interestingly, when the fire performances of TPU/10 EG and TPU/40 HH/10 EG composites are compared, TPU/10 EG composite shows higher pHRR, THE, pMLR and lower FPI values than those of TPU/ 40 HH/ 10 EG. When the fire performances of TPU/ 20 EG and TPU/ 30 HH/ 20 EG composites are compared, TPU/20 EG composite shows lower pHRR, THE, pMLR and higher FPI values than those of TPU/ 30 HH/ 20 EG. As a result of cone calorimeter test, the synergistic interaction between expandable graphite and huntite and hydromagnesite is observed at low percentage of expandable graphite (10 %). At high concentration of expandable graphite (20%), the antagonistic interaction between expandable graphite and huntite and hydromagnesite is observed.

### 4.3 Flammability Properties

The flammability characteristics of composites are determined by LOI and UL94 ratings. The relevant data are given in Table 4.3.

**Table 4.3** LOI values and UL-94 ratings of composites

<b>SAMPLE</b>	<b>LOI</b>	<b>UL-94</b>
<b>TPU</b>	21.2	NR
<b>TPU/40 HH</b>	21.6	NR
<b>TPU/50 HH</b>	25.7	V1
<b>TPU/60 HH</b>	31.2	V0
<b>TPU/10 EG</b>	22.2	NR
<b>TPU/ 20 EG</b>	25.2	V1
<b>TPU/ 45 HH/ 5 EG</b>	24.4	V1
<b>TPU/ 40 HH/ 10 EG</b>	24.8	V0
<b>TPU/30 HH/ 20 EG</b>	27.7	V0
<b>TPU/25 HH/ 25 EG</b>	32.6	V0

**NR:** Not rated

TPU resin has LOI value of 21.2 % and burns to clamp during the UL-94 test. The LOI value steadily increases as the added amount of huntite and hydromagnesite increases and reaches 31.2% with the addition of 60 wt% HH. UL-94 rating of TPU increases to V1 and V0 with the addition of 50 and 60 wt% HH, respectively. The flame retardant effect of huntite and hydromagnesite mainly arises from endothermic decomposition, dilution effect in the gas phase via water and CO<sub>2</sub> release and the formation of protective char layer in the condensed phase [50, 88]. The LOI value of pure TPU increases from 21.2 to 25.2% with the addition of 20% expandable graphite and UL-94 rating increases to V1. The flame retardant effect of expandable

graphite mainly arises from the fluffy protective char formation in the condensed phase [113,114]. When huntite and hydromagnesite and expandable graphite are used together, LOI value increases steadily as the ratio of expandable graphite increases in the flame retardant mixture. The highest LOI value of 32.6% is achieved at a ratio of 1:1. The highest UL-94 rating (V0) is achieved at a ratios of 4:1, 3:2 and 1:1. According to the flammability test results, the synergistic interaction is observed between expandable graphite and huntite and hydromagnesite.

#### **4.4 Mechanical Properties**

In order to understand the mechanical properties of composites, tensile testing and DMA analysis are carried out. SEM analyses are also performed on the freeze fractured surfaces of selected composites. To observe the fracture surfaces of the composites gives precious information related to the dispersion of fillers and their interface properties. The related SEM micrographs are shown in Figure 4.11. The tensile test data of composites are listed in Table 4.4.

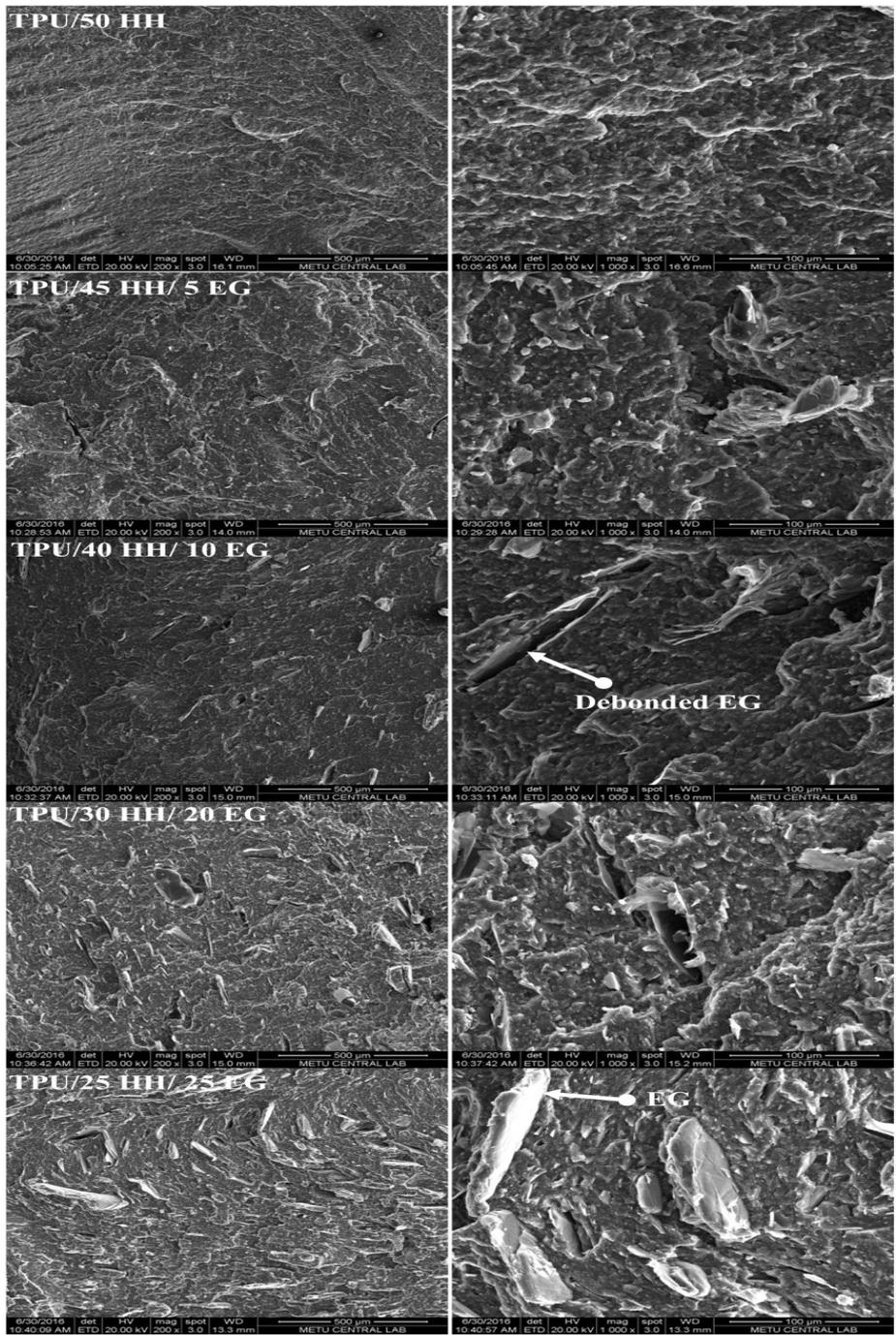


Figure 4.11 SEM images of freeze fractured surfaces of selected composites

**Table 4.4** Tensile properties of composites

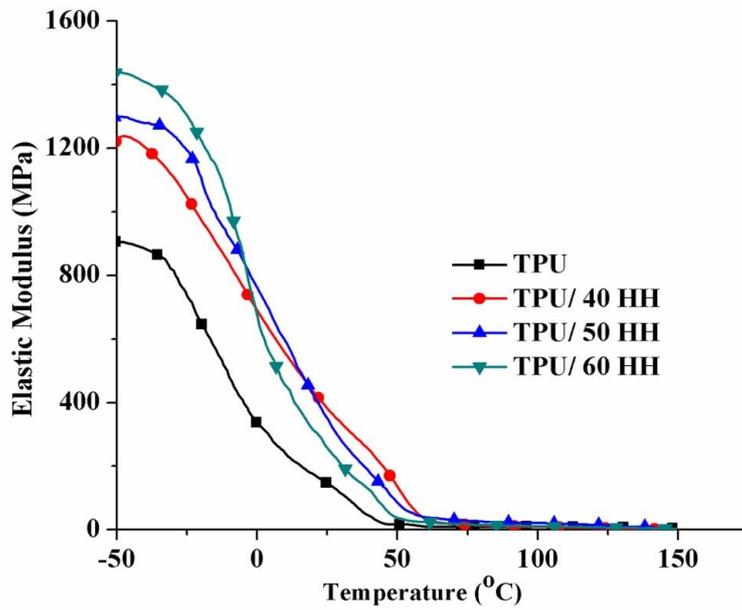
<b>SAMPLES</b>	<b>Tensile Strength (MPa)</b>	<b>Elongation at break ( % )</b>
<b>TPU</b>	24.8±2.2	424.0±22.3
<b>TPU/40 HH</b>	8.0±0.2	61.6±14.8
<b>TPU/50 HH</b>	9.3±0.8	21.4±1.3
<b>TPU/60 HH</b>	9.4±0.3	7.76±1.3
<b>TPU/10 EG</b>	11.2±0.3	332±1.1
<b>TPU/ 20 EG</b>	8.9±0.1	26.1±1.7
<b>TPU/45 HH/ 5 EG</b>	7.6±0.3	106.7±3.6
<b>TPU/40 HH/10 EG</b>	7.0±0.1	79.1±2.4
<b>TPU/30 HH/ 20 EG</b>	9.0±0.4	65.8±1.7
<b>TPU/25HH/ 25 EG</b>	9.6±0.3	44.6±1.5

The tensile strength of the pristine TPU reduces over 60 % with the addition of huntite and hydromagnesite at three different concentrations. The reduction in tensile strength arises from the non-uniform dispersion of huntite and hydromagnesite in TPU due to the poor interfacial interaction between them (see. Figure 4.11). The percent elongation at break value of pristine TPU reduces as the concentration of huntite and hydromagnesite increases owing to the restriction of the polymer chain mobility. Similar trends are also observed in mineral based flame retardants filled polymers in the previous studies [24, 87, 88, 120].

When expandable graphite and huntite and hydromagnesite are used together, tensile strength reduces up to 10 wt % EG loading with respect to TPU/50 HH composite. The tensile strength increases with further the addition of expandable graphite (20 and 25%), and these composites have approximately the same tensile strength of TPU/50 HH when the standard deviations are considered.

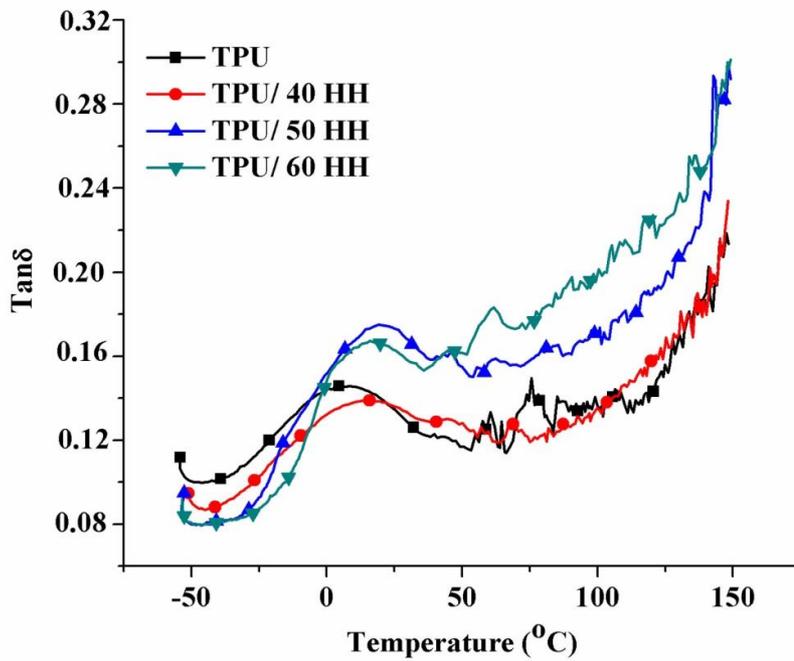
The tensile strength of a particulate filled composite depends mainly on the amount of the filler, the adhesion between filler and matrix and the shape of the filler [121]. It is thought that the adhesion between expandable graphite and TPU and particulate filler geometry affects predominantly the tensile strength at low and high loadings of expandable graphite, respectively. As seen from Figure 4.11, pull out expandable graphite particles are the indication of the poor adhesion between expandable graphite and TPU. The weak interfacial adhesion causes the reduction in tensile strength of composites at low loadings of expandable graphite. The plate like structure of expandable graphite, which has high load bearing capacity than particulate fillers like huntite and hydromagnesite, causes increase in tensile strength at high loadings [122].

The elastic modulus and  $\tan \delta$  versus temperature graphs of pristine TPU and huntite and hydromagnesite containing TPU based composites are shown in Figure 4.12 - 4.13.



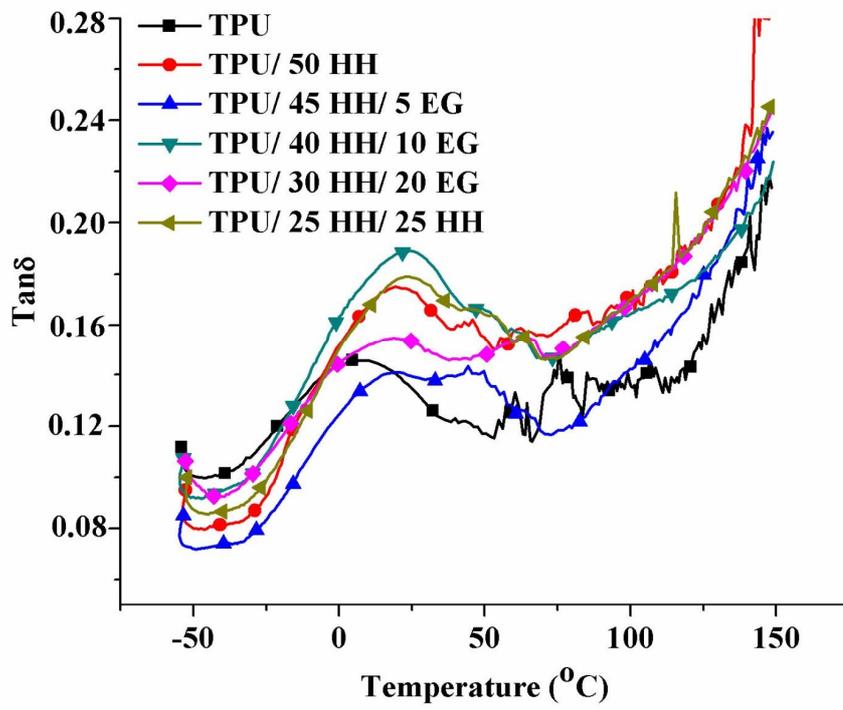
**Figure 4.12** Elastic modulus versus temperature graphs of pristine TPU and huntite and hydromagnesite composites

The elastic modulus of a material is related with its load bearing capacity. A general declining trend in elastic modulus is observed for all samples as the temperature increases due to the thermal transitions occurred in the TPU matrix. The elastic modulus of the pure TPU is improved with the addition of huntite and hydromagnesite and stays higher up to 50 °C. Above 50 °C, no considerable difference is observed in elastic modulus values of pristine TPU and huntite and hydromagnesite containing TPU composites. It is well known fact that the filler with higher stiffness than the matrix can increase the elastic modulus of the composites [119, 120, 123].

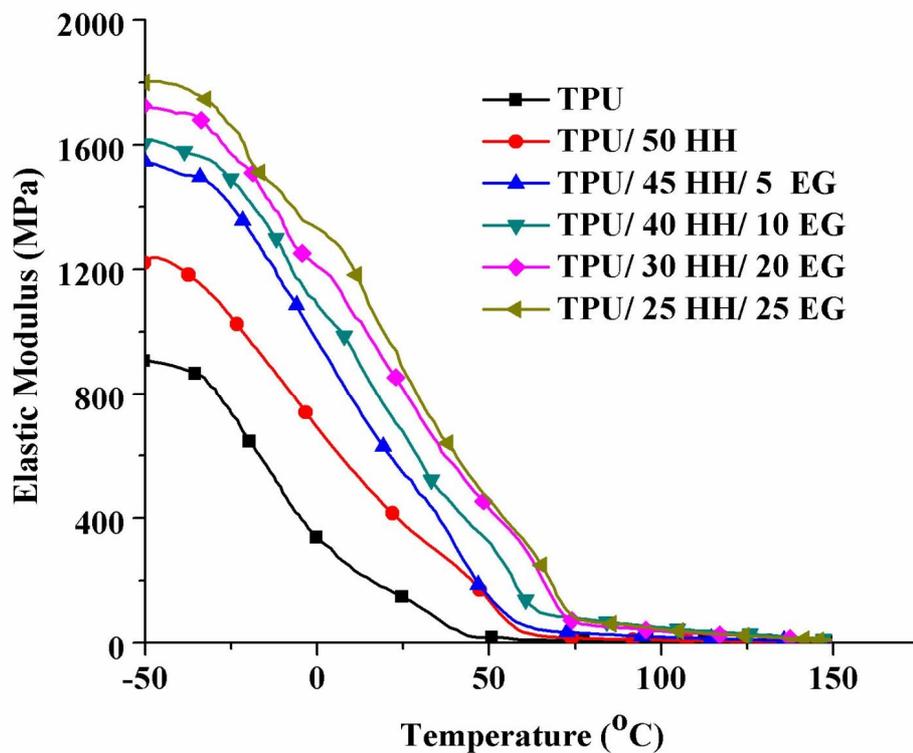


**Figure 4.13** Tan  $\delta$  versus temperature graphs of pristine TPU and huntite and hydromagnesite composites

The peak tan  $\delta$  gives information about the major viscoelastic transitions in the matrix material. As from Figure 4.13, the pristine TPU has  $T_g$  value of 5 °C. With addition of 50 wt% HH,  $T_g$  of pristine TPU increases at about 15 °C. The shifting of  $T_g$  to higher temperatures can be associated with the decreased mobility of the matrix chains [124]. 50 and 60 wt% HH containing TPU composites have higher peak tan  $\delta$  than pristine TPU. The high magnitude peak tan  $\delta$  is the indication of the higher damping at interfaces due to the poor adhesion between huntite and hydromagnesite and expandable graphite [125-127]. The tan  $\delta$  and elastic modulus versus temperature graphs of huntite and hydromagnesite and expandable graphite containing TPU based composites are shown in Figures 4.14 - 4.15.



**Figure 4.14** Tan  $\delta$  versus temperature graphs of pristine TPU, huntite and hydromagnesite and expendable graphite composites



**Figure 4.15** - Elastic modulus versus temperature graphs of pristine TPU, huntite and hydromagnesite and expandable graphite composites

The elastic modulus of the TPU/50 HH composite is improved as the added amount of expandable graphite increases and stays higher up to 75 °C. It is thought that the increase in elastic modulus stems from the plate like structure of expandable graphite which has high load bearing capacity than particulate filler (huntite and hydromagnesite) [122].

#### **4.5 Comparison of Flammability Properties and Mechanical Properties of Composites**

As seen from Table 4.4 Huntite and Hydromagnesite additions to TPU decreases the mechanical properties dramatically however the flammability properties are improved.

Similarly, presence of expandable graphite in TPU causes a drop in mechanical properties conversely flame retardant characteristics of expandable graphite filled composites increased.

In the case of both Huntite Hydromagnesite and expandable graphite additions to TPU together also show decreasing trend in mechanical parameters. Higher amount of Huntite Hydromagnesite exhibited more reduction in mechanical properties. At low percentage of EG concentrations the synergistic interaction between EG and HH was occurred, however at higher amounts of EG, the antagonistic interaction between EG and HH was observed. As the amount of EG increase, in both Huntite Hydromagnesite and expandable graphite additions to TPU, flammability properties of composites are improved.

As a result, mechanical properties drop rapidly with the addition of Huntite hydromagnesite and expandable graphite, oppositely the flame retardance properties increases as compared with pristine TPU.

**Table 4.5** Comparison of flammability properties and mechanical properties of composites

SAMPLE	Flammability Properties			Mechanical Properties	
	LOI	UL-94	pHRR (kW/m <sup>2</sup> )	Tensile Strength (MPa)	Elongation at break (%)
<b>TPU</b>	21.2	NR	668	24.8±2.2	424.0±22.3
<b>TPU/40 HH</b>	21.6	NR	370	8.0±0.2	61.6±14.8
<b>TPU/50 HH</b>	25.7	V1	290	9.3±0.8	21.4±1.3
<b>TPU/60 HH</b>	31.2	V0	182	9.4±0.3	7.76±1.3
<b>TPU/10 EG</b>	22.2	NR	189	11.2±0.3	332±1.1
<b>TPU/ 20 EG</b>	25.2	V1	134	8.9±0.1	26.1±1.7
<b>TPU/ 45 HH/ 5 EG</b>	24.4	V1	168	7.6±0.3	106.7±3.6
<b>TPU/ 40 HH/ 10 EG</b>	24.8	V0	167	7.0±0.1	79.1±2.4
<b>TPU/30 HH/ 20 EG</b>	27.7	V0	155	9.0±0.4	65.8±1.7
<b>TPU/25 HH/ 25 EG</b>	32.6	V0	133	9.6±0.3	44.6±1.5



## CHAPTER 5

### CONCLUSIONS

This study deals with the effect of EG on flame retardant, thermal and mechanical properties of HH containing TPU. The results of current study show that the addition of 60 wt % HH is enough for achieving the highest UL-94 rating (V0) with a LOI value of 31.2%. HH shows its flame retardant effect through the endothermic decomposition, the dilution effect in the gas phase and the formation of thermally stable char in the condensed phase. According to the flammability test results, the synergistic interaction is observed between HH and EG. The maximum LOI value is observed at a ratio of 1:1 (HH:EG) and the highest UL-94 rating (V0) is observed at a ratios of 4:1, 3:2 and 1:1. According to the mass loss calorimeter test results, TTI does not change, pHRR, THE and pMLR values reduce and FPI value increases as the added amount of HH increases. When EG and HH are used together, the synergistic interaction between EG and HH was observed at low percentage of EG (10 %). At high concentration of EG (20%), the antagonistic interaction between EG and HH was observed. According to the mechanical test results, the addition of HH reduced the tensile strength and elongation at break values and increased the elastic modulus and the glass transition temperature of pristine TPU. The addition of EG negatively affected the tensile strength at low loadings up to 10 wt % EG and the tensile strength increased as the further addition of EG (20 and 25wt%). The elastic modulus of 50 wt% HH containing TPU composite was further improved as the added amount of EG increased.



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