

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE
ENGINEERING AND TECHNOLOGY

**EFFECTS OF HUNTITE/HYDROMAGNESITE ON CAPACITY OF FLAME
RETARDANCY, MECHANICAL AND PHYSICAL PROPERTIES OF
POLYPROPYLENE**

M.Sc. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

SEPTEMBER, 2012

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

**HUNTİT/HİDROMANYEZİTİN POLİPROPİLENİN ALEV GECİKTİRİCİ
KAPASİTESİ, MEKANİK VE FİZİKSEL ÖZELLİKLERİNE ETKİLERİ**

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To my family,

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ABBREVIATIONS

PP	: Polypropylene
FR	: Flame Retardant
H/HM	: Huntite/Hydromagnesite
ATH	: Aluminium Tri Hydrate
MDH	: Magnesium Hydroxide
ABS	: Acrylonitrile Butadiene Styrene
EVA	: Ethylene Vinyl Acetate
SAN	: Styrene Acrylonitrile
MBS	: Methyl Methacrylate Butadiene Styrene
PET	: Polyethylene Terephthalate
PVC	: Polyvinyl Chloride
PTFE	: Polytetrafluoroethylene
LDPE	: Low-Density Polyethylene
HIPS	: High Impact Polystyrene
HBCD	: Hexabromocyclododecane
PMMA	: Poly (methyl methacrylate)
HDPE	: High-Density Polyethylene
EPDM	: Ethylene Propylene Diene Monomer
MCHP	: Magnesium Carbonate Hydroxide Pentahydrate
ZS	: Zinc Stearate
APP	: Ammonium Polyphosphate
PER	: Pentaerythritol
ASTM	: American Society for Testing and Materials
IEC	: International Electrotechnical Commission
ISO	: International Organization for Standardization
BS	: British Standards
LOI	: Limiting Oxygen Index
UL	: Underwriters Laboratory
GWT	: Glow Wire Temperature
GWIT	: Glow Wire Ignition Temperature
GWFI	: Glow Wire Flammability Index
L/D	: Length/Diameter
MPa	: Mega Pascal
SEM	: Scanning Electron Microscopy
FTIR	: Fourier Transform Infrared Spectroscopy
XRD	: X-ray Diffraction
TGA	: Thermal Gravimetric Analysis
MFI	: Melt Flow Index
MFR	: Melt Flow Rate
HB	: Horizontal Burning

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EFFECTS OF HUNTITE/HYDROMAGNESITE ON CAPACITY OF FLAME RETARDANCY, MECHANICAL AND PHYSICAL PROPERTIES OF POLYPROPYLENE

SUMMARY

Polymers, due to their low cost, ease of process, and also range of properties, are widely used to produce a wide variety of materials found in many applications in daily life. Especially polypropylene, which is an important polymer of polyolefins, has taken place of conventional materials rapidly due to common usage in engineering, chemical, and electrical industries.

Additives are added to polymers, depending on the usage areas, in order to provide the required functional properties. Additives should be added into polymers in optimum amounts not to lose desired functional properties. Flame retardants, heat and UV stabilizers, colorants, antioxidants, and fillers are known as major auxiliary chemicals for polymers. Reduction of fires caused by plastic materials are widely investigated in many research studies after polymers has taken place of conventional materials such as metal, wood, and glass. Also material losses which are increasing due to fires in recent years, have revealed once again the importance of the usage of flame retardant additives in final products. In case of fire in order to reduce losses of life and property, the addition of flame retardant and smoke suppressant additives into polymers has increased rapidly. Flame retardant additives play an essential role for improving the flame resistance of polymers. Since the halogenated flame retardant additives release toxic gas to environment, halogen free flame retardants, which are non toxic and environmentally harmless, are preferable in recent years. In research studies about flame retardant systems in order to increase flame resistance of polymers, environmental friendly systems are also preferred.

In this research study, polypropylene that has wide range of applications was used. Due to the wide usage of polypropylene at houses and work places, flame retardancy of this material should be provided using environmental friendly flame retardant additives. Aiming the flame retardancy of polypropylene, usage of a flame retardant system comprising huntite and hydromagnesite, of which reserves are widely located in Turkey, was suggested. These minerals processed by Minelco are on the market with the trade name of Ultracarb. Huntite and hydromagnesite minerals are naturally occurring mixture. Mixtures prepared by Minelco comprise varying proportions of huntite and hydromagnesite. These materials prepared as commercial products can contain large amount of huntite or hydromagnesite. And their mixtures can be coated with stearic acid or silicone.

Four different commercial grades of huntite and hydromagnesite mixtures were used. Ultracarb 1250 has a high content of huntite (65-70%). Ultracarb 1253 also comprises higher huntite content (65-70%) with silicone coated. Hybercarb 2090 comprises the highest amount of huntite (75-80%). LH15 has also higher hydromagnesite content (55-60%).

In this study, in order to determine the ideal formulation, mixtures of huntite and hydromagnesite were fed to co-rotating twin-screw extruder at 30-40-50-60%

loading levels with the screw speed of 100 rpm at 185°C by using polypropylene melt processing method. Sixteen samples were prepared with this method then they were molded to obtain standard test samples (test bar, plate, tensile and impact specimens) by using injection molding method. With these test samples, flame retardant performances of huntite and hydromagnesite and the effect of mechanical properties of these additives on polypropylene were evaluated with the aforementioned ratios. Density, FTIR (Fourier Transform Infrared), XRD (X-ray Diffraction) and melt flow index (MFI) tests were conducted to determine the structural and morphological properties of the test samples. Tensile, Izod impact and three point bending tests were also carried out to evaluate the mechanical properties of the test samples. Thermal properties were determined according to thermogravimetric analysis (TGA) and deformation under load HDT-Vicat test results. In order to investigate huntite and hydromagnesite minerals distribution on the test sample surfaces, SEM micrographs of these samples were evaluated. Additionally, flame retardant performance of the samples were determined according to limit oxygen index (LOI), glow wire, and UL 94 horizontal flammability test results.

According to density measurement results of sixteen different test samples, density test results showed a steady increase with increasing H/HM loading level. It was also observed that there was not any difference between the mixtures that contains different percentage of huntite and hydromagnesite minerals at the same loading level. FTIR analysis was conducted for high proportion (55-60%) of hydromagnesite containing LH15 material and for the mixture of this material with PP in the ratio of 60%. A very sharp band occurred at 3647 cm^{-1} which must be due to an almost free O-H vibration. With the aim of determining huntite and hydromagnesite percentage in four different huntite/hydromagnesite mixtures, XRD analysis was conducted. Percentage amount of huntite and hydromagnesite minerals were calculated evaluating XRD peaks. Melt flow index value of the samples were determined under standard temperature and pressure values. Rheology is a significant parameter for processability and molding of the product, so controlling of this parameter is critically important. Granules of sixteen different samples were molten at the temperature of 230°C and a load of 2.16 kg was applied on them. It was observed that melt flow index of the materials was decreased with increasing the additive amount in the composite. Distribution of the mixture in PP was evaluated based on SEM analysis. SEM observations showed that during extrusion hydromagnesite particles were well dispersed than huntite particles in polypropylene composites. No interaction was observed between huntite/hydromagnesite and polypropylene except mechanical adhesion between filler and polypropylene.

The brittleness of the composite materials increased and tensile strengths of the test samples decreased with increasing the additive percentage in the composite. Elongation values at tensile point were also decreased due to increasing amount of additives in the composite. It was observed that each mixture containing high amount of huntite and hydromagnesite comprised the same mechanical properties. It was also indicated that the silicone coated huntite/hydromagnesite mixture did not show any significant effect on mechanical properties of the composite. The results were almost same for both mixtures. According to three point bending test results it can be said that with the increase in additive amount in the composite, brittleness of the test sample increased and the strength decreased. Elongation values also decreased due to increasing amount of additives in the composite. It was found that the impact

strength of the samples was larger than that of neat PP at 30% loading level. There was not any significant difference between impact strengths of neat PP and PP composite at 40% loading level. The impact strength values of huntite and hydromagnesite mixtures, that were fed to the system above 50% proportion, were smaller than that of pure PP. Silicone coated mixture showed almost same results comparing to uncoated huntite/hydromagnesite mixtures at all loading levels. Considering flame retardant performance of huntite/hydromagnesite minerals and PP mixtures, it was pointed out that the mixture comprising high amount of hydromagnesite, was more effective than that of the mixture comprising high amount of huntite at all loading levels. It was found that the remaining amount of inorganic material increased with increasing of huntite/hydromagnesite amount in the composite at 900°C by evaluating TGA results. It was also observed that the hydromagnesite mineral started decomposing endothermically before the huntite mineral and showed an effective performance by cooling the polymer surface. When we investigated the vicat softening point by the addition of H/HM particles Vicat A values were not affected too much. Vicat B values of polypropylene composites increased with addition of H/HM.

In LOI test, the mixture that contains higher amount of hydromagnesite presented the highest value with 24.3% oxygen index at the loading level of 60%. LOI values of the polypropylene composites increased by increasing of huntite/hydromagnesite ratio in the composite. In glow wire test, it was observed that the mixtures containing high amount of hydromagnesite and huntite mineral (U1250, U1253, and LH15) achieved both of tests (750°C and 850°C) at 60% loading level except H2090. By determining the ratio of huntite/hydromagnesite mixture in the composite as 30%, it was obtained that only the highest amount of hydromagnesite mixture succeeded in the test at 750°C. UL94 horizontal flammability test results showed that polypropylene composites containing higher hydromagnesite content had more effective performance than that of the mixture comprising higher huntite content for each loading level.

In order to improve flame retardancy properties of polypropylene, zinc borate and LH 15 (huntite/hydromagnesite mixture) were used together. 10% zinc borate and 50%LH 15 filled polypropylene composite was prepared by the twin screw co-rotating extruder and injection molded test specimens were subjected to the mechanical, thermal, and flammability tests. Test results can explain as; the addition of zinc borate into the PP/LH 15 matrix caused an improvement in inflammability properties.

HUNTİT VE HİDROMANYEZİTİN POLİPROPİLENİN ALEV GECİKTİRİCİ KAPASİTESİ, MEKANİK VE FİZİKSEL ÖZELLİKLERİNE ETKİLERİ

ÖZET

Polimerler, düşük maliyetleri, kolay işlenebilirlikleri ve farklı özelliklerinden dolayı, günlük hayatta birçok uygulama alanı bularak, çeşitli malzemelerin üretiminde kullanılmaktadır. Özellikle poliolefin sınıfına ait önemli bir polimer olan polipropilen mühendislik, beyaz eşya, kimya ve elektrik sektörlerinde kullanılarak geleneksel malzemelerin yerini almaktadır.

Polimerlere, kullanım alanlarına bağlı olarak, gerekli fonksiyonel özellikleri kazandırmak amacıyla katkı maddeleri eklenmektedir. İstenilen özellikleri sağlamak için, katkı maddelerinin polimerlere uygun miktarda katılması gerekmektedir. Alev geciktiriciler, ısı ve UV sabitleyiciler, renklendiriciler, antioksidanlar, renklendiriciler ve dolgular polimerlerin başlıca yardımcı maddeleri olarak bilinmektedir. Polimerlerin metal, tahta ve cam gibi geleneksel malzemelerin yerini almasından sonra, plastik malzemeden kaynaklanan yangınların azaltılması, yapılan araştırmalarda önemli bir yer tutmaktadır. Ayrıca son yıllarda yangınlardan dolayı artan maddi ve manevi kayıplar, malzemelerde alev geciktirici katkı maddesi kullanımının önemini bir kez daha ortaya koymuştur. Yangınlarda can ve mal kaybını azaltmak için yanmayı önleyici/geciktirici ve duman bastırıcı katkı maddeleri ilavesi günümüzde sürekli olarak artmaktadır. Alev geciktirici katkı maddeleri, polimerlerin aleve dayanımının arttırılmasında önemli bir rol oynamaktadır. Halojen içeren alev geciktirici katkı maddeleri yandıkları zaman çevreye zehirli gaz vermeleri nedeniyle yerlerini halojen içermeyen alev geciktirici katkı maddelerine bırakmaktadır. Halojen içermeyen katkı maddeleri zehirsiz olup çevreyi olumsuz yönde etkilememektedir. Son yıllarda polimerlerin aleve dayanıklılığını arttırmak için kullanılan yanmayı önleyici sistemleri konu alan araştırmalarda da özellikle çevre dostu sistemler tercih edilmektedir.

Bu çalışmada günümüzde evlerde ve işyerlerindeki geniş kullanım alanı olan polipropilenin aleve dayanımının, çevre dostu alev geciktirici katkı maddeleri yardımıyla sağlanması için doğal mineral huntit ve hidromagnezit alev geciktirici sistemi üzerine çalışılmıştır. Huntit ve hidromanyezit mineralleri Türkiye’de geniş bir reserve sahiptirler. Ülkemizde bu mineraller Minelco firması tarafından işlenerek Ultracarb ticari adı ile piyasada yer almaktadır. Huntit/hidromanyezit mineralleri doğada bir karışım halinde birlikte bulunmaktadır. Minelco firması tarafından hazırlanan karışımlar çeşitli oranlarda huntit ve hidromanyezit içermektedir. Ticari olarak hazırlanan bu ürünler, farklı oranlarda huntit veya hidromanyezit içerebilmektedir. Ayrıca kullanım alanları ve istenilen özelliklere uygun olarak huntit ve hidromanyezit karışımlarının yüzeyleri stearik asit veya silikon ile de kaplanmış olarak piyasaya sürülebilmektedir.

Bu çalışmada, huntit ve hidromanyezit yüzdeleri farklı 4 ticari karışım kullanılmıştır. Ultracarb 1250 yüksek oranda (% 65-70) huntit minerali içeren bir karışımdır.

Ultracarb 1253 yüksek oranda (%65-70) huntit içeriğinin yanı sıra yüzeyi silikon ile kaplıdır. Hybercarb 2090, karışımların içerisinde en yüksek (%75-80) huntit içeriğine sahip olan karışımdır. LH15 ise yüksek oranda (%55-60) hidromanyezit içeriğine sahiptir.

Bu çalışmada, ideal formülü belirlemek amacıyla, bu huntit ve hidromanyezit karışımları %30-40-50-60 yükleme seviyelerinde polipropilene eriyik karıştırma yöntemiyle, çift vida ekstruderde 185°C’ de ve 100 rpm hızda eklenmiştir. Böylece hazırlanan 16 adet örnekten, 185°C’de enjeksiyon yöntemiyle standart (çubuk, plaka, darbe ve çekme) test numuneleri basıldı ve bunlar kullanılarak huntit ve hidromanyezit oranının, polipropilen üzerindeki alev geciktirici performansı ve mekanik özelliklere etkisi incelendi. Numunelerin, fiziksel ve morfolojik özelliklerinin belirlenmesi amacıyla yoğunluk, infrared spektroskopisi (FTIR), X ışınları kırınımı (XRD) ve eriyik akış indeksi (MFI) testleri, mekanik özelliklerini belirlemek için çekme, darbe ve 3 nokta eğme testi yapılmıştır. Isısal özellikler termal gravimetrik analiz (TGA) ve yük altında deformasyon sıcaklığı HDT-Vicat sonuçlarına göre değerlendirilmiştir. Ayrıca huntit/hidromanyezit minerallerinin malzeme yüzeyinde dağılımını tespit etmek amacıyla Tarayıcı Elektron Mikroskobu (SEM) görüntüleri de incelenmiştir. Numunelerin alev geciktirici performansı limit oksijen indeksi (LOI), kızgın tel testi ve UL 94 yatay yanmazlık testi ile belirlenmiştir.

16 adet farklı numunenin yoğunluk sonuçlarına bakıldığında, numune içerisindeki katkı maddesi miktarının artırılmasıyla yoğunluğunun da kararlı olarak arttığı görülmüştür. Farklı yüzdelerde huntit ve hidromanyezit minerallerini içeren karışımların, aynı yükleme seviyelerindeki yoğunlukları arasında fark olmadığı tespit edilmiştir. FTIR analizi sadece yüksek oranda hidromanyezit içeren (%55-60) LH15 malzemesine ve bu malzemenin %60 oranında PP ile karışımı için yapılmıştır. 3647 cm^{-1} ’de hidromanyezit mineralindeki O-H gruplarından kaynaklanan keskin bir pik görülmüştür. XRD analizi 4 farklı huntit/hidromanyezit karışımı içerisindeki huntit ve hidromanyezit yüzdeleri tespit etmek amacıyla yapılmıştır. Huntit ve hidromanyezit mineralinin XRD analizinde verdiği pikler belirlenerek karışım içerisindeki mineral yüzdeleri tespit edilmiştir. Malzemelerin eriyik akış indeksi değerleri belirli sıcaklık ve basınç koşulları altında belirlenmiştir. Akışkanlık, ürünün işlenmesinde ve kalıplanmasında kritik bir öneme sahip olan, bu nedenle de kontrolü oldukça önemli parametrelerden biridir. 16 adet farklı numunenin granülleri 230°C sıcaklıkta eritilerek üzerine 2.16 kg yük uygulanmıştır. Kompozit içerisindeki katkı malzemesinin artmasıyla malzemenin erime akış indeksinin düştüğü ölçülmüştür. SEM analizi sonuçlarında da kompozit içerisindeki katkı maddesinin artırılmasıyla malzemenin polipropilen içerisinde nasıl bir dağılıma gösterdiği belirlenmiştir. SEM sonuçlarına göre polipropilen içerisinde hidromanyezit mineralleri, huntit minerallerinden daha iyi bir dağılıma göstermektedir.

Çekme deneyi sonuçlarına göre kompozit içerisindeki katkı maddesi oranının artmasıyla birlikte malzemenin kırılabilirliği artmaktadır. Bununla birlikte kopma dayanımı da azalmaktadır. Kopma anındaki uzama değerleri de katkı maddesi ilavesiyle birlikte azalmaktadır. Yüksek oranında hidromanyezit içeren karışım ile yüksek oranda huntit minerali içeren karışımlar mekanik özellikler açısından benzer özellikler göstermiştir. Yüzeyi silikon ile kaplanmış huntit/hidromanyezit karışımının da mekanik özellikler üzerine iyileştirici etkisinin olmadığı tespit edilmiştir. Sonuçlar arasında çok büyük farklar görülmemiştir. Aynı şekilde 3 nokta eğme sonuçlarına göre kompozit içerisindeki katkı maddesi miktarı arttıkça malzemenin kırılabilirliği

artmakta ve malzemenin dayanımı azalmaktadır. Uzama miktarı kompozit içerisindeki katkı maddesi miktarının artmasına bağlı olarak azalmaktadır. Malzemelerin Izod darbe dayanımının, %30 oranında katkı maddesi yükleme seviyesinde, saf polipropilenden yüksek olduğu bulunmuştur. %40 yükleme seviyesinde, saf polipropilenin darbe dayanımı ile polipropilen kompozitin arasında belirgin bir fark görülmemiştir. Huntit ve hidromanyezit karışımlarının sisteme %50'den fazla yüklenmesi durumunda, darbe dayanımı saf polipropilen ile karşılaştırıldığında azalma göstermektedir. Yüzeyi silikon ile kaplı karışım, bütün yükleme seviyelerinde diğer kaplamasız huntit/hidromanyezit karışımlarıyla benzer değerleri göstermiştir. Huntit/hidromanyezit minerallerinin PP ile karışımının alev geciktirici performansı araştırıldığında yüksek oranda hidromanyezit içeren karışımın her yükleme seviyesinde yüksek huntit içeren karışımdan daha etkili özelliklere sahip olduğu tespit edilmiştir.

Termal gravimetrik analiz (TGA) sonuçlarına göre kompozit içerisindeki huntit/hidromanyezit miktarının artırılmasıyla 900°C'de geriye kalan inorganik madde miktarının arttığı görülmüştür. Ayrıca hidromagnezit minerali huntit mineralinden önce endotermik olarak ayrışmaya başlayarak polimer yüzeyini soğutup aktif bir performans göstermiştir. Polipropilen içerisindeki huntit/hidromagnezit oranının artmasıyla birlikte kalan inorganik malzeme miktarı artmaktadır. Vicat test sonuçları değerlendirildiğinde, Vicat A metodunda, saf polipropilen ile katkılı malzeme karşılaştırıldığında fark görülmemiştir. Vicat B metoduna göre ise polipropilen içerisindeki huntit/hidromanyezit oranının artırılmasıyla sıcaklığın saf polipropilene göre artış gösterdiği gözlemlenmiştir.

Limit oksijen indeks (LOI) testine göre %60 yükleme oranında, yüksek hidromanyezit içeren karışım %24.3 oksijen indeks ile en yüksek değeri göstermiştir. Buna bağlı olarak kompozit içerisindeki huntit/hidromanyezit miktarı arttıkça LOI değeri artmaktadır. Yüksek hidromagnezit minerali içeren karışımın daha yüksek LOI değerine sahip olmasıyla birlikte, hidromagnezit mineralinin, huntit mineralinden daha etkili olduğu görülmektedir. Kızgın tel testi sonuçlarına göre H2090 haricinde, yüksek oranda hidromanyezit ve huntit mineralini içeren karışımlar (U1250, U1253 ve LH15) %60 yükleme seviyesinde, 750°C ve 850°C testlerini geçmiştir. Kompozit içerisindeki huntit/hidromanyezit karışımı %30 olarak belirlendiğinde, sadece yüksek hidromanyezit içeren karışımın 750°C testini geçtiği görülmüştür. UL 94 yatay yanmazlık test sonuçlarına göre her yükleme seviyesi için yüksek oranda hidromanyezit içeren karışım (LH15), yüksek oranda huntit içeren karışımlara (U1250, U1253, H2090) göre daha aktif bir performans göstermiştir. Yatay durumda alevin numune üzerindeki ilerlemesinde azalma tespit edilmiştir.

Polipropilenin alev geciktirici özelliklerini arttırmak amacıyla LH 15 ve çinko borat (ZnB) beraber kullanılmıştır. Çinko borat duman bastırıcı özelliğe sahip iyi bir alev geciktirici katkı maddesidir. Alev geciktirici katkı maddeleri ile kullanıldığında iyi sinerjik etkiler göstermektedir. LH 15 karışımının içerisindeki hidromagnezit miktarı huntit miktarından fazladır. Huntit/hidromagnezit karışımı (LH 15) ve çinko borat arasındaki sinerjik etkinin belirlenmesi amacıyla, polipropilen ile birlikte kompozit hazırlanmıştır. %10 çinko borat ve %50 LH 15 içeren polipropilen kompozit çift vidalı ekstruder ile hazırlanmıştır. Enjeksiyon ile kalıplama işlemi yapılan test numunelerine mekanik, termal ve yanmazlık testleri yapılmıştır. Test sonuçlarına göre çinko borat içeren polipropilen kompozit, mekanik ve yanmazlık özellikler açısından %60 oranında LH 15 içeren polipropilen kompozitten daha iyi sonuçlar göstermiştir.

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]. The improvement of polymeric materials, or plastic as an engineering material began to as a result of extended research within the 20th century. Bakelite is known as the first synthetic resin, which was found in 1907, that is commonly used today in components for the electrical and electronic industries. In 1926, the work of Staudinger obtained a breakthrough for thermoplastic materials. The scientific foundation for the systematic study of plastics was initiated by his pioneering research into the long chain molecular structure of plastics. Depending on the industrial usage, polymeric materials can be divided into the following groups: plastics, rubber, synthetic fibers, polymeric coatings, and polymeric additives. Plastics can be divided into two general classes: commodity plastics (such as polyolefines, polystyrene, polyvinyl chloride, diene elastomers, epoxies, resins etc.) and high performance engineering plastics (such as polyamides, polycarbonates, acetals, polysulfones, fluoropolymers etc.). Plastics can be used as an engineering material instead of conventional materials such as metal, wood, stone, glass, and ceramic. They are very useful for many applications such as automotive industry, the electronic sector, the packaging and manufacturing of consumer goods [2].

At present, polypropylene (PP) is the most widely used commodity thermoplastic polymer in many different commercial applications, compatible with many processing techniques. In addition, it is known as one of the fastest growing classes of commodity thermoplastics, with a market share growth of 6-7%. Its strong growth rate is based on moderate cost and favorable properties. PP is useful for many applications such as fibers, films, filaments, and injection molding parts for automobiles, rigid packaging, appliances, medical equipment, food packaging and consumer products. It can be alternative materials for glass, metal, and engineering plastics such as ABS, polycarbonate, polystyrene, nylon and used large appliances such as ovens, dishwasher, refrigerators, and washing machine. Flame retardancy

properties of PP must be improved by the use of flame retardants for applications in the construction, automotive, appliances, and electronics industries [3].

Fire is unique destructive force of nature and known as physical and chemical phenomenon. The interaction between the flame, its fuel, and the surrounding can be strongly nonlinear, and quantitative estimation of the process involved is often complex. The burning process and the processes of interest in an enclosure fire mainly involve mass fluxes and heat fluxes to and from the fuel and the surroundings [4].

Every day in Europe there is about 12 fire victims and 120 people severely injured and the World Health Organisation reports that there are approximately 300,000 deaths per year, globally from fire-related burns. In the USA in 2009, over 1.3 million fires were attended by public fire services, which resulted in 3,010 civilian deaths and 17,050 civilian injuries. According to common indicators of fire statistics in the countries of the world in 2003 year, in Turkey there are approximately 505 deaths [5].

To provide protection from fires and to increase escape time when fire happens, methods to increase the flame retardancy of commercial polymers have been improved. A plastic flame retardant (FR) is a unique chemical compound incorporated into a plastic. Since its aim is to inhibit the ignition and/or retard the burning of that plastic material. In plastic formulations, employment of flame retardants must achieve at least one of several tasks during the fire. These include;

- increasing the ignition temperature
- reduction of the rate of burning
- reduction of the flame spread
- reduction of the smoke generation.

Many types of flame retardants which can be inorganic, organic, mineral, halogen containing or phosphorus-containing are used in consumer products. In recent years, halogen free flame retardants replaced conventional halogenated flame retardants in plastic materials. Halogen containing flame retardants have significant disadvantages which are related to the formation of smoke, toxic gasses and corrosive decomposition product. In contrast, mineral flame retardants provide in part

extremely low smoke values. They absorb toxic and corrosive gasses and generate nothing but water, carbon dioxide and harmless metal oxide. Most halogen-free flame retardants have environmentally friendly profile. Especially minerals have been used as flame retardant in plastic applications for many years. The following properties are ideally required for the successful commercial use of flame retardant filler:

- Low toxicity
- Ready availability and low cost
- Available with small particle sizes, with defined morphology and ideally low surface area and capable of being used at high filler loadings
- Low levels of solubility, extractable salts, and of potentially detrimental impurities (such as those causing premature polymer degradation)
- Colorless
- A significant endothermic decomposition in the temperature range 100°C–300°C, with release of at least 25% by weight of water and/or carbon dioxide, depending on the polymer, its mechanism of decomposition, and inherent resistance to combustion [6].

Huntite and hydromagnesite minerals are defined as natural mixtures that have some useful filler properties for plastic applications. Huntite is calcium magnesium carbonate, while hydromagnesite is hydrated magnesium carbonate. The main application in polymers is as fire retardant filler, with a mechanism of endothermic decomposition with release of water and carbon dioxide. 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. Ultracarb is also known as brand name of huntite and hydromagnesite mixtures which Minelco sells the mixed mineral as a fire retardant. It includes varying proportions of huntite and hydromagnesite [7].

Huntite/hydromagnesite represents another magnesium containing source for mineral flame retardants. These minerals are similar to brucite based flame retardant, this group of materials was introduced to the market in the late 1980s. Huntite/hydromagnesite has no uncomplicated metal hydroxide structure, but consists of two distinct carbonates. Endothermic decomposition starts at about 250°C

liberates water steam and carbon dioxide and results in Ca and Mg oxide as solid end products. Flame retardant efficiency is similar to that of Aluminium trihydrate (ATH) and Magnesium hydroxide in most applications. Huntite is not as effective flame retardant as hydromagnesite. For flame retardants applications the hydromagnesite ratio should not be lower than 35 to 40%. A formulation of huntite/hydromagnesite (60%) in ethylene vinyl acetate (EVA) polymer (40%) shows a correlation of hydromagnesite content to oxygen index only below 40% ratio [8].

At present, economically important reserves of huntite and hydromagnesite are found in Turkey and Greece. In Turkey, the age of these deposits is estimated at between two to three million years. The size of these reserves is tens of million of tonnes [9]. The commercially used deposits in northern Greece hold some millions of tonnes reserves. The deposits normally consist of natural blends of the two minerals huntite and hydromagnesite with varying ratios. The level of impurities is very low, the most important ones are other white carbonate minerals such as aragonite, calcite, and dolomite [8].

In this study, flame retardancy capacity of PP were investigated using four different types of Ultracarb (U1250, U1253, H2090, and LH15) which comprise of varying proportions of huntite/hydromagnesite. In addition, silicone coated mixture of huntite and hydromagnesite with higher huntite content were used. The mixtures of huntite/hydromagnesite (H/HM) were incorporated into PP at different loading levels (30-40-50-60%) in order to investigate the effect of huntite and hydromagnesite on various properties of polymeric composites, such as flame retardancy and mechanical properties. The effects of the ratio of two minerals in polymeric compounds were evaluated in terms of flame retardancy and mechanical properties of PP compounds and the results were compared to silicon coated type Ultracarb and also zinc borate (%10) and LH 15 (%50) were added to polypropylene to improve flame retardancy properties.

2. FLAMMABILITY OF POLYMERS AND FLAME RETARDANTS

2.1 Polymers and Classification

Polymers which are so common in our everyday lives used to make commercial products as diverse as clothing and compact disks, calculators and styrofoam cups, packing for food, and insulation. In addition, plastics play such an important role in the industrialized world. We may have moved from the age of metals into the age of plastics [1].

Polymers are called as the compounds of light weight, high strength, flexible, chemical resistant with special electrical properties. They can be converted into an attractive choice of wide variety of colours, strong solid articles, transparent glass like sheets, flexible rubber-like materials, soft foams, smooth and fine fibres, jelly-like food materials etc. In addition, polymers can be used to seal joints, bear loads, fill cavities, jerk resistant in between glasswares, and the bond objects [10].

Polymers can be separated into two classes; natural and synthetic. Protein fiber, cotton, cellulose and wool are known as common examples of natural polymer. Synthetic polymers can be divided into different classifications depending on the structure, property, processing characteristics, type of polymerization mechanisms or applications. The terms polymer and polymeric material encompass very large, broad classes of compounds, both natural and synthetic, with a wide variety of properties. Because of the extraordinary range of properties of polymeric materials.

The polymers can be divided into two parts based on their thermal processing behavior as thermoplastics or thermosets. Thermoplastics are polymers which melt when heated and resolidify when cooled, while thermosets are those which do not melt when heated but, sufficiently high temperature, decompose irreversibly. There is a useful chemical distinction between the two groups. Thermosets are crosslinked materials, consisting of an extensive three-dimensional network of covalent chemical bonding, while thermoplastics include essentially linear or lightly branched polymer molecules [11]. The classification of polymers is indicated in Figure 2.1.

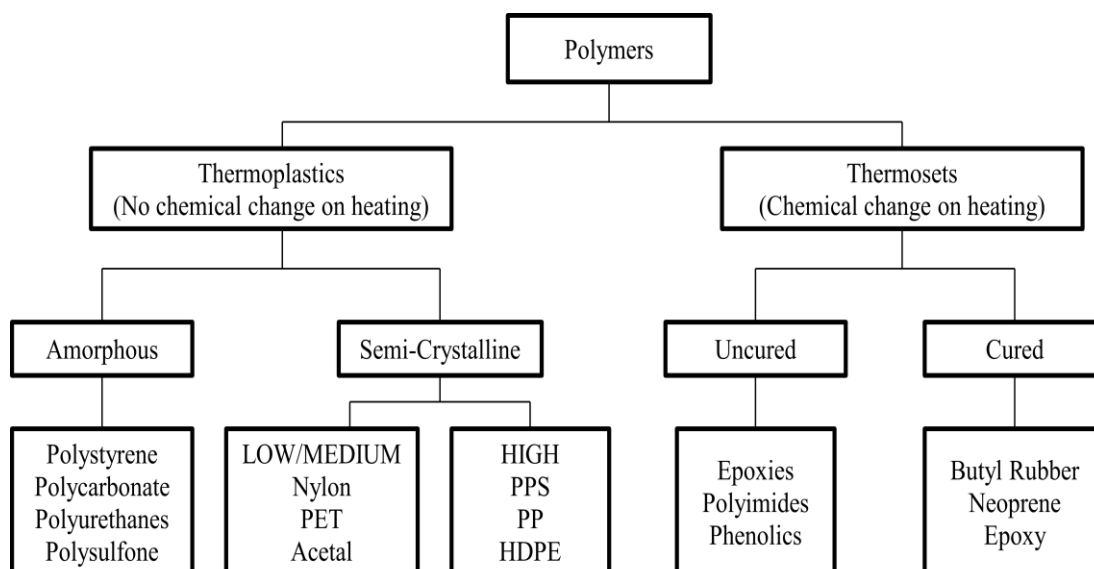


Figure 2.1 : Classification of polymers [12].

A polymer is built up from numerous smaller molecules. The small molecules used as the basic building blocks for these large molecules are defined as monomers. In addition, monomers are known as repeating unit. The repeat units form a polymer. Molecule structure is very important for polymers. For example Polyethylene (repeating unit: $-(CH_2-CH_2)-$) and polypropylene (repeating unit: $-(CH(CH_3)-CH_2)-$) are the most widely used synthetic polymers that are thermoplastics. Polystyrene (repeating unit: $-(CH(Phenyl)-CH_2)-$) is indicated as the most important aromatic hydrocarbon polymer. A number of styrenic copolymers including acrylonitrile-butadiene-styrene terpolymers (ABS), styreneacrylonitrile polymers (SAN) and methyl methacrylate butadiene styrene terpolymers (MBS) are also important. Cellulosics, polyacrylics and polyesters are the most important and widely used oxygen-containing polymers. Poly (methyl methacrylate) (repeating unit: $-(CH_2-C(CH_3)(CO-OCH_3))-$; PMMA) which is defined as the main polyacrylic widely used as a substitute for glass. Polyethylene terephthalate (PET), or polybutylene terephthalate is the most important polyesters.

Nitrogen-containing materials are known as nylons (polyamides) (repeating unit: $-CO-NH-$), polyurethanes (repeating unit: $-NH-COO-$) and polyacrylonitrile (repeating unit: $-(CH_2-CH-CN)-$).

Poly (vinyl chloride) (PVC, repeating unit: $-(CH_2-CHCl)-$) is the most important chlorine-containing polymer and polytetrafluoroethylene (PTFE) is the widely used fluorine-containing polymer [13].

2.2 The Burning of Polymers

2.2.1 Fire dynamics and combustion

The scientific description of fire phenomena in quantitative terms is called as fire dynamics. Combustion is explained as the rapid oxidation of a substance which is accompanied by rapid release of energy. Chemical combination of a substance with oxygen is defined as oxidation. Fire which involves chemical reactions between combustible species and oxygen from the air is known as physical and chemical phenomenon. Another definition is that fire is a simpler definition of combustion. Oxidizer is necessary for combustion to occur. When exposed to heat, pressure, or both, oxidizer will liberate oxygen that will subsequently become available to support the combustion of the fuel. A fuel is explained as anything that will burn.

Fire is presented as a triangle. There are three parts to the fire triangle theory. The fire triangle is presented in Figure 2.2. Oxidizer, fuel and energy are important factors for this combustion cycle that is called the fire triangle. This combustion cycle must be closed and present at the same time for a fire to exist. In addition, fuel, oxygen, and heat are the three sides of the original fire triangle.

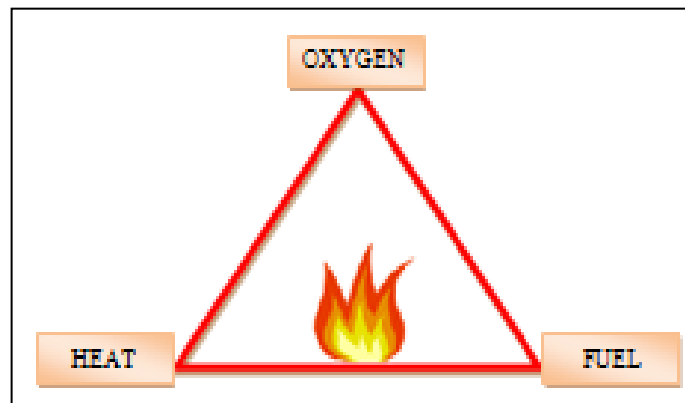


Figure 2.2 : Fire triangle [14].

According to fire triangle theory, when fuel, an oxidizer, and energy are brought together in a one place in the proper amounts of and forms, a fire will occur. The fuel which is defined as being in the ignitable must also be available in the proper amount. It must be present in a gas or vapor form to burn. The percentage of gas and vapor in air between upper and lower flammable limits is known as the flammable range. A maximum percentage of gas or vapor in air is defined as the upper flammable limit. A minimum percentage of gas or vapor in air is defined as the lower

flammable limit. The upper and lower flammable limits are important factors for combustion to occur.

The oxidizer portion must be in the proper form to support combustion. It will be atmospheric oxygen. It can be oxygen released from an oxidizing agent or one of the halogens. In addition, the energy is also important factor to increase the temperature of the fuel to its ignition temperature. The ignition temperature is explained as the minimum temperature to which a fuel must be raised before it will ignite. When all the conditionals is ensured, the material will become hotter and hotter until its ignition temperature is reached and the fire begins [14].

The combustion process is conducted by such variables as rate of heat production, rate of heat transfer to the surface, surface area, and rates of decomposition. In addition, Figure 2.3 illustrates combustion process. Flame retardancy of polymeric materials which may be evolved in the heating stage is improved by flame retardants that cause the formation of a surface film of low thermal conductivity and/or high reflectivity that reduces the rate of heating. It is also improved by flame retardants that might serve as a heat sink by being preferentially decomposed at a low temperature. And eventually, it is evolved by flame retardant coatings that upon subject to heat may intumesce into a foamed surface layer with low thermal conductivity properties. Transformation of a plastic into char and limit production of combustible carbon containing gases can be improved by a flame retardant. At the same time, thermal conductivity of the surface will be decreased by char. Therefore, the decomposition products can also be altered by flame retardants.

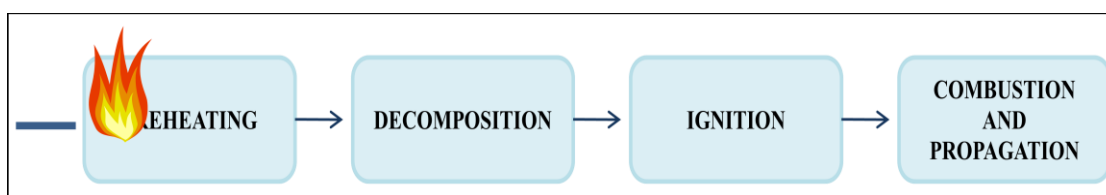


Figure 2.3 : Combustion process illustration [14].

2.2.2 Behaviour of polymeric materials in fires

Combustion is explained as a fast, self accelerating exothermal redox process that may be of either a chain or a thermal nature, depending on the cause of initiation and development. The flammability properties of natural and synthetic polymeric materials are determined by the ability of such materials to ignite and spread and combustion process [15].

If many polymers exposed to some suitable ignition sources, they will undergo self-sustained combustion in air or oxygen. The main sources of ignition are generally nonpolymeric materials such as matches, cigarettes, torches, or electric arcs, but polymers are most responsible for the propagation of a fire. A highly complex combustion system is created by a burning polymer. Chemical reactions can occur in three interdependent regions that are within the condensed phase, at the interface between the condensed phase and gas phase, and in the gas phase [16].

Heating of the polymer, decomposition, ignition and combustion are called as a cycle of coupled events of polymer combustion. The polymer is heated to a specific temperature at which it starts to decompose and gives out gaseous products that are usually flammable and diffuse into the flame zone above the burning polymer. When an ignition source is available, they will undergo combustion in the gas phase and liberate more heat. Under these conditions, some of the heat is transferred back to the polymer surface. More volatile polymer fragments are produced to sustain the combustion cycle [16].

Natural and synthetic polymer will decompose or pyrolyse evolving flammable volatiles when they exposed to source of sufficient heat. If the temperature is high enough to ignite, they will mix with air. Figure 2.4 shows simple representation of polymer combustion processes.

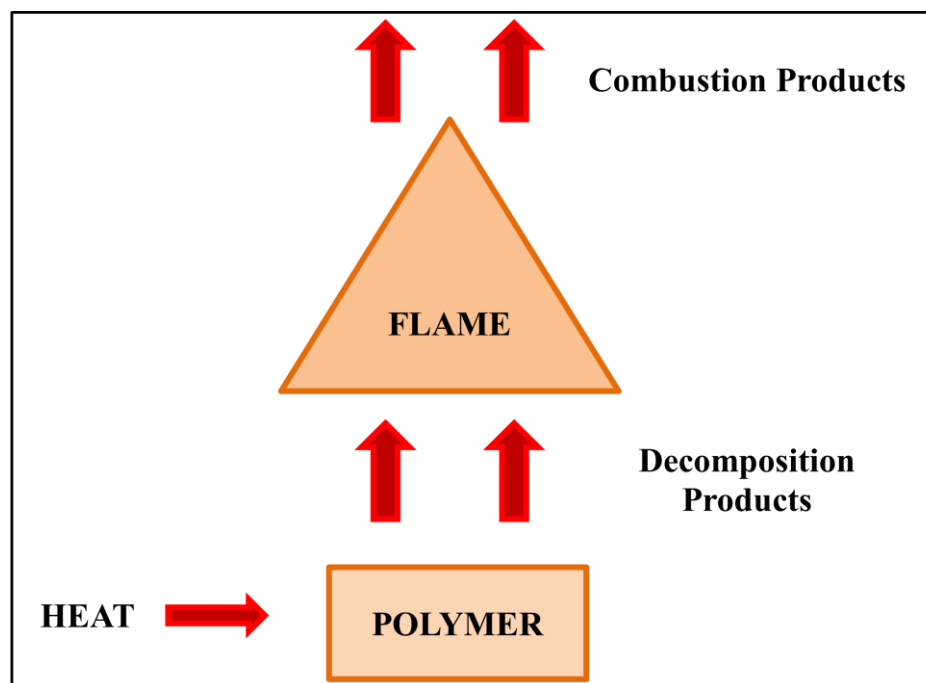


Figure 2.4 : Polymer combustion process [16].

The presence of an external source such as a spark or a flame (flash ignition) causes ignition. Ignition can occur spontaneously. If the heat evolved by this ignited flame is sufficient to keep the decomposition rate of the polymer above that required to maintain the concentration of the combustible volatiles, i.e. the 'fuel', within the flammability limits for the system, then a self-sustaining polymer combustion cycle will be established.

Several processes and/or parameters, such as burning rates (solid degradation rate and heat release rate), spread rates (flame, pyrolysis, burnout, smolder), ignition characteristics (delay time, ignition temperature, critical heat flux for ignition), product distribution (in particular, toxic species emissions), smoke production help to explain the burning behavior of plastics [4].

2.2.3 Thermal decomposition of polymers

Degradation of polymers comprises all the changes in the chemical structure and physical properties of the polymers due to external chemical stresses caused by chemical reactions. Biodegradation, pyrolysis, oxidation, and mechanical, photo and catalytic degradation are defined as broader terms for polymer degradation [17].

The two different mechanisms of degradation of polymers are described as depolymerisation and statistical fragmentation of chains. Polymer has many different bonds and types of bonds that can break. The bonds that tend to break first are the ones that form the weakest link in the chain. This explains why most polymers decompose at a temperature substantially lower than comparable small molecules when there are irregularities that can perform as weak points where degradation starts. Side-group elimination, random scission and depolymerisation is defined as three major pathways of thermal degradation of polymers [17].

Side-group elimination forms in two steps. The first step is the elimination of the side groups attached to a backbone of the polymer. For example, the first step of thermal degradation of PVC is the elimination of the side groups to form hydrogen chloride. When the side groups removed, a polyene macromolecule remains [17].

Random scission involves the formation of a radical at some point on the polymer backbone, producing small repeating series of oligomers usually differing in chain length by the number of carbons. Statistical fragmentation is important mechanism of degradation of polymers. Polymers that do not depolymerise, decompose by thermal

stress into fragments that break again into smaller fragments and so on. The degree of polymerization decreases without the formation of free monomeric units. Initiation of statistical fragmentation is formed by chemical, thermal or mechanical activation or by radiation [17].

Depolymerisation is defined as a free-radical mechanism in that the polymer is degraded to the monomer or comonomers that make up the (co)polymer. Polymethacrylate and polystyrene degrade by this mechanism. The formation of a free radical on the backbone of the polymer causes the polymer undergo scission to form unsaturated small molecules and propagate to the free radical on the polymer backbone. The conditions of depolymerisation are similar to statistical fragmentation. The mechanism of depolymerisation proceeds until the equilibrium between monomer and polymer at given temperature is reached in a closed reaction system [17]. Table 2.1 shows a listing of the decomposition and ignition temperatures for common polymers [13].

Table 2.1 : Decomposition and ignition temperatures for common thermoplastic polymers [13].

Polymer	Decomposition range/°C	Flash ignition temperature/°C	Autoignition temperature/°C	ΔH_C/kJ kg⁻¹
LDPE	340-440	340	350	46.5
Polypropylene	330-410	350-370	390-410	46.0
Polystyrene	300-400	345-360	490	42.0
PVC(rigid)	200-300	390	455	20.0
PMMA	170-300	300	450	26.0
Cellulose(cotton)	280-380	210	400	17.0

2.2.3.1 Decomposition and properties of polypropylene

Polyolefins are produced with a variety processes and are some of the largest volume commodity polymers. Polypropylene (PP) is known as an important polyolefin. In this work, flame retardancy properties of PP are investigated so decomposition, properties and applications of PP are given is in this section. PP can be used in many different commercial applications. It is a thermoplastic material that is compatible with many processing techniques. PP is defined as one of the fastest growing classes of commodity thermoplastics, with a market share growth of 6-7%/year [3].

PP can be in three forms that are described as atactic, isotactic and syndiotactic. In isotactic form, all methyl groups are attached to the one side of c-c backbone. In syndiotactic, methyl groups are placed at regular intervals and on the either side of backbone. Isotactic form has maximum crystallinity. The molecule structure of PP is showed in Figure 2.5.

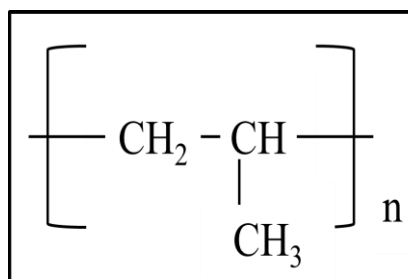


Figure 2.5 : Molecule structure of PP [18].

PP is useful material having outstanding physical, chemical, mechanical, thermal and electrical properties. It has lower impact strength strength when compared to low or high density polyethylene.

Glass transition temperature: -10°C

Melting temperature: 173°C

Amorphous density at 25°C: 0.85g/cm³

Crystalline density at 25°C: 0.95g/cm³

Molecular weight of repeat unit: 42.08 g/mol

PP is described as useful plastic that used in consumer sectors in house wares, furniture, appliances, luggage, toys, battery cases and other durable items for home, garden or leisure uses. Other applications comprise hoods, orthopedic devices, structural covers, light tables, lab. tables, rinse and etch housing for electronic industry. In addition, it has useful applications in automotive sector. Bumpers, cladding, and exterior trim are made of this material [18].

PP is known as one of the most oxidatively unstable of the polyolefins. It is very vulnerable to oxidative degradation under the influence of elevated temperature and sunlight because of the existence of tertiary carbon atoms. The free radical degradation of PP includes initiation, propagation, chain branching and termination steps leading to non-radical products. Thermal dissociation of chemical bonds forms

at initiation step, whereas the key reaction in the propagation is the reaction of the polymer alkyl radicals with oxygen to form polymer peroxy radicals in a very fast reaction. The next propagation step is defined as abstraction of a hydrogen atom by the polymer peroxy radical to yield hydroperoxide polymer (POOH) and new alkyl radical. The chain branching of POOH results in the formation of very reactive polymer alkoxy radicals and hydroxyl radicals. The polymer oxy radicals can be involved in termination reactions [19]. The mechanism of thermal decomposition of PP is indicated in Figure 2.6.

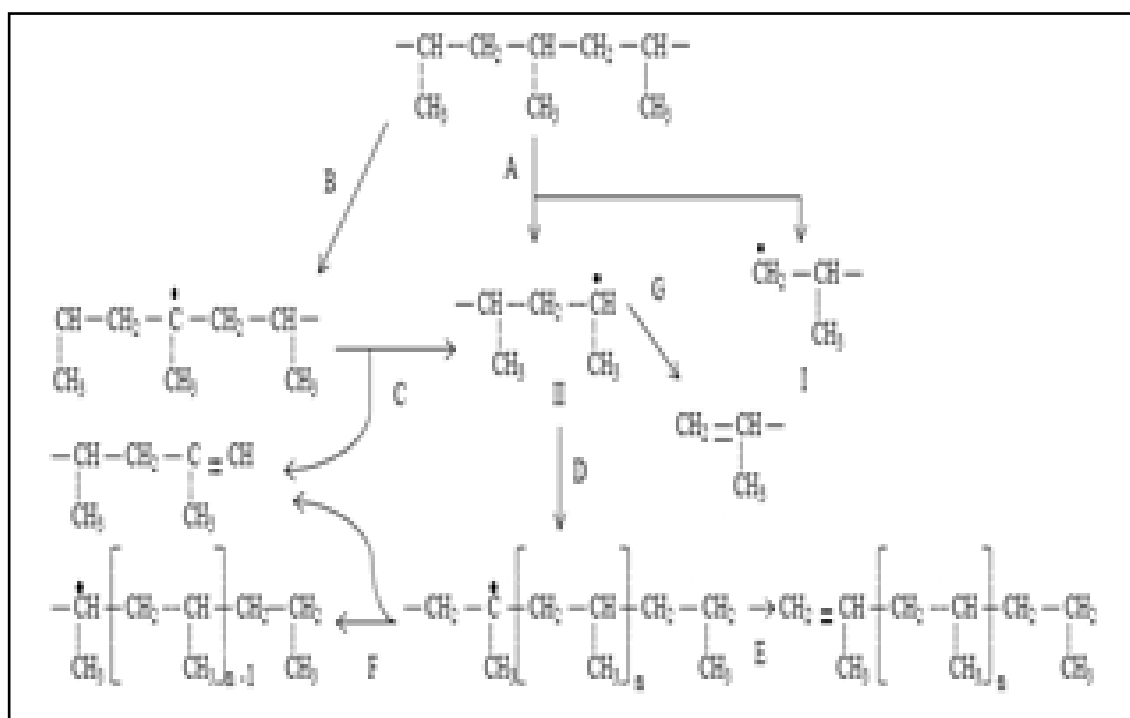


Figure 2.6 : The thermal decomposition mechanism of PP [19].

The initiation reaction (A) which occurs by random scission of the main chain generates two types of radicals that are known as primary (I) and secondary (II). During the decomposition, the generation of radical II is more desirable than the generation of radical I since the former is also generated by intermolecular and intramolecular radical radical transfer to tertiary carbon followed by β - scission (B, C, D and E) [19].

2.3 General Flame Retardant Mechanisms

Combustion process should be prevented or even suppressed by a flame retardant. Depending on their nature, they perform chemically and/or physically in the solid,

liquid, or gas phase. During a particular stage of the combustion process, for example, during heating, decomposition, ignition, or flame spread, flame retardants interfere with combustion. They should be considered as a complex process in which many individual stages occur simultaneously with one dominating but they don't occur singly [4].

Flame retardants are different from one another in terms of chemical structure and their general mechanisms of action are appropriate several classes of flame retardants. Gas-phase-active and condensed-phase-active flame retardants are normally recognized the first line of separation. Gas-phase-active flame retardants perform primarily through scavenging free radicals that are responsible for the branching of radical chain reactions in the flame. It is known as chemical mechanism of action in the gas phase. Other flame retardants produce large amounts of incombustible gases which dilute flammable gases and sometimes dissociate endothermically. In addition, they decrease the temperature by absorbing heat. Combustion is retarded by this effect that may eventually result in extinguishment of the flame. It is called as the physical mechanism of action in the gas phase.

Condensed-phase mechanisms of action are more numerous than the gas-phase mechanisms. Charring is known as the most common condensed-phase-action. Chemical interaction of the flame retardant and the polymer or physical retention of the polymer in the condensed phase could promote charring. Along with that charring could also be promoted by catalysis or oxidative dehydrogenation.

Aluminium hydroxide and magnesium hydroxide are flame retardants which show almost exclusively a physical mode of action. On the other hand, there is no single flame retardant that will act exclusively through a chemical mode of action. Chemical mechanisms are always accompanied by one or several physical mechanisms that can be most commonly endothermic dissociation or dilution of fuel. Synergistic can often be combinations of several mechanisms [20].

2.3.1 Physical mode of action

There are several ways in which the combustion process can be retarded by physical action:

- By cooling. The additive can degrade endothermally. Endothermic reactions cool the material to a temperature below that required for supporting

combustion process. ATH performs under this principle, and its efficiency is determined the amount incorporated in the polymer.

- By forming protective layer. The additives can form protective layer that is called physical barrier. It can reduce the heat transfer from the heat source to the material. This effect is known as principle of intumescence phenomenon. Depending on the their pyrolysis, phosphorus additives can form a protective vitreous barrier. The same effect can be observed using boric acid based additives, inorganic borates, or low melting glasses.
- By dilution. Additives and inert substances, which evolve inert gases on decomposition, dilutes the fuel in the solid and gaseous phase so that the lower ignition limit of the gas mixture is not exceed. Release of water vapour and carbon dioxide may dilute the radicals in the combustion process [4].

2.3.2 Chemical mode of action

The most important chemical reactions interfering with the combustion process occur in the gas and condensed phases.

- Reaction in the gas phase. The radical reactions of the combustion process occur in the gas phase. Flame retardants or its degradation products interrupt mentioned reactions. The exothermic processes that occur in the flame is stopped, this system cools down. The supply of flammable gases is reduced and suppressed [4]. However, highly toxic and irritant partially burnt products, including carbon monoxide (CO) are generated by flame reactions that generally increase the toxicity of the fire gases while reducing fire growth. Free radical inhibitors are released by flame retardant chemicals at pyrolytic temperatures, and the radical mechanism of the combustion process that occurs in the gas phase is interrupted by the flame retardant [21].
- Reaction in the condensed phase. Two types of reaction occur in this phase. Firstly, the flame retardant can accelerate breakdown of the polymer. Secondly, a layer of carbon (charring) is created by flame retardants to form on polymer surface. For example, the dehydrating action of the flame retardant produces double bonds in the polymer. These form the carbonaceous layer via cyclizing and cross-linking processes [4].

2.4 Basic Flame Retardants of Polymeric Materials

The main task of flame retarding polymers is to enhance the ignition resistance of the material, to reduce flame spread rates and to reduce amounts of toxic and smoke products in case burning. All flame retardants have important effects on the technical properties of plastic materials. The aim for product development is to find a compromise between desired improvement in fire safety and minimal reduction of other properties. The desired properties for flame retardants are listed in the following:

- High efficiency to reduce negative effects on properties and costs,
- Compatibility with polymer and other additives,
- Thermal stability at processing temperature,
- Low tendency to bleed out or to evaporate,
- UV-stability
- Colour and odourless,
- Resistance to ageing and hydrolysis,
- No corrosion of equipment,
- Environmental safety and no toxicity,
- Recyclable.

There are two types of additives that are known as reactive and additive flame retardants. Additive flame retardants are used especially in thermoplastics, but also in thermosets. If they are compatible with the plastic they act as plasticisers, otherwise they are considered as fillers. They are used in polyolefins, polyvinylchloride, and polystyrene to polymers with a heterogeneous chain polyurethanes, polyesters, polycarbonates, polyphenylene ethers, and polyamides in terms of the application ranges from polymers with a pure carbon chain structure. They can be easily and cheaply incorporated into the polymers and do not change their characteristics significantly when they are compared to reactive flame retardants. Reactive flame retardants are known as tailor-made products for certain polymers, preferred for polymers with a heterogeneous chain such as epoxy resins or polyurethanes. Chemical reactions are necessary to incorporate into the polymer chain for this class of flame retardants. Oligomeric and polymeric flame retardants are prepared using

reactive flame retardants. They are used mainly in thermosets (especially polyesters, epoxy resins, and polyurethanes) in which they can easily be incorporated [4,22].

Combinations of additive or reactive flame retardants can generate an additive. This additive can create synergistic or antagonistic effect. The synergistic effect can observe when they are used together with specific flame retardants. The flame retardants/synergist systems have achieved great importance in practical use because they are usually less expensive than flame retardants used alone [22].

There are many flame retardants that work in a number of different ways. Some flame retardants are effective on their own, other products are used mainly or only as synergistic, acting to enhance the effect of other types of flame retardant. To understand how flame retardants work it is first necessary to see how materials burn. Solid materials do not burn directly, they must be first decomposed by heat (pyrolysis) to release flammable gases. Visible flames appear when these flammable gases burn with the oxygen (O_2) in the air. If solid materials do not break down into gases, then they will only smoulder slowly and often self extinguish, particularly if they “char” and form a stable carbonaceous barrier which prevents access of the flame to the underlying material. However, as we all know, even materials such as wood do in fact burn, because once ignited the heat generated breaks down long-chain solid molecules into smaller molecules which transpire as gases. Figure 2.7 shows how combustion process works with flame retardant system [5].

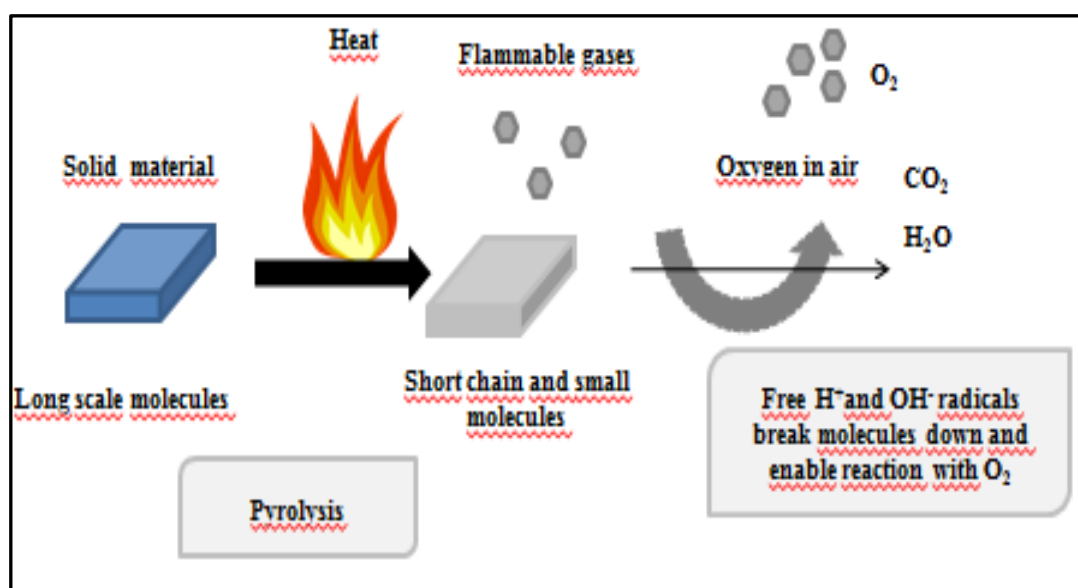


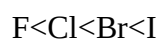
Figure 2.7 : Combustion process of solid material including flame retardant [5].

The gas flame itself is maintained by the action of high energy radicals that is H and OH in the gas phase which decomposes molecules to give free carbon which can react with oxygen in air to burn to CO₂, producing heat energy [5].

Halogenated (chlorine and bromine), phosphorus-containing, and bromine-containing phosphorus compounds, red phosphorus, nitrogen containing, silicone, and inorganic metal compounds (such as antimony trioxide used as synergist); hydrated minerals; and others are known as commercially available flame retardants.

2.4.1 Halogenated flame retardants

Halogenated flame retardants are used for purposes of reducing combustibility of polymer materials. There are three types of halogenated flame retardants that are called as derivatives of compounds with aliphatic, cycloaliphatic and aromatic structures. The nature of halogen atoms is varied in each type of structure. Reactive type of flame retardant (on account of the functional groups, they are able to become part of the polymer structure) and the nonreactive type (these do not react chemically with a molecule) are used as flame retardants. The effectiveness of flame retardation reactions using halogenated compounds with similar structures increases in the order [15]:



Halogenated flame retardants which are known as reactive type or nonreactive type added to or reacted with the base polymer. Reactive flame retardants become a part of the polymer either by becoming a part of the backbone or by grafting onto the backbone. The choice of a reactive flame retardant is more complicated than the choice of an additive type. Halogenated flame retardants vary in terms of thermal stability [15].

Halogenated flame retardants perform in the gas phase. However, halogenated flame retardants can be effective also in the condensed phase. Bromine is more effective than chlorine because its weaker bonding carbon enables it to interface at a more favourable point in the combustion process. HBr is the effective agent that is liberated over a narrow temperature range so that it is available at high concentration in the flaming zone. HCl is formed over a wider temperature range and so it is less effective.

Halogenated flame retardants perform by interfering with the radical mechanism taking place in the gas phase. The high-energy OH and H radicals formed by chain branching:



At first the halogenated flame retardant breaks down to;



where X is either Cl or Br. The halogen radical reacts to form the hydrogen halide;



which in turn interferes with the radical mechanism:



The high energy H $\cdot$ and OH $\cdot$ radicals are removed by reaction with HX and replaced with low-energy X radicals. HX produces the actual flame retardant effect. The hydrogen halide consumed is regenerated by reaction with hydrocarbon. HX performs as a catalyst.



Figure 2.8 and 2.9 indicate specific halogenated flame retardants that used in polymeric systems.

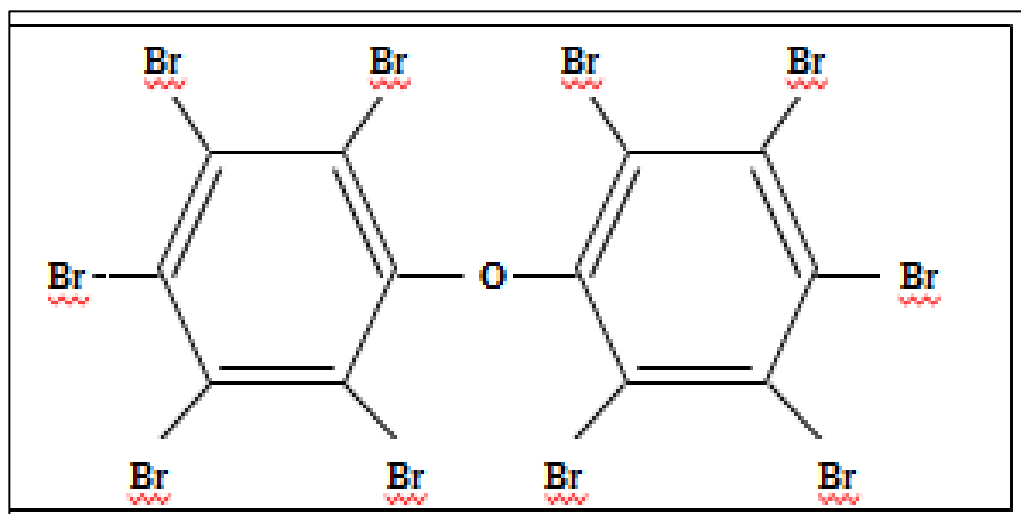


Figure 2.8 : Chemical structure of DECA [15].

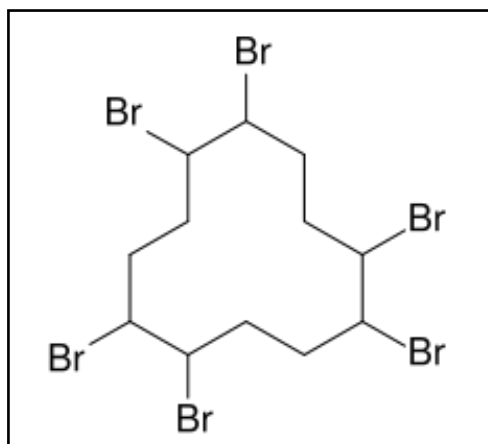


Figure 2.9 : Chemical structure of HBCD [15].

2.4.2 Antimony trioxide

Antimony trioxides (Sb_2O_3) have no effect on flame retardancy properties when they use alone. It is effective synergist for halogenated flame retardants. It performs as a catalyst and facilitates the breakdown of halogenated flame retardants to active molecules. It also reacts with the halogens to produce volatile antimony halogen compounds, which are themselves directly effective in removing the high energy H^+ and $\text{OH}^\cdot$ radicals which feed the flame phase of the fire, thus reinforcing the flame suppressing effect of the halogenated flame retardants [5].

Combination of antimony trioxide and halogenated flame retardant shows one of the most important synergistic flame retardant combinations. Synergism is very important factor to create a larger effect of combination of polymer additives than that expected from individual contribution [6].

2.4.3 Phosphorus flame retardants

Phosphorus-containing flame retardants perform in the condensed phase (including both and the solid phases, since various degrees of melting are involved at fire temperatures). The amount of carbonaceous residue or char formed by one or both two mechanisms is increased by phosphorus-containing compounds. There are two char forming mechanisms: redirection of the chemical reactions involved in decomposition in favor of reactions yielding carbon rather than carbon monoxide and carbon dioxide and formation of a surface layer of protective char [15].

Phosphorus flame retardants play important role in the production of low flammability polymeric materials. They are used widely for polymeric systems but they have not been completely studied in terms of polymer combustion process in all

stages. The generally mentioned action mechanisms of phosphorus flame retardants have not been confirmed by experiments [15].

The phosphorus flame retardants are used for some halogens. They may have synergistic effect in polymeric systems. In this way, environmental impact of halogens can be minimal with provided synergistic effect [23].

2.4.4 Melamine flame retardants

Melamine based flame retardants only find limited application in polymers, e.g. melamine in polyurethane and melamine cyanurate in polyamides. Melamine and derivatives are known as developed systems and used in intumescent systems [22].

Melamine cyanurate is mainly used in unfilled PA6 and 66 UL 94 V-0 grades and in thermoplastic polyurethane and high impact polystyrene (HIPS). Melamine based HALS products are used as flame retardants in polyolefins [4].

Melamine includes 67wt% nitrogen in the molecule with high thermal stability. Melamine also forms stable salts with strong acids. Melamine itself, melamine cyanurate, melamine phosphate, melamine pyrophosphate, and melamine polyphosphate are commercially available for various flame retardant applications. The mechanism of melamine salts is different from the mechanism of flame retardant action of melamine. Melamine phosphates contain phosphorus in the molecule so they have specific advantages.

Under normal conditions, melamine is used in flexible polyurethane combination with chloroalkyl phosphates and in intumescent coatings in combination with ammonium polyphosphate and pentaerythritol [24].

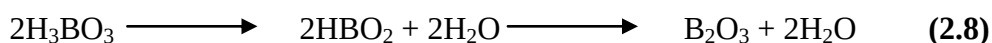
2.4.5 Silicon flame retardants

The use of relatively small amount of silicon compounds in the polymeric systems can improve their flame retardancy. They are known as environmentally friendly additives since their use leads to a reduction in the harmful impact on environment when compared with existing materials [23].

2.4.6 Boron flame retardants

Boron based flame retardants can be effective in the condensed phase, and in some cases, in the gas phase as well. The use of mixtures of boric acids and borax as flame

retardants for cellulose and zinc borate for PVC and some engineering plastics is a major application of borates. Boron based flame retardants perform by endothermic, stepwise release of water and formation of a glassy coating protecting the substrate. Boric acid shows dehydrating and charring action with oxygen-containing substrates. This action is similar to the polyphosphoric acid resulting from phosphate esters. The glassy coating and the pronounced tendency to char protect the substrate successfully against oxygen attack and heat [22]. Thermal decomposition mechanism of boric acid is given in Equation 2.8.



Boric acid and sodium borate are two of the oldest known flame retardants that are used primarily to flame-retard cellulose such as cotton and paper. They are effective in these applications and inexpensive. Because of their water solubility, the use of these borates is limited to products for which nondurable flame retardancy is acceptable.

Combination of antimony trioxide and zinc borate is used as flame retardant. Their use leads to development of flame retardancy properties of polymeric systems. The multifunctional zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) is very effective fire retardant synergist of halogens in polymers. In addition, zinc borate can be used as a flame retardant, smoke suppressant and afterglow suppressant. In contrast to ATH, zinc borate promotes char formation in burning polymer [25].

Zinc borate is useful synergist with both MDH and ATH. In polymer system, improved char and inorganic barrier formation is established. In addition, studies have confirmed the zinc borate enhancement of the action of ATH in polyolefins [26].

2.4.7 Metal hydrate flame retardants

Some inorganic compounds are useful for use as flame retardants in polymeric materials because such compounds can be effective in the range of decomposition temperatures of the plastic, mainly between 150 and 400°C. The most widely used inorganic flame retardants such as aluminium and magnesium hydroxide affect the combustion process via physical means. Nevertheless halogen containing flame retardants affect the combustion process chemically in the polymeric systems. In

addition, the effects of red phosphorus and ammonium polyphosphate are depended on both mode of action.

Unlike organic compounds, inorganic compounds do not evaporate under the influence of heat; rather they decompose, giving off non-flammable gases like water, carbon dioxide, sulphur dioxide, hydrogen chloride, mostly in endothermic reactions. They perform by diluting the mixture of flammable gases and by shielding the surface of the polymer against oxygen attack in the gas phase [22].

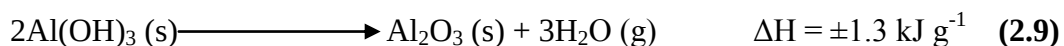
Inorganic hydroxides or mixed hydroxide inorganic salts that can be used as flame retardants in many types of polymers can release water upon heating above 200°C. ATH and MDH are two of the most commonly known inorganic flame retardants [20].

2.4.7.1 Aluminium trihydrate (ATH)

ATH has considerable potential as halogen-free flame retardant additive for polymers, together with a combined smoke suppressing capability. It can undergo an endothermic dehydration by releasing 34.6 wt% water in the temperature range 220-250°C. In addition, it is used in applications where high filler content is technically possible and processing temperatures do not exceed 180°C. It is low cost, environmentally acceptable and easy to incorporate into polymeric systems. ATH can be effective flame retardant and smoke suppressant at high loadings (typically 40 to 60% by weight). Filling levels must be higher than 60% weight to achieve suitable flame retardancy.

ATH is, by weight, the largest commercially manufactured flame retardants. It can use in wire and cable insulation and other elastomeric products, synthetic marble and synthetic onyx, latex for carpet back-coatings, phenolics, epoxies, and saturated polyesters.

ATH begins to decompose in the temperature range from 180 to 200°C. Aluminium oxide and water is decomposition products of ATH. ATH is formulated as $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The residue of aluminium builds up to create a protective barrier.



It has also been reported that the filler decomposition temperature will be increased when it surrounded by molten polymer. For example, ATH starts to decompose at

190°C, whereas, when water does not start to be lost until the temperature reaches 250°C in an ethylene-vinyl acetate copolymer (EVA) in a common cable industry formulation [27].

2.4.7.2 Magnesium hydroxide

Magnesium hydroxide performs as a flame retardant and smoke suppressant. Like alumina trihydrate, it functions by release of water vapour at elevated temperature, which absorbs heat and dilutes the combustible gases. Magnesium hydroxide (330-340°C) has the higher decomposition temperature than aluminium trihydrate (210-220°C) and magnesium hydroxide can be processed at higher temperatures than those using ATH. Again high loadings, desired levels of flame retardancy are achieved in the range 50-60 %.

MH is known as the second most widely used fire retardant filler. It is more expensive than ATH, but has a higher decomposition temperature (about 300°C). This property makes it more appropriate for use in thermoplastic applications where elevated processing temperatures are encountered [6].

MH can be used in plastics processed at higher temperatures than ATH, like polypropylene and engineering plastics. High loadings are necessary to increase fire performance requirements of plastics because it can heavily affect the plastic properties.



Especially, MH is used in certain wire and cable applications, in polypropylene and polyamides. For example, about 60-65% magnesium hydroxide in polypropylene is necessary to meet the UL 94 V0 test [22].

2.4.7.3 Huntite/Hydromagnesite (Ultracarb)

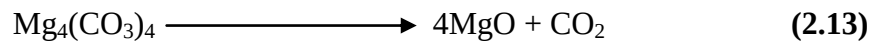
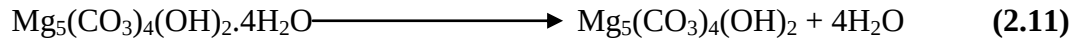
Ultracarb is a natural mineral that includes huntite and hydromagnesite mixtures. This is mined in Greece and Turkey and sold by Minelco Company. It is approximately equal mixture of huntite, $\text{Mg}_3\text{Ca}(\text{CO}_3)_4$ and hydromagnesite, $\text{Mg}_5(\text{CO}_3)(\text{OH})_2 \cdot 4\text{H}_2\text{O}$. Ultracarb is used as a flame retardant in wire and cable applications [7]. It can be alternative to ATH in PVC, halogen free, and rubber applications. It comprises of varying proportions of huntite and hydromagnesite. The

main focus of this thesis is huntite/hydromagnesite mixtures. They are incorporated into polymer system to enhance flame retardancy [28].

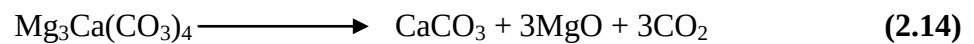
Hydromagnesite is known as basic magnesium carbonate, while huntite is mixed calcium magnesium carbonate. These materials which show a platy structure seem to occur together in fairly equal proportions [29].

Huntite and hydromagnesite minerals which have a similar history in terms of flame retardant applications as magnesium hydroxides combine high purity, naturally fine particle size, and reasonable costs. They are used either alone or in combination with other mineral flame retardants to create synergism. These two minerals are important for wire and cable applications. Especially, they ensure good properties and processing in a wide range of PVC compounds [8].

The decomposition of huntite and hydromagnesite has been discussed by various authors. Huntite particles have platy morphology, while hydromagnesite particles have a blocky morphology. Hydromagnesite has three decomposition stages between about 220°C and 550°C, releasing water and carbon dioxide leaving a magnesium oxide residue. Mechanisms show how hydromagnesite thermally decomposes. These three steps are associated with cumulative mass losses of 15.45%, 19.31% and 57.08%.



Huntite also decomposes via two step process; releasing carbon dioxide over a temperature range of approximately 450°C and 800°C. These two steps are associated with cumulative mass losses of 37.5% and 50.0% respectively. Decomposition steps of huntite are indicated at the following mechanisms.



Ultracarb is known as trade name of huntite/hydromagnesite mixture that gives off both water and carbon dioxide when heated, with a minor loss at about 230°C, and major losses at about 420 and 550°C, the endotherm being about 1000j/g and total

weight loss being about 53%. It may have cost advantage and provide approximately the same physical properties to a polyolefin as does ATH [30].

Huntite and hydromagnesite minerals are used in polymeric systems to improve flame retardancy properties. However, potential fire retardant fillers are suitable for polymers. These potential fillers are illustrated at Table 2.2.

Table 2.2 : Potential fire retardant fillers [9].

Potential Material(Common Names and Formula)	Onset of Decomposition (°C)	Volatile Content (%w/w)		
		Total	H ₂ O	CO ₂
Nesquehonite (MgCO ₃ .3H ₂ O)	70-100	71	39	32
Alumina trihydrate (Al(OH) ₃)	180-200	34.5	34.5	0
Basic magnesium carbonate, hydromagnesite (4MgCO ₃ .Mg(OH) ₂ .4H ₂ O)	220-240	57	19	38
Sodium dawsonite (NaAl(OH) ₂ CO ₃)	240-260	43	12.5	30.5
Magnesium hydroxide (Mg(OH) ₂)	300-320	31	31	0
Calcium hydroxide Ca(OH) ₂	430-450	24	24	0
Boehmite AlO(OH)	340-350	15	15	0
Magnesium phosphate octahydrate Mg ₃ (PO ₄) ₂ .8H ₂ O	140-150	35.5	35.5	0
Calcium sulphate dehydrate, gypsum (CaSO ₄ .2H ₂ O)	60-130	21	21	0

2.4.8 Intumescent flame retardants

Intumescent flame retardants have been improved as alternatives for the halogenated flame retardants. Because these flame retardants, upon heating, promote the formation of char which provides insulation from heat and oxidative degradation. An intumescent flame retardant has been improved which can be incorporated in a thermoplastic prior to molding. Phosphoric acid, phosphorus oxide, pentaerythritol and melamine are used for intumescent system [31].

Ammonium polyphosphate (APP), pentaerythritol (PER) and melamine system is well known intumescent flame retardant, which was first used in fire retardant intumescent coatings. It is mainly combined of inorganic acid sources (e.g. ammonium polyphosphate, etc.), carbonifics (e.g. pentaerythritol, sorbitol, etc.) and spumifics (e.g. melamine, etc.). This system is used in thermoplastics to provide lower flame retardant efficiency, lower thermal stability and lower water resistance compared with halogenated flame retardants [32].

2.5 Flammability Tests

Flammability tests are very important to determine flammability properties of polymeric materials. They are conducted by standards which are known as ASTM, ISO etc. Table 2.3 shows standards for flammability tests.

Table 2.3 : Flammability standards and testing.

Test Methods	Flammability Test Standards
1) Glow Wire Test	*ASTM D6194-10 Standard test method for glow-wire ignition of materials.
2) UL 94 Test	*ASTM D635-10 Standard test method for rate of burning and/or extent and time of burning of plastics in a horizontal position. *ASTM D3801-10 Standard test method for measuring the comparative burning characteristics of solid plastics in a vertical position.
3) Limiting Oxygen Index	*ASTM D2863-10 Standard test method for measuring the minimum oxygen concentration to support candle-like combustion of plastics (Oxygen index)
4) Cone Calorimeter Test	*ASTM E1354-11 Standard test method for heat and visible smoke release rates for materials and products using an oxygen consumption calorimeter. *ISO 5660-1 Reaction-to-fire tests- heat release smoke production and mass loss rate- Part 1: heat release rate (cone calorimeter method) *ISO 5660-2 Reaction-to-fire tests- heat release smoke production and mass loss rate- Part 2: Smoke production rate.

2.5.1 Limiting oxygen index (LOI)

The ignition and flammability of ignitable polymeric materials was stated for many years using a variety of small scale tests, many of which involved burners. The limiting oxygen index test was improved in the 1960s. This test is also known as the ‘Critical Oxygen Index’ test. The minimum percentage of oxygen in the test atmosphere needed to support ignition and flaming combustion of the test material is measured by the limiting oxygen index test [33].

ASTM D2863-97 or BS ISO 4589-2 is used to determine oxygen index. The specimen size and shape is not as strictly specified as in the UL 94 test, but usually bars of about 100x65x3 mm are used in testing of rigid plastics. The specimen is replaced in a candle-like fashion vertically at the axis of a glass chimney and clamped at the bottom. A controlled mixture of nitrogen and oxygen feed to the chimney. The flame is applied to the top of the specimen until entire top surface is ignited. If the specimen does not ignite in less than 30s, the concentration of oxygen is then enhanced, in steps with repeated trial ignitions, until the specimen represents stable candle-like combustion for more than 3 min after removal the ignition source. By iteration of these steps, limiting oxygen index is determined [30]. Table 2.4 lists the limiting oxygen index values for some commercial different plastics.

Table 2.4 : LOI values of different plastics [30].

Plastic	LOI, % Value
ABS	18.0-39.0
HDPE (non FR)	16.0-18.0
HDPE (with FR)	26.0-27.0
LDPE (non FR)	16.0-18.0
LDPE (with FR)	26.0-27.0
Nylon-6	31.8
Polypropylene(PP)	17.5-18.0
Polystyrene	18.3-19.0
PVC (rigid)	21.6

2.5.2 Glow wire test

In Europe, the flammability of polymeric materials is commonly tested by glow wire test which is defined IEC 60695-2-10/13. The glow wire test (GWT) uses a heated hairpin-configuration resistance wire which is pressed, using a sliding rig, against the specimen for 30 seconds and then pulled back. The specimen is replaced to test apparatus. The glow wire temperature is measured at which the specimen either ignites on contact or in 30 seconds after withdrawal and it is also noted whether burning droplets ignite a paper placed below the specimen [30].

The specimen is presumed to have passed the glow wire test if one of the following occurs:

- If there is no flame and no glowing;
- If flames or glowing of the specimen, of the surrounding and of the layer below, extinguish within 30 seconds after removal of the glow wire and the surrounding parts and the layer below have not burned away completely [34].

In addition, the glow wire ignition temperature (GWIT) is also known as wire temperature where the specimen ignites with a flame of 5 seconds duration or more. The glow wire flammability index (GWFI) is the temperature at which the flames burn for less than 30 seconds [30].

2.5.3 UL 94 flammability test

UL 94 flammability test is known as Underwriters Laboratory test that is one of the most important UL standards relating to fire safety test methods and requirements and contains several tests [4].

This test is also depicted in ASTM D3801-10 that is used to measure and describe the response of materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions [35].

The UL 94 test provides an assessment of flammability for a variety of thermoplastic materials. It is the most widely accepted flammability performance test for plastic materials. The UL 94 test actually comprises several test methods which are known as vertical and horizontal burning tests. The vertical burn method is the most common method where a test specimen (a bar of 13 mm by 125 mm by varying

thickness) is ignited while suspended 10 mm above a calibrated methane (Bunsen) burner. Five test specimens are prepared to apply flame twice for 10 seconds. The amount of burn time is recorded to classify test specimens. The flammability performance is described through one of three ratings, V0, V1 or V2 dependent on the number of seconds of after-flame burn time for each specimen, the total after flame burn time for all specimens, the afterglow time [36]. Figure 2.10 shows the basic vertical test apparatus. Horizontal test apparatus is given in Figure 2.11.

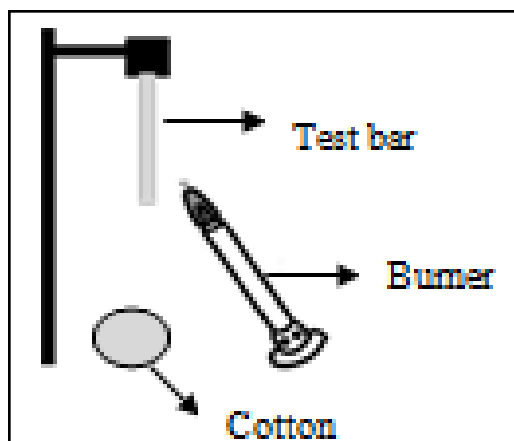


Figure 2.10 : UL 94 vertical test apparatus [36].

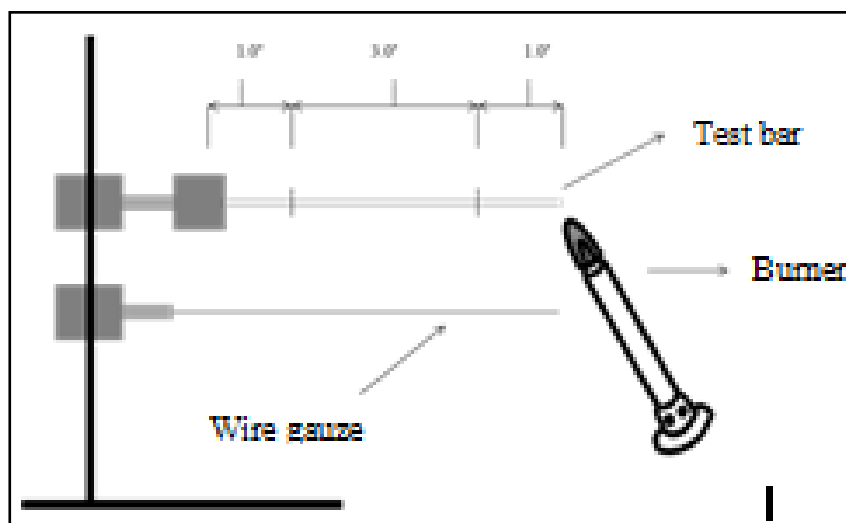


Figure 2.11 : UL 94 horizontal test apparatus [36].

2.5.4 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis is important and useful in the analysis of compounded plastic samples and involves continuous weighing of a small sample in a controlled atmosphere as the temperature is increased at a programmed linear rate. In addition, TGA is very simple technique to analysis the filler content of a polymer compound.

This test helps to obtain accurate quantifications of the principal compound constituents such as plasticizer, polymer and organic species. By the use of the temperature maxima at which weight events occur it is also possible to use the technique to obtain some qualitative assignments for the plasticizer and polymer and the weight loss of a material is measured as a function of its temperatures [37].

2.5.5 Cone calorimeter test

The cone calorimeter is one of the most important and effective tests to evaluate the flammability properties of polymeric materials. Under forced flaming conditions, sample plates 100x100 mm in size are investigated in this method. Several important parameters which include time to ignition, heat release rate, peak heat release rate, total heat release, mass loss rate, and specific extinction area (SEA) can be obtained from cone calorimeter test. Peak heat release rate is known to be the most important criteria to describe flammability properties of natural and synthetic polymeric materials. Other data such as smoke release and CO production can be obtained from this test to evaluate fire hazard of polymeric materials. This test is described in ISO 5660 standard to determine the use of the cone calorimeter test as shown in Figure 2.12. [38].

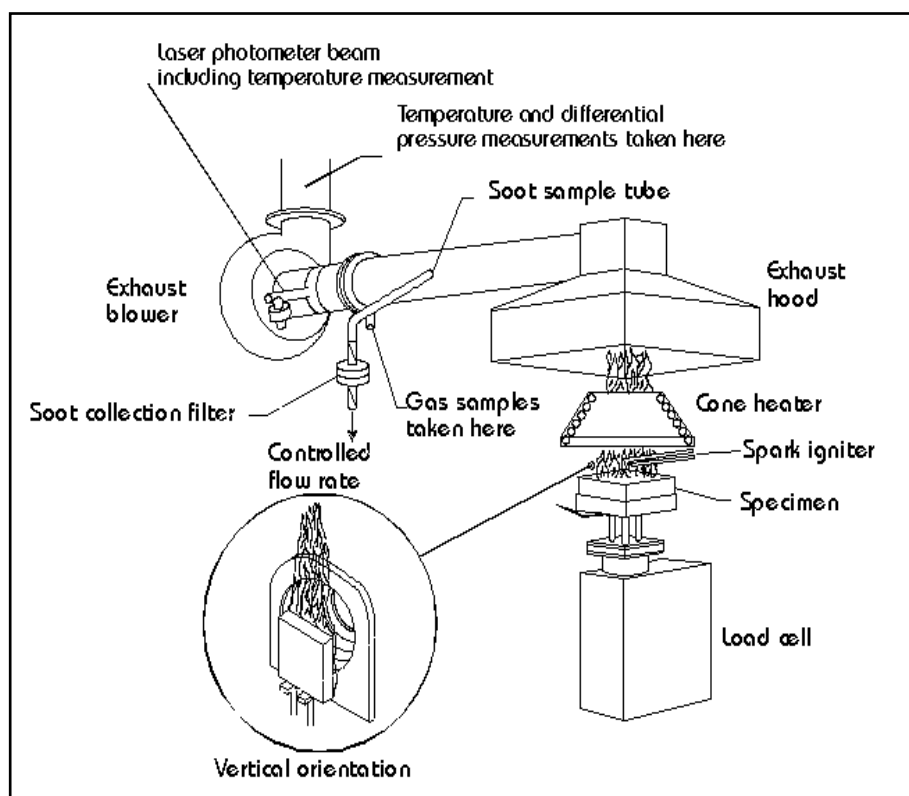


Figure 2.12 : Cone calorimeter test [38].

2.6 Literature Overview of Huntite/Hydromagnesite Minerals

In this section, literature overview about flame retardant systems and huntite/hydromagnesite minerals is stated. The use of polyolefines, especially polypropylene in automotive, construction, and other industries is limited by its high combustibility. To improve flame retardancy performance of polypropylene is badly needed in numerous applications.

Marosfoi and co-workers investigated fire retardancy behavior of polypropylene-magnesium hydroxide-clay composites of different morphologies. They reported that combination of montmorillonite and sepiolite type of clays resulted in the increased time to ignition, and markedly decreased heat release rate. In addition, they said that nanofillers-nanofillers interaction played important role in fire retardant mechanism of polypropylene [39].

Green published an overview on the past, present and future of fire retardant chemicals and usage in industry. Fire retardants such as bromine and chlorine compounds, non halogen and halogenated phosphates and antimony oxides were evaluated in terms of marketing concepts and specialty. He reported that ATH was the largest growing flame retardant, with about a 5% growth per year [40].

Shen and their colleagues reports that zinc borates can be used as flame retardant, smoke suppressant, afterglow suppressant, and anti-tracking agent in both halogenated and halogen-free polymers. Zinc borates have synergistic effect when used with halogen sources. They go to say that zinc borates are multifunctional flame retardants in halogen free polymers [41].

Liang and Zhang stated that aluminium hydroxide and magnesium hydroxide were used as a flame retardant in PP which used as the matrix resin. In addition, zinc borate was used as a flame-retardant synergist. Fire retardancy properties were evaluated in terms of oxygen index, burning velocity and smoke density. Their results indicated that oxygen index increased with an increase of the filler content. The burning velocity and smoke density decreased with increase of the filler content [42].

Wu and Shu investigated the influence of zinc borate mechanism on intumescent flame retardancy system. They reported that zinc borates were used anti-dripping agent and smoke suppressant in intumescent system with LDPE [43].

Chiu and Wang investigated the flammability properties of an intumescent fire retardant polypropylene added with magnesium hydroxide. The results showed that the intumescent flame retardant ammonium polyphosphate-filled polypropylene had superior flammability properties but higher carbon dioxide (CO) concentration and smoke density. By adding some magnesium hydroxide additives in intumescent fire retarded polypropylene, the smoke density and CO concentration decrease. They reported that intumescent system and magnesium hydroxide additives are effective on improving combustion properties for polypropylene [44].

Almeras and their colleagues investigated intumescent process with addition of ammonium polyphosphate/Polyamide-6 system in many polymers blends. Combination of fillers in PP can modify the properties of the polymeric matrix. They also investigated that the effect of fillers (talc and calcium carbonate) on the fire performance of the polypropylene/ammonium polyphosphate/Polyamide-6 blend. Talc increases and calcium carbonate decreases in the fire performance of the blend [45].

Kirschbaum reports that huntite is not very effective flame retardant on its own because of its high decomposition temperature, over 400°C. In addition, he says that mixture of huntite and hydromagnesite has effective fire retardant performance to metal hydroxides such as ATH in EVA [46].

Georgiades stated that combination of huntite and hydromagnesite minerals containing less than 40 % of hydromagnesite attempted to accomplish a UL 94 rating at acceptable loading levels in polypropylene and EVA. Blends of the minerals containing between 10% and %67 hydromagnesite indicated that there was no important difference in the flame retardant effect once the hydromagnesite content exceeded 42%. He continues to say that a 50/50 mixture of huntite and hydromagnesite minerals containing higher proportion of huntite are important and effective smoke suppressant for polymeric systems [47].

Clemens detailed the effect of the ratio of huntite and hydromagnesite minerals. His work was carried out using polypropylene. The work showed that hydromagnesite represented significantly greater flame retardant performance than the huntite. Fire retardancy was investigated in terms of UL 94 and LOI. He also reported that a higher proportion of huntite improved impact properties of polypropylene [48].

Rigolo conducted his work using polypropylene and suggested some comparisons between a synthetic magnesium carbonate hydroxide pentahydrate (MCHP) and commonly used mineral based flame retardants ATH and magnesium hydroxide. Rigolo asserted that MCHP was more effective than magnesium hydroxide in terms of LOI and UL 94 test [49].

Haurie stated that a 2 wt% coating of stearic acid on synthetic hydromagnesite enhanced oxygen index to 32.9% compared to 24.5% for uncoated sample in EVA. It is also reported that the increased loading level enhanced oxygen index value and presence of stearic acid improved tensile strength and elongation at break [50].

Morgan investigated effectiveness of various magnesium carbonate based flame retardants including mixture of natural huntite and hydromagnesite, synthetic hydromagnesite, magnesium carbonate, calcium carbonate and magnesium hydroxide in terms of peak heat release rates. He also reported that magnesium hydroxide and synthetic hydromagnesite showed equal performance to reduce peak heat release rates. Combination of natural hydromagnesite and an unknown quantity of huntite has positive effective of reducing the peak heat release rate, at the cost of reducing the time to ignition, when compared to synthetic hydromagnesite [51].

Inglethorpe details that huntite has useful effect and properties in terms of flame retardancy. It is also reported that small particle size of huntite may improve the flame retardant properties of mineral when compared to big particle size of hydromagnesite [52].

Toure has published that blends of huntite and hydromagnesite minerals have positive efficiency at high loading levels. In addition, he also investigated fire retardancy properties of huntite and hydromagnesite minerals in halogenated formulations (antimony trioxide/decabromodiphenyl oxide filled PP-PE copolymer). Their endothermic decomposition mechanism is very effective to reduce heat transfer to substrate [53].

Hollingberry and Hull make brief about decomposition temperatures of huntite and hydromagnesite minerals. Huntite and hydromagnesite minerals are known as natural blends. They state that huntite has platy structure. Hydromagnesite begins to decompose at 220°C and have three decomposition steps while huntite begins to decompose at 450°C and two decomposition steps. During decomposition reactions

approximately 54% of the mass of the huntite and hydromagnesite mixture is released as water and carbon dioxide. The metal oxide residue performs as a physical and thermal barrier to further decomposition of the underlying polymer [54].

Yılmaz and Çelik have investigated particle size of huntite and hydromagnesite minerals and increasing the mineral content of a polymer composite (EVA). They state that huntite and hydromagnesite have advantages such as noncorrosiveness, low smoke production, low combustion, and recyclability and decreasing the particle size of the minerals improves protection against fire [55].

Haurie investigated flame behaviour of natural synthetic hydromagnesite in LDPE/EVA blend. It was also compared to natural blends of huntite and hydromagnesite minerals. In conclusion, he reported that the synthetic hydromagnesite indicated an effective flame retardant performance with an increase of the time to ignition as well as the LOI value in comparison with mineral hydromagnesite-huntite filled samples and magnesium hydroxide [56].

Hongchang Han and their colleagues searched suitable surface modifiers for synthetic hydromagnesite. Zinc stearate (ZS) and stearic acid were chosen as the surface modifier and investigated the properties of synthetic hydromagnesite with different surface modifier content. They stated that 2 wt% coating of stearic acid on synthetic hydromagnesite was suitable for applications [57].

Kangal and Güney searched separation conditions for huntite from associated mineral. And also, the influence of modifying reagents like sodium silicate and carboxymethyl cellulose on surface properties of huntite were investigated. In conclusion, they reported that huntite concentrates were produced with 97-98% huntite contents and 76-86% recoveries [58].

3. EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene

Polypropylene (PP) was used as a main polymer matrix, grade HJ325MO from Borouge, Austria with the melt flow index of 50 g/10 min (MFI; 230°C/ 2.16 kg) and density 0.910 g/cm³.

3.1.2 Huntite/Hydromagnesite (Ultracarb)

All the samples of natural huntite/hydromagnesite (H/HM), which were used to improve flame retardancy properties of PP, were supplied by Minelco with trade name Ultracarb. Their deposits are located in south western Turkey. The different types of grades comprise of varying proportions of huntite and hydromagnesite. Hybercarb 2090 (H2090) consists of huntite (a platy magnesium calcium carbonate) and hydromagnesite (hydrated magnesium carbonate) with the higher huntite content. It is not surface treated. LH 15 consists of huntite and hydromagnesite. This grade contains mainly hydromagnesite but does still contains a proportion of huntite. Ultracarb 1250 (U1250) and Ultracarb 1253 (U1253) contain huntite and hydromagnesite with higher huntite content. Table 3.1 shows the commercial grades and percentage of huntite and hydromagnesite minerals in the natural mixtures used in this study according to XRD results. They were characterized with XRD to determine their contents. Particle sizes of the two minerals range from 2.5 to 23 µm. Particle size distribution of mixtures are given in Table 3.2.

Table 3.1 : Percentage of huntite and hydromagnesite in the natural mixtures according to XRD results.

Commercial name	Huntite content (%)	Hydromagnesite content (%)
Ultracarb 1250 (U1250)	65-70	30-35
Ultracarb 1253 (U1253)	65-70	30-35
Hybercarb 2090 (H2090)	75-80	20-25
LH15	40-45	55-60

Table 3.2 : Particle size distribution profile of mixtures.

Particle size (microns)	U1250	U1253	LH 15	H2090
d ₉₈	18	16.5	16.5	23
d ₅₀	2.5	3	3	2.5

3.1.3 Zinc Borate

Commercial zinc borate was supplied by MELOS A.S. to increase flame retardancy properties of PP with LH 15. Zinc borate is an inorganic compound, a borate of zinc. It is a white crystalline or amorphous powder insoluble in water. Zinc borate is primarily used as a flame retardant in plastics. Particle size of zinc borate powders range from 5 to 45 μm .

3.2 Equipment

3.2.1 Twin-screw extruder

In this study, in order to form well mixed compound intermeshing, co-rotating twin-screw extruder was used; PRISM TSE24 IIC, with the screw diameter 24mm and L/D ratio 28:1 (shaft length/screw diameter) at Arcelik's laboratory.

Two Brabender DSR28 gravimetric feeders, degassing port connected to the Edwards rotary vacuum pump by hoses, water bath and fixed length pelletizer or chopper are known as equipments of PRISM TSE24 extruder. It has seven modular barrel segments with length of 96 mm or 4D. The barrel can be separated in the middle easy screw removal and cleaning purpose. Figure 3.1 indicates the seven modular barrel and twin screw of extruder. Electrical resistances and water cooling channels controlled by thermoregulator which are connected to each modular barrel zone to ensure play important role to control the set temperature. Thermocouples are brought together at the 3rd, 5th, and 7th zone of barrel up to the internal surface to melt temperature of polymeric materials. Inlet zone is defined as the first barrel that is cooled down to prevent the messing up of the polymers through the walls of barrel and screw. Polymeric materials melt in the barrels by effect of heat and pressure. The gases occurred during compounding are removed and one degassing unit is connected to the Edwards rotary vacuum pump by hoses at the 6th barrel zone. Die takes place with a three-strand hole at the forward end of the extruder [59,60]. Details of PRISM TSE24 extruder are given in Table 3.3.



Figure 3.1 : PRISM TSE24 IIC Twin-screw extruder.

Table 3.3 : PRISM TSE24 Twin screw extruder data sheet.

	Units	PRISM TSE24
Screw diameter	mm	24
Typical output	kg/h	2 to 50
Maximum screw speed	rpm	1000
L/D (shaft length/screw diameter)	-	28:1
Channel depth	mm	5.15
Screw diameter/channel depth	-	5.15
Screw/barrel clearance	mm	0.2
Shaft center line distance	mm	18.75
Shaft center line/radius ratio	-	1.5625
Total area	cm ²	8.5
Screw area	cm ²	4.7
Free area	cm ²	3.8
Total volume	cm ³	511
Free volume	cm ³	228
Barrel peripheral surface area	cm ²	830
Surface area/total volume	m ² /liter	0.14
Surface area/Free volume	m ² /liter	0.31
Max. channel shear rate @ 1000 rpm	s ⁻¹	244
Max. power	kW	9
Max. torque/shaft	Nm	43

The polymer melt can go out of the extruder. It can be cooled down into a water bath and obtained as spaghettis that are cut into small pieces called granules by the fixed length pelletizer or chopper. This system is also known as the classical way of spaghettis pelletizing. Figure 3.2 shows Prism granulating unit.



Figure 3.2 : Prism granulating unit.

Two K-ton gravimetric feeders and one Brabender side feeder are ready for use in the extruder as shown in Figure 3.3. They can be controlled by K-Tron computer interfaced software and Prism own controller system. Gravimetric feeders are calibrated according to its manual handbooks before each production process.

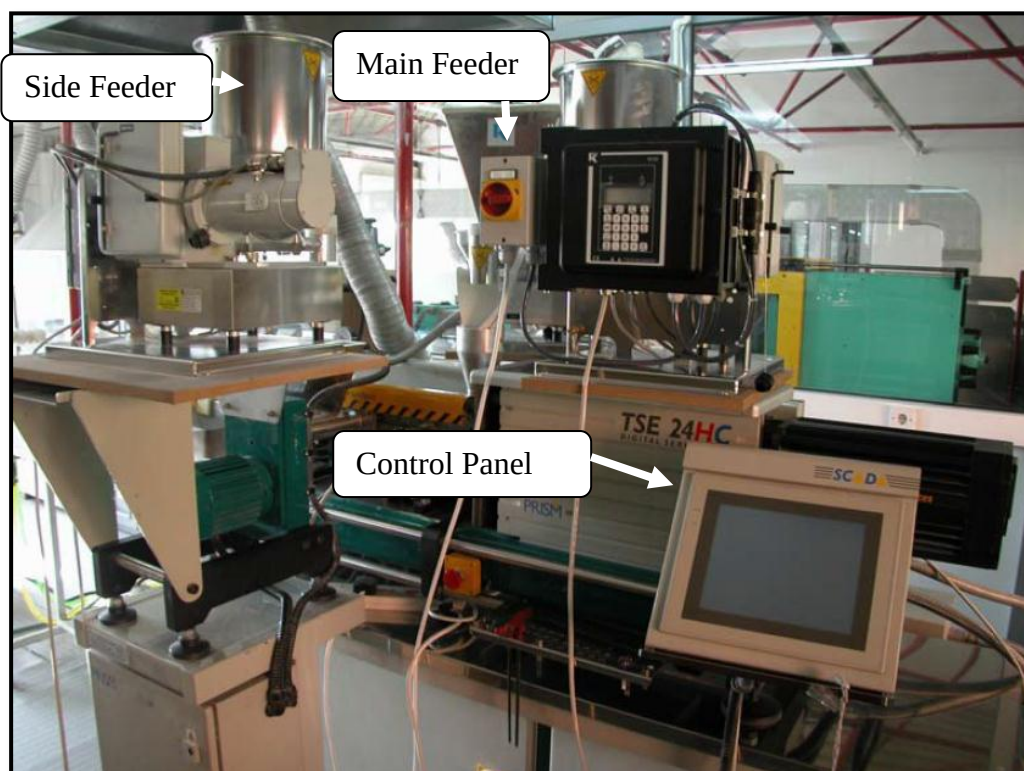


Figure 3.3 : PRISM TSE24 IIC Twin-screw extruder with gravimetric feeder.

3.2.1.1 Screw configuration

The extruder screw profile was configured to accomplish good melting and mixing of polymers by high shear, high residence time in the reaction zones, and venting close to the outlet of the extruder. The screws of the extruder were designed to be six zones;

- raw material intake and solid conveying zone
- plasticizing zone (first kneading block)
- melt conveying zone
- further homogenization zone (second kneading block)
- degassing zone
- pressure built up zone

3.2.2 Injection molding machine

Arburg Allrounder 320C injection machine was used to produce specimens according to ISO standards as shown in Figure 3.4. Injection unit consists hopper, heat controlled barrels-cylinder, screw and motor [59,60]. Technical specifications of the Arburg injection machine are given in the Table 3.4.

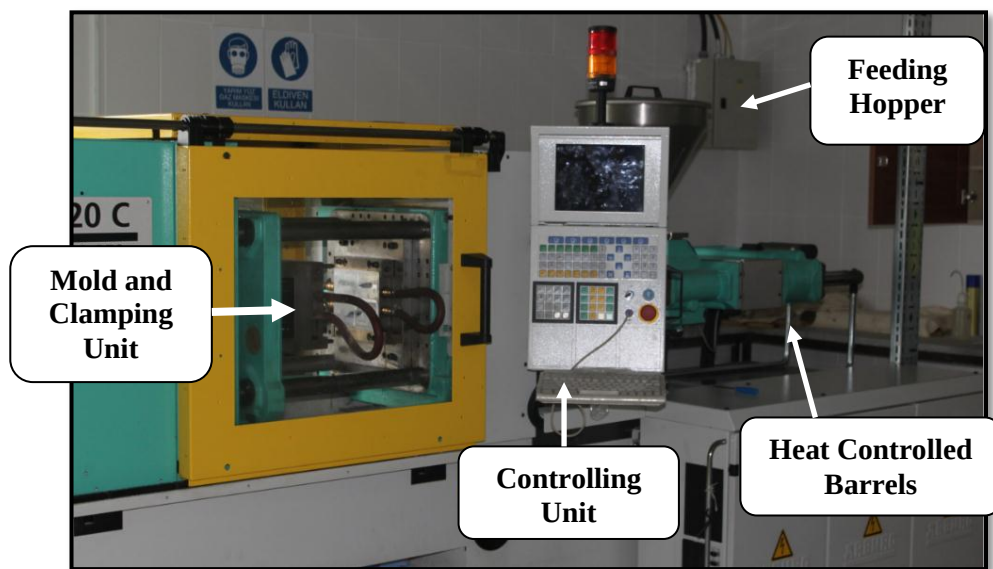


Figure 3.4 : Arburg Allrounder 320C injection machine.

Table 3.4 : Specifications of Arburg Allrounder 320C injection machine.

	Unit	
Screw diameter	mm	30
Max. injection pressure	bar	1068
Max. volumetric displacement	cm ³	71.4
Wax. Shot weight	g	70
Hydraulic motor power	W	1800
Max. clamping force	tonnes	30
Max. screw speed	rpm	115
Screw back pressure	bar	25

3.2.3 Pyknometer

The density of specimens was measured with AccuPyc 1330 Pyknometer as shown in Figure 3.5.



Figure 3.5 : Pyknometer illustration.

3.2.4 Fourier transform infrared (FTIR)

FTIR (The Excalibur FTS 3000 MX spectrometer) spectrums of polypropylene composites was recorded to determine the organic components in the samples. FTIR spectrometer is shown in Figure 3.6.



Figure 3.6 : FTIR spectrometer.

3.2.5 X-ray diffraction (XRD)

XRD analysis of mixtures of H/HM was performed using X'Pert PRO X-ray diffractometer as shown in Figure 3.7.



Figure 3.7 : X-ray diffraction instrument.

3.2.6 Melt flow index machine

The flow behavior of molten polymer is defined as an important factor affecting the processability of polymers. Melt flow index (MFI) or melt flow rate (MFR) is described by flow properties of the molten polymers and is measured by using Zwick 4106 testing machine as shown in Figure 3.8. This test is applied at a fixed temperature and under load that is predefined according to the polymer type. The testing device is equipped with heating cylinder, temperature control equipment, piston, die, and loading unit. The die, which is located at the bottom of heating cylinder and applied onto the piston, can move downward within the cylinder. It has a diameter of 2.095 ± 0.005 mm.

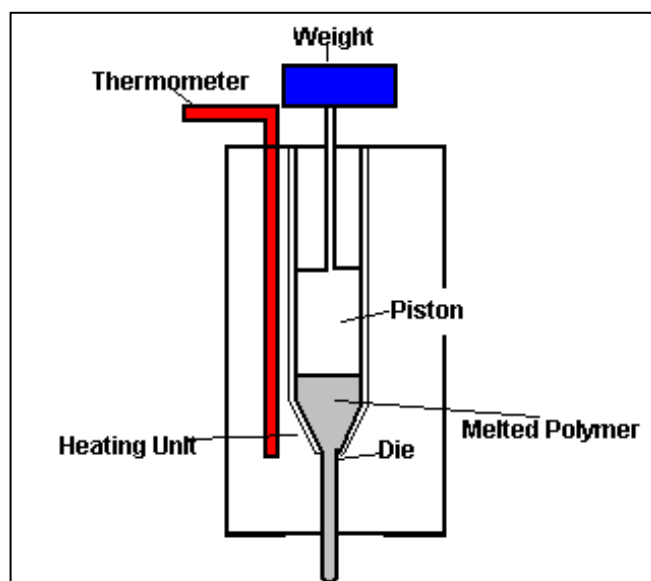


Figure 3.8 : Melt flow test illustration [59].

3.2.7 Scanning Electron Microscopy (SEM)

Investigation of the morphology of polypropylene composites was done by a scanning electron microscope (Jeol JSM 6400) as shown in Figure 3.9.



Figure 3.9 : Jeol JSM 6400 SEM instrument.

3.2.8 Mechanical test machine

Tensile properties of specimens were measured by using Zwick universal tensile testing machine Z020 equipped with 20 kN load cell as load indicator and long stroke extensometer as extension indicator. Testing speed was set to 50 mm/min and gauge length (L_0) was set to 70 mm. Tensile test sample is indicated in Figure 3.10.

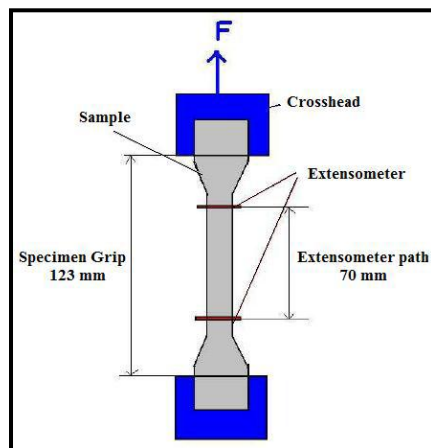


Figure 3.10 : Tensile test sample [59].

3.2.9 Three point bending test machine

Flexural properties of polypropylene composites were investigated by using Instron 4505 universal testing machine equipped with 10 KN load cell as load indicator and three point bending fixture. Three point bending test machine was used to determine

flexural properties of polypropylene composites. Three point bending test is illustrated in Figure 3.11.

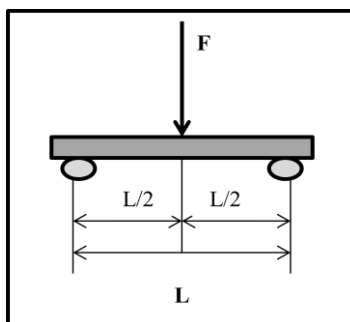


Figure 3.11 : Three point bending testing illustration [59].

3.2.10 Izod impact test machine

Izod impact strength of specimens was measured by using Zwick/Roell Izod impact machine as shown in Figure 3.12.



Figure 3.12 : Izod impact testing machine.

3.2.11 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) of polypropylene composites were carried out by using Q500 thermal gravimetric analyzer as indicated in Figure 3.13.



Figure 3.13 : Thermal gravimetric analyzer.

3.2.12 Vicat softening point testing machine

Vicat softening temperature of compounds was measured using The Instron HDT&Vicat machine as shown in Figure 3.14.



Figure 3.14 : Vicat softening point testing machine.

3.2.13 Limiting oxygen index (LOI) flammability tester

This test was carried out by using limiting oxygen index test apparatus (Fire Testing Technology) equipped with test chimney, specimen holders, gas measurement and control devices, flame igniter, timing device, fume extraction system, and gas supplies as shown in Figure 3.15.



Figure 3.15 : Limiting oxygen index tester.

3.2.14 Glow wire tester

Glow wire test was carried out by using PTL Glow – wire test apparatus to determine the fire resistance. This test method measures and describes the response or materials, products, or assemblies to heat and flame under controlled conditions, but does not by itself incorporate all factors required for fire hazard or fire risk assessment of the materials, products, or assemblies under actual fire conditions.

PTL Glow wire test apparatus is equipped with glow wire, thermocouple, temperature indicator, supply circuit, test fixture, indicator board and test chamber as shown in Figure 3.16.

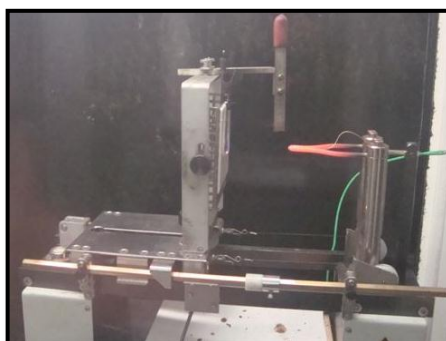


Figure 3.16 : Glow wire tester.

3.2.15 UL 94 horizontal flammability tester

Rate of burning and time of burning of self supporting plastics in a horizontal position were measured by using CEAAT flammability tester as shown in Figure 3.17. This test method was developed for polymeric materials used for parts in devices and appliances. The CEAAT flammability tester is equipped with test chamber, test fixture, laboratory burner, gas supply, wire gauze, timing device and flexible specimen support fixture.



Figure 3.17 : UL 94 horizontal tester.

3.3 Experimental Procedure

3.3.1 Compounding recipes

Formulations of compounds, containing polypropylene (PP) and mixtures of huntite and hydromagnesite (H/HM) (4 different grades; U1250, U1253, H2090, and LH15) were processed using co-rotating twin-screw extruder. Polypropylene composites

were prepared with varying the H/HM percentages (30, 40, 50, and 60 wt.%) in the formulation given below in Table 3.5. The effects of H to HM weight ratio in the H/HM grades and H/HM loading level on the flame retardancy performance and mechanical properties of composites were investigated. LH 15 and Zinc Borate were used together to increase flame retardancy properties of PP at 60 wt% loading level. Zinc borate were added to LH 15 to determine synergistic effect in polymeric composite.

Table 3.5 : Formulations containing huntite and hydromagnesite produced in extrusion process.

Samples	PP (weight per cent)	U1250 (weight per cent)	U1253 (weight per cent)	H2090 (weight per cent)	LH15 (weight per cent)	ZnB (weight per cent)
PP	100	-	-	-	-	-
PP+U1250	70	30	-	-	-	-
	60	40	-	-	-	-
	50	50	-	-	-	-
	40	60	-	-	-	-
PP+U1253	70	-	30	-	-	-
	60	-	40	-	-	-
	50	-	50	-	-	-
	40	-	60	-	-	-
PP+H2090	70	-	-	30	-	-
	60	-	-	40	-	-
	50	-	-	50	-	-
	40	-	-	60	-	-
PP+LH15	70	-	-	-	30	-
	60	-	-	-	40	-
	50	-	-	-	50	-
	40	-	-	-	60	-
PP+LH15+ZnB	40	-	-	-	50	10

3.3.2 Compounding procedure and compounding process parameters

The homopolymer PP was fed into extruder from inlet zone with using first feeder. The mixtures of H/HM (U1253 or U1250 or H2090 or LH15 or LH15+ZnB) were separately fed into extruder from second (side feeder) and third feeders. Second feeder is also known as side feeder and located at the side of extruder. Third feeder is described as gravimetric feeder. The feeders were calibrated to obtain weight percent metering. The compounded materials were taken from the extruder via the holes of the die and cooled down in water bath and the pelletized by pelletizer. The properties of final product are affected process parameters that are known as temperature, screw

Tensile, flexural, Izod impact, UL 94 and LOI test specimens were produced with Arburg Allrounder 320C injection machine according to ISO standards. General process parameters and injection molding machine illustration are given in Figure 3.19.

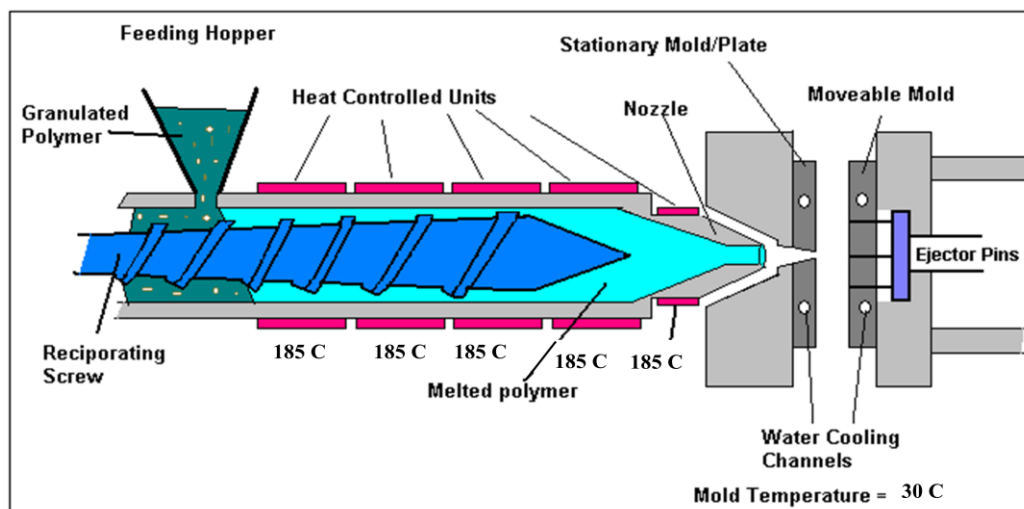


Figure 3.19 : General process parameters and illustration of injection molding machine [60].

Mold temperature during the injection process was kept constant as 30°C with a water cooling chiller; Piovan ST092. Molds of the injection molding machine are given in Figures 3.20 and 3.21.



Figure 3.20 : Injection molds of tensile specimens according to the ISO R 527[61].

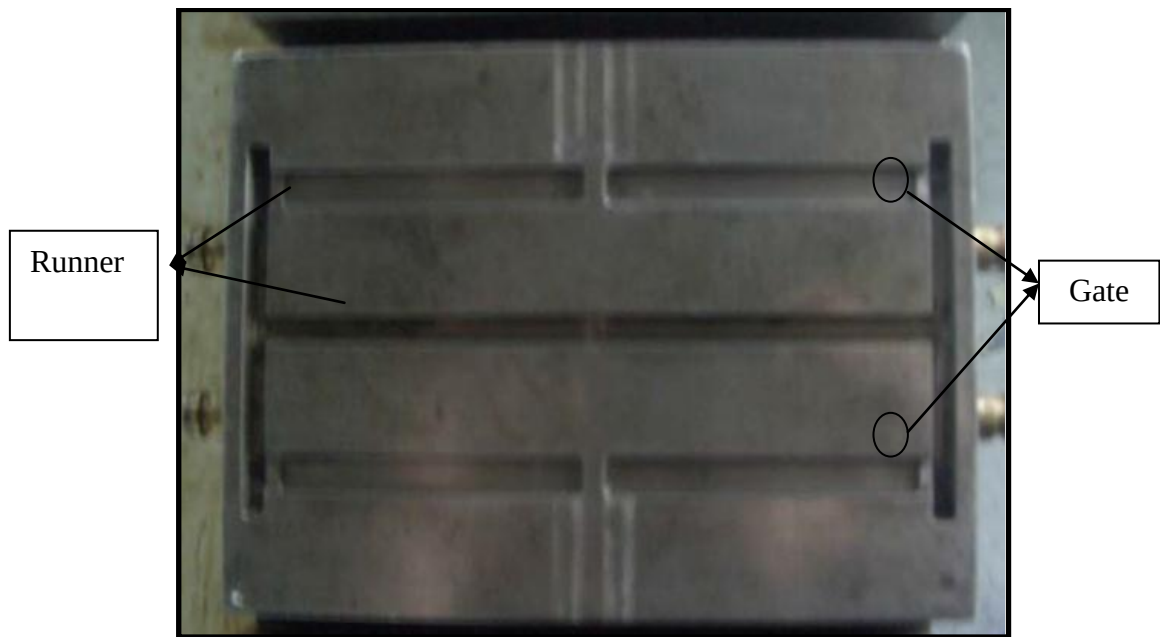


Figure 3.21 : Injection molds of flexural and impact specimens according to the ISO 178 [62].

3.4 Characterization

3.4.1 Structural and morphological properties

3.4.1.1 Measurement of density

The density of specimens was determined according to the procedure explained in ISO 1183 [63]. This method is also known as Pyknometer method. The specimen was weighed in the air first and then placed in the AccuPyc 1330 Pyknometer. The volume of specimens was calculated using this machine by first vacuuming the air in the measuring vessel and then filling up the vessel with nitrogen (N_2).

3.4.1.2 Fourier transform infrared (FTIR) analysis

FTIR analysis was performed over the range of 400 to 4000 cm^{-1} at room conditions. Samples were prepared to determine the organic components in the samples. Higher hydromagnesite content (LH15; 55-60%) sample and LH15 filled PP composites at 60% loading levels were characterized by FTIR.

3.4.1.3 X-ray diffraction (XRD) analysis

XRD technique was used for structural analyses of the mixtures of H/HM. The ratios of huntite and hydromagnesite in the mixtures (4 different grades; U1250, U1253,

H2090, and LH15) were determined by using XRD equipment at 40 kV, 40 mA with CuK_α radiation ($1.5405 \text{ \AA}$) by 2θ at a scan rate of $2^\circ/\text{min}$. Structural analyses of LH15 filled PP at 60 wt% loading level was determined by using XRD analysis.

3.4.1.4 Measurement of melt flow index

The flow behavior of molten polymer is defined as an important factor affecting the processability of polymers. Melt flow index (MFI) or melt flow rate (MFR) is described by flow properties of the molten polymers and measured according to ISO 1133 test standard [64].

The test temperature and weight were set to 230°C and 2.16 kg, respectively for 4 different grades of Ultracarb filled polypropylene. After cleaning the cylinder and piston, 6 grams of test samples in pellet form were fed into the preheated cylinder. The material was compressed by hand pressure to ensure the charge is free from air during charging. 1 kg of preload was applied via the piston for 4 minutes, then 2.16 kg of test weight was applied. The molten polymeric material was discharged from the die. The rate of the discharged material was measured by cutting off the extrudate at a time interval of 30 seconds. At least three cut-offs were weighed using a weighing balance with an accuracy of 0.001 g. The melt flow rate expressed in grams per the reference time (10 minutes), is given by Equation 3.1.

$$\text{MFI}(230^\circ\text{C}, 2.16\text{kg}) = (S \times M) / t \quad (3.1)$$

Where S is the reference time of 600 seconds; M is the average mass of the cut-offs, in grams; and t is the cut-off time interval of 30 seconds.

3.4.1.5 Scanning electron microscopy (SEM) analysis

The aim is to examine the interface between polypropylene and naturally occurring huntite and hydromagnesite particles and filler dispersion in the matrix. Injection molded test bars having dimensions of $4 \pm 0.2 \text{ mm}$, $10 \pm 0.2 \text{ mm}$, $80 \pm 0.2 \text{ mm}$ were left in a desiccator for at least 48 hours to get rid of post crystallization or physical aging and any hydrolysis effect. 2 mm notched test specimens were submerged in liquid nitrogen for 2 hours and broken with a sudden impact. The fractured surfaces were coated with carbon before the SEM investigation to provide electro conductivity.

3.4.2 Mechanical properties

3.4.2.1 Determination of tensile properties

Test specimens were left in a heat controlled room at a temperature of $23 \pm 2^\circ\text{C}$ and 50 % humidity for at least 48 hours to prevent the specimens from the post crystallization or physical aging effects.

Tensile properties of polymeric compounds were investigated by using tensile test specimens described as test specimens ‘Type One’ according to ISO / R 527 [61]. Normal specimens were used to measure tensile properties. The test was carried out at standard conditions, i.e., $23 \pm 2^\circ\text{C}$ and 50 % humidity.

The thickness and width within the parallel portion of specimens were measured by a screw micrometer reading at least 0.02 mm. After the measurement, the specimen was fixed to self-aligning grips of the tensile test machine with a distance of 123 mm between grips. The extensometer was attached to the specimen over the parallel portion of the grip and the machine was started. The loads and corresponding deformations were recorded at the time interval of 0.2 seconds.

Tensile properties were measured as follow:

- Tensile stress or yield stress is indicated as σ_y (tensile load per unit area of original cross section within the narrow parallel portion). Tensile stress expressed in Newton per square millimeter (N/mm^2) is the first point on the load / extension curve at which an increase occurs without an increase in load.
- Tensile strain or percentage elongation at yield is indicated as ϵ_y . Tensile strain is the percentage elongation corresponding to tensile point.
- Elastic modulus or Young modulus is calculated from the slope of the line in this region where stress is proportional to strain.

3.4.2.2 Determination of flexural properties

The test was carried out at standard conditions, at temperature of $23 \pm 2^\circ\text{C}$ and 50 % humidity. Flexural properties of polypropylene composites were determined according to ISO 178 standard [62]. Similar to tensile test specimens, injection molded test bars having dimensions of 4 ± 0.2 mm, 10 ± 0.5 mm, 80 ± 0.5 mm were

kept within a desiccators for at least 48 hours to prevent post crystallization or physical aging and any hydrolysis effects. Span of two lower arms of bending fixture was set to 60 mm. Testing speed was set to 5 mm/min and the extension was measured from travel of traverse of testing machine.

The thickness and width were measured by screw micrometer reading at least 0.02 mm. Then, the specimen was laid to lower arms of the bending fixture fixed to stationary testing machine base. The third arm of the fixture fixed to movable traverse of testing machine was slowly contacted with test piece at mid-span and the machine was started. The loads and corresponding deformations were recorded at the time interval of 0.2 seconds. Following tensile properties were measured:

- Flexural stress or flexural yield stress designated as σ_f is calculated as follows:

$$\sigma_f = (3 \times F \times L) / (2 \times b \times h^2) \quad (3.2)$$

- where F is applied load in meganewtons (MN), L is the span length, b is the width and h is the thickness of specimen in meters. Flexural stress is express in megapascal (MPa) or newton per square millimeter (N/mm²).
- Flexural strain is the distance over which the top of specimen surface at mid-span has deviated during flexure from its original position and is designated as ϵ_{FY} .
- Flexural modulus or apparent modulus of elasticity (E_b) is calculated from initial linear portion of the load extension curve by using at least five values of the deflection and load. E_b is calculated as follows:

$$E_b = (L^3 \times F) / (4 \times b \times h^3 \times Y) \quad (3.3)$$

- where L is span length, b and h are the width and thickness of the specimen respectively, F is the load at a chosen point on the initial linear portion of the load –deflection curve, Y is the deflection corresponding to load F. L, b, h and Y are in millimeter and F is in Newton, then E_b is in N/mm².

3.4.2.3 Determination of Izod impact strength

Izod impact strength of specimens was determined according to ISO 180 standard [65]. It is similar to tensile test specimens. Injection molded test bars having dimensions of 4 ± 0.2 mm, 10 ± 0.2 mm, 80 ± 0.2 mm were kept in a desiccators for

at least 48 hours to prevent post crystallization or physical aging and any hydrolysis effect. The thickness and width were measured by screw micrometer reading at least 0.02 mm. Then, 2 mm notch with notch base radius 0.25 ± 0.05 mm was machined at mid-span of specimen. The test specimen and the notch were defined in the ISO standard as type 1A. Blank test (i.e. without a specimen in place) was performed to ensure the total friction losses.

The specimen was placed into test machine grips in such a way that the notched surface was faced to the impact point. The pendulum was then released and the impact energy was recorded after making correction for frictional losses. The Izod impact strength, in kilojoules per square meter (KJ/m^2), as calculated as follow:

$$\text{Izod Impact Strength} = A_k / (X \times Y_k) \times 10^3 \quad (3.4)$$

where A_k is the impact energy, in joules, absorbed by the test specimens and it is corrected for frictional losses. X is the thickness, in millimeters, of specimen. Y_k is the difference of width and notch depth, in millimeters.

3.4.3 Thermal properties

3.4.3.1 Determination of thermal stability

Thermal gravimetric analysis (TGA) of the mixtures of H/HM (4 different grades), zinc borate and polypropylene composites were carried out by using Q500 thermal gravimetric analyzer from 30°C to 900°C at a heating rate 20°C/min . Nitrogen was used as a carrier gas with a constant flow rate during analysis.

3.4.3.2 Measurement of Vicat softening point

According to ISO 306 standard, Vicat softening temperature of compounds was determined [66]. Specimen with 4 ± 0.2 mm thickness and minimum 10 mm^2 surface area was submerged within a heating bath filled with transformer oil at 23°C . Hardened steel, circular cross section indentation tip with area of $1.000 \pm 0.015 \text{ mm}^2$ was located in the middle of the specimen. The temperature measurement bulb was located near to the specimen. After five minute, with the indentation tip still in position, the weight was added to the load carrying plate which had direct connection with the indentation tip via a stainless steel rod. The weight was arranged so that the

total force on the specimen is $50 \pm 1\text{N}$. The temperature of bath was increased at a uniform rate of $50 \pm 5\text{ K/h}$, while the liquid was stirring.

The temperature of bath at which the indenting tip had penetrated into the test specimen by $1 \pm 0.01\text{ mm}$ beyond its starting point was recorded at Vicat Softening temperature for Method A or Method B depending of the weight used.

3.4.4 Flame retardant properties

3.4.4.1 Determination of oxygen index

Oxygen index was determined according to ASTM D2863-10 standard [67]. This test method provides for the measuring of the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that will just support flaming combustion of plastics. The test was carried out at standard conditions, at temperature of $23 \pm 2^\circ\text{C}$ and 50 % humidity. In addition, each test specimen was kept for at least 40 h at $23 \pm 2^\circ\text{C}$ and 50 % humidity.

Initial concentration of oxygen was selected to determine limiting oxygen index. It was depended upon the difficulty of ignition or the period of burning before extinguishing in air. Oxygen concentration that was used as the volume percent measured and recorded.

3.4.4.2 Determination of glow wire ignition temperature

Test specimens were kept at temperature of $23 \pm 2^\circ\text{C}$ and $50 \pm 5\%$ relative humidity for at least 40 hours prior to testing. Thickness of specimens must be 0.25 mm or greater than 6.4 mm.

The specimen was mounted in the test so that the surface that comes in contact with the tip of the glow-wire was vertical and any losses to supporting means were insignificant. The pre-selected glow-wire temperature was maintained for at least 60 seconds prior to conducting the test. The specimen was brought in contact with the tip of the glow-wire at an applied force of $1.0 \pm 0.2\text{ N}$ for $30 \pm 1\text{ s}$. For the purpose of this test, ignition will be deemed to have occurred if either sustained flaming occurs or the tissue paper on the indicator board placed underneath the apparatus exhibits flames caused by particles falling from the test specimen [68].

3.4.4.3 Determination of UL 94 flammability rating

Rate of burning and time of burning of self supporting plastics in a horizontal position were measured according to ASTM D-635 standard [69]. Specimens shall be 125 ± 5 mm long by 13.0 ± 0.5 mm wide, and provided in the minimum thickness and in the 3.0 mm thickness. Test specimens were kept at temperature of $23 \pm 2^\circ\text{C}$ and 50 ± 5 % relative humidity for at least 48 hours prior to testing.

The specimen to be tested was exposed to burner flame for 30 s without changing its position. If the specimen continues to burn, with a flame or glowing combustion, after removal of the test flame, record the elapsed time (t), in seconds, for the flame front to travel from the 25 mm reference mark to 100 mm reference mark and record the burned length (L), as 75 mm. If the flame front passes the 25 mm reference mark but does not reach the 100 mm reference mark, record elapsed time and burning length, in millimeters between the 25 mm reference mark and where the flame front stopped. Linear burning rate (V), in milimetres per minute is calculated for each specimen where the flame front reaches the 100 mm reference mark using the following equation:

$$V = 60L/t \quad (3.5)$$

L is defined as the burned length, in millimetres. And also t is time, in seconds.

The behavior of specimens shall be classified HB (HB = horizontal burning) if, there are no visible signs of combustion after the ignition source is removed or the flame front does not pass the 25 mm reference mark or the flame front reaches the 100 mm reference mark and the linear burning rate does not exceed 400 mm/min for specimens having a thickness between 3 and 13 mm or 75 mm/min for specimens having a thickness less than 3 mm.

4. RESULTS AND DISCUSSION

4.1 Polypropylene/Mixtures of Huntite and Hydromagnesite and Their Properties

Four different commercial grades of huntite and hydromagnesite mixtures were used. Ultracarb 1250 has a high content of huntite (65-70%). Ultracarb 1253 also comprises higher huntite content (65-70%) with silicone coated. Hybercarb 2090 comprises the highest amount of huntite (75-80%). LH15 has also higher hydromagnesite content (55-60%). The effectiveness and the loading level of mixtures of huntite/hydromagnesite (H/HM) (U1250, U1253, H2090, and LH15) were investigated by adding of Huntite/hydromagnesite to PP at specified mixing conditions in Section 3.3.2. Four different grades of Huntite/hydromagnesite were mixed to PP as 30 - 40 - 50 - 60 % ratios for preparing sixteen polymeric composite samples. These produced samples were molded as test specimen and they were tested as described in Section 3.

4.1.1 Structural and morphological properties results

4.1.1.1 Measurement of density

Measurement of density was done as defined in section 3.4.1.1. Density test results showed a steady increase with increasing Huntite/hydromagnesite loading level (30-40-50-60 wt.%). Huntite (magnesium calcium carbonate) has a density of approximately 2.70 g/cm^3 compared to approximately 2.24 g/cm^3 for hydromagnesite (basic magnesium carbonate). Huntite/hydromagnesite is an inorganic mixture and has a higher density of 2.50 g/cm^3 than that of polypropylene, which is 0.9028 g/cm^3 . Therefore, the incorporation of Huntite/hydromagnesite into the polypropylene matrix resulted in processing composites with higher density. The highest loading of 60 wt.% Huntite/hydromagnesite increased the density up to 1.5 g/cm^3 . The results indicated that there were no significant differences for the same

loading levels in the density values. Test results are given in Table 4.1 and Figure 4.1.

Table 4.1 : Test results of density measurements of neat polypropylene and mixtures of H/HM filled polypropylene.

Samples	H/HM loading levels (%)	Density (g/cm ³)
Neat PP	0	0.9028 ± 0.0008
PP+U1250	30	1.1164 ± 0.0003
	40	1.2175 ± 0.0062
	50	1.3310 ± 0.0034
	60	1.4678 ± 0.0025
PP+U1253	30	1.0991 ± 0.0030
	40	1.2254 ± 0.0055
	50	1.3329 ± 0.0011
	60	1.4664 ± 0.0049
PP+H2090	30	1.0933 ± 0.0045
	40	1.2144 ± 0.0084
	50	1.3309 ± 0.0066
	60	1.4915 ± 0.0054
PP+LH15	30	1.0916 ± 0.0035
	40	1.2070 ± 0.0071
	50	1.3202 ± 0.0059
	60	1.4361 ± 0.0067

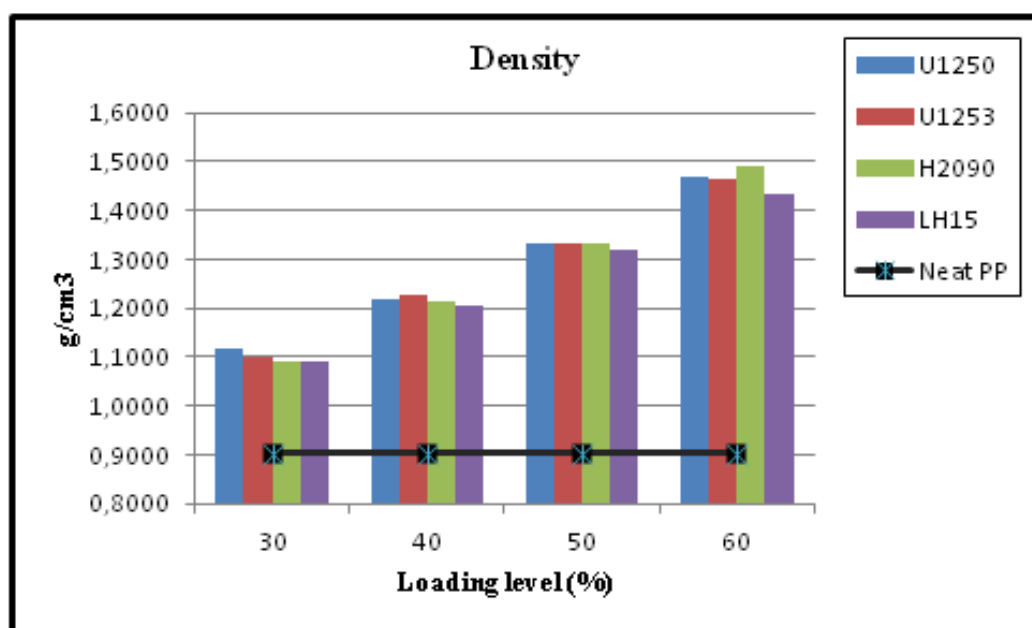


Figure 4.1 : Density measurement results of H/HM filled PP.

4.1.1.2 Fourier Transform Infrared (FTIR) analysis

FTIR analysis was used to examine the chemical composition and structure of materials. In this study, LH15 (higher hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) content) filled PP at 60wt.% loading levels, and LH 15 were characterized to obtain FTIR spectra. The structural and characteristic groups of materials were determined. FTIR spectra were recorded in the absorbance mode. The FTIR spectra of samples were presentend in Figures 4.2, 4.3, 4.4.

In this study, a very sharp band occurred at 3647 cm^{-1} which must be due to an almost free O-H vibration. The pair of strong sharp bands occurred at 3515 cm^{-1} and 3450 cm^{-1} in the spectrum (Figure 4.2, Figure 4.3, and Figure 4.4). The FTIR spectra of calcium magnesium carbonate shows characteristic with a very intense broad band centering at $2750\text{--}4000\text{ cm}^{-1}$. Magnesium carbonate indicates lower intensity absorptions at $550\text{--}700\text{ cm}^{-1}$. In addition, polypropylene shows peaks at 2922 cm^{-1} due to the methyl ($-\text{CH}_3$) groups. These results are in aggrement with literature [55,70].

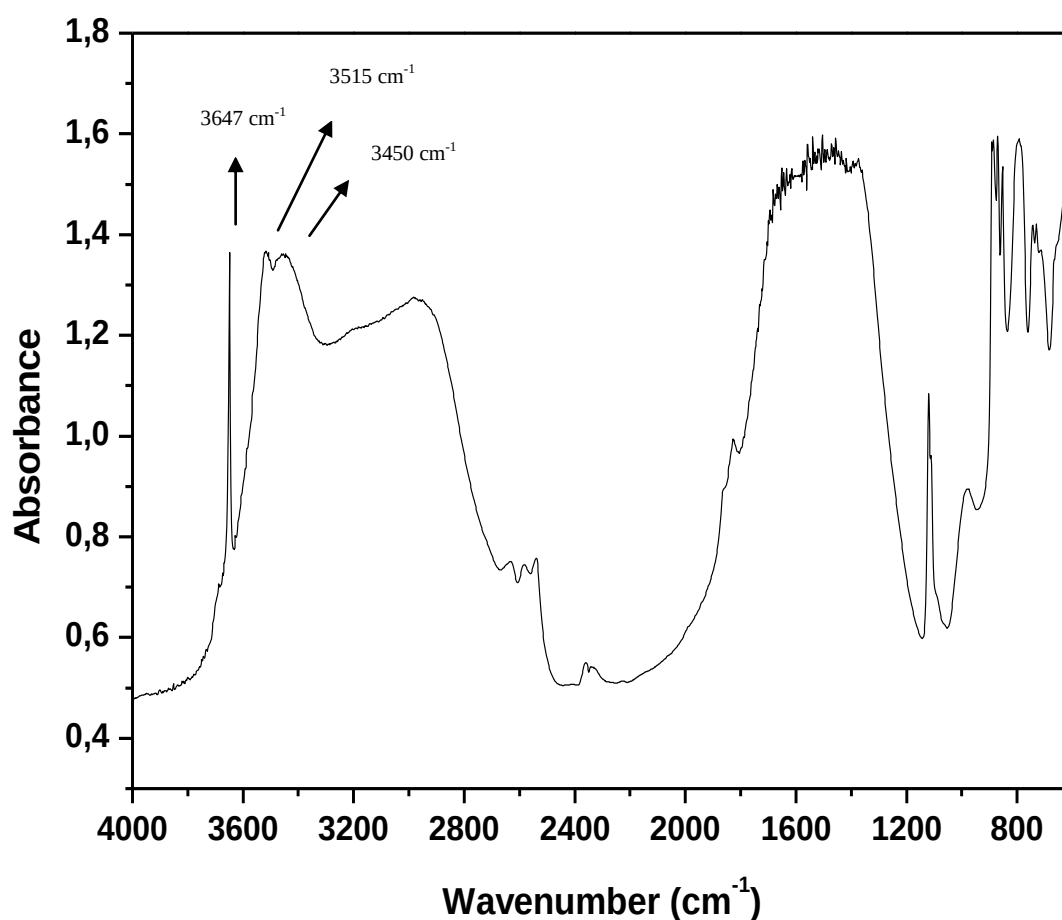


Figure 4.2 : FTIR analysis of LH15.

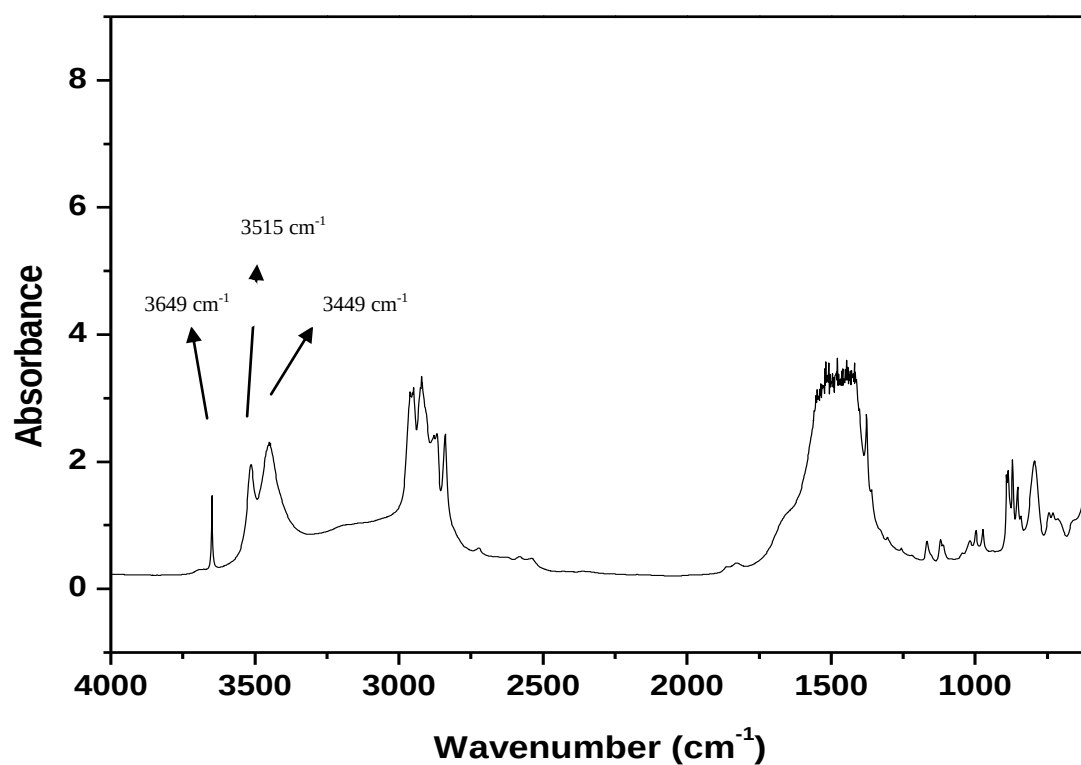


Figure 4.3 : FTIR analysis of LH15 filled PP at 60% loading level.

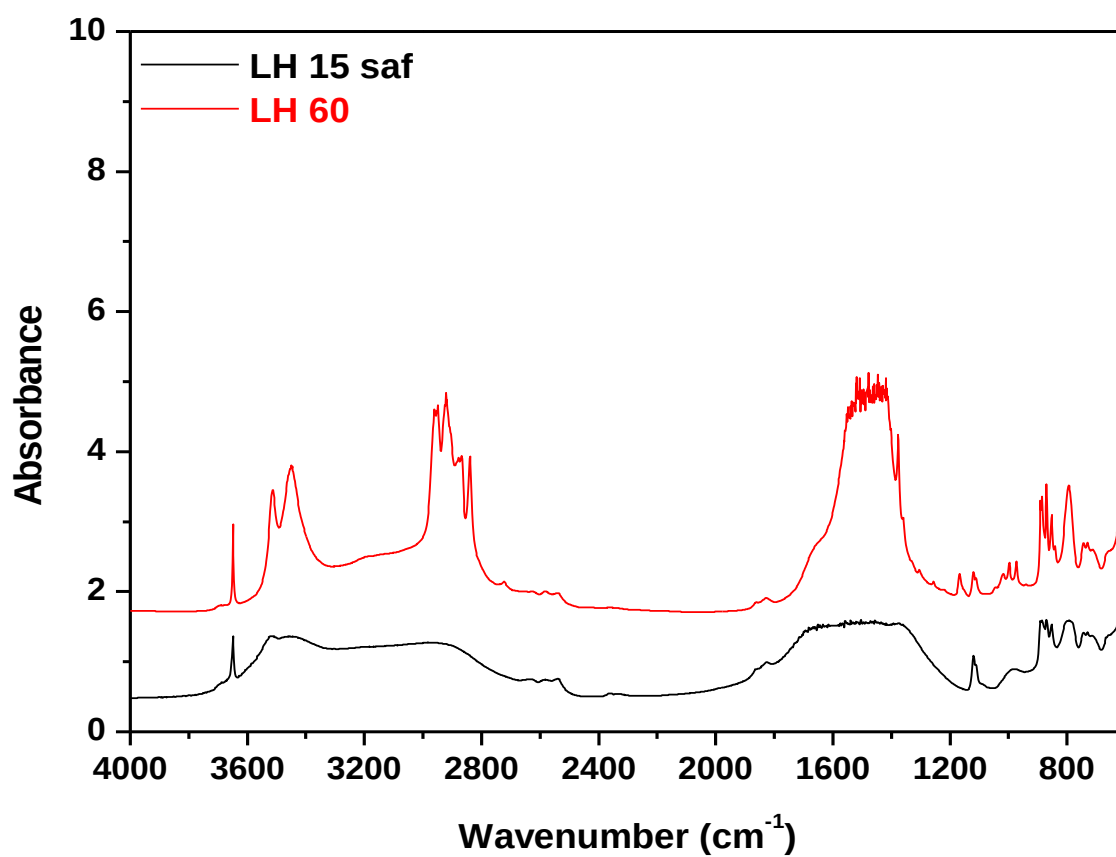


Figure 4.4 : FTIR analysis of LH 15 and LH15 filled PP at 60% loading level.

4.1.1.3 X-ray Diffraction (XRD) analysis

Structural investigation was done according to the procedure explained in section 3.4.1.3. XRD pattern of mixtures of H/HM (4 different grades; U1250, U1253, H2090, LH15) is indicated in Figures 4.5, 4.6, 4.7, 4.8. The ratios of huntite and hydromagnesite in the mixtures were found from these results. U1250 consists of three distinct phases such as hydromagnesite, huntite and dolomite. It includes higher huntite content (65-70%). U1253 is silicone coated a mixture of H/HM with higher huntite content (65-70%). It consists of two distinct phases such as hydromagnesite and huntite. LH15 comprises higher hydromagnesite content (55-60%). H2090 includes much higher huntite content (75-80%) than other samples.

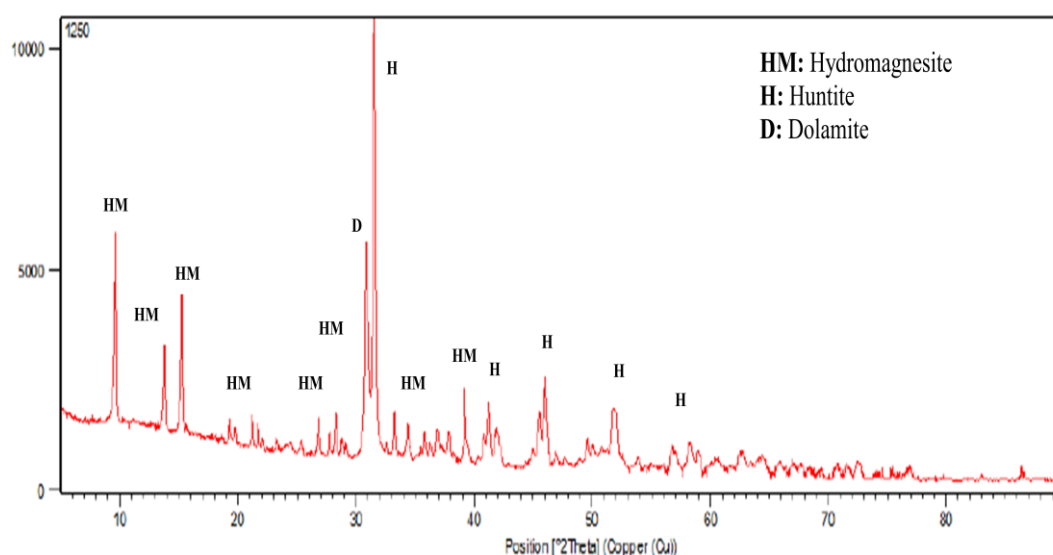


Figure 4.5 : XRD pattern of U1250 with higher huntite content.

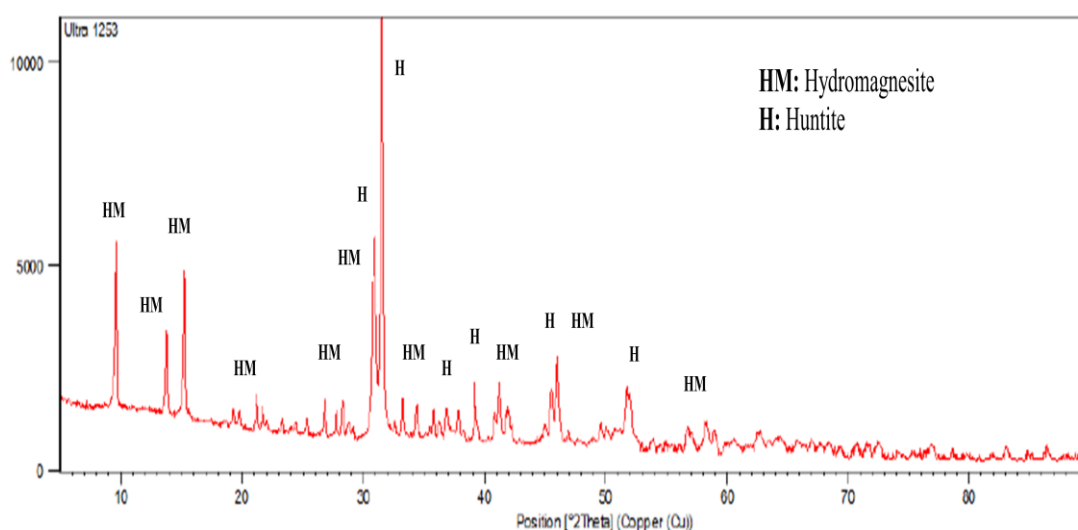


Figure 4.6 : XRD pattern of U1253 with higher huntite content and silicone coated.

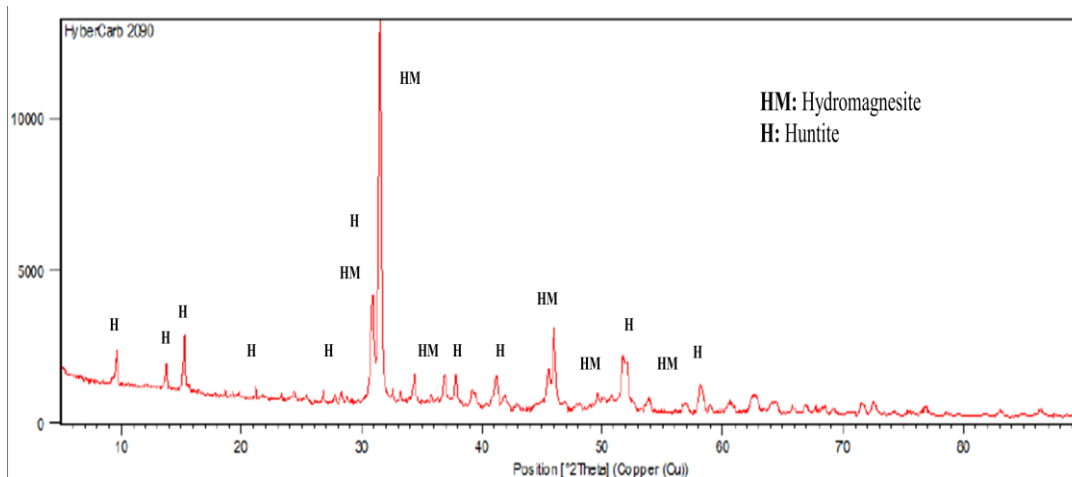


Figure 4.7 : XRD pattern of H2090 with higher huntite content.

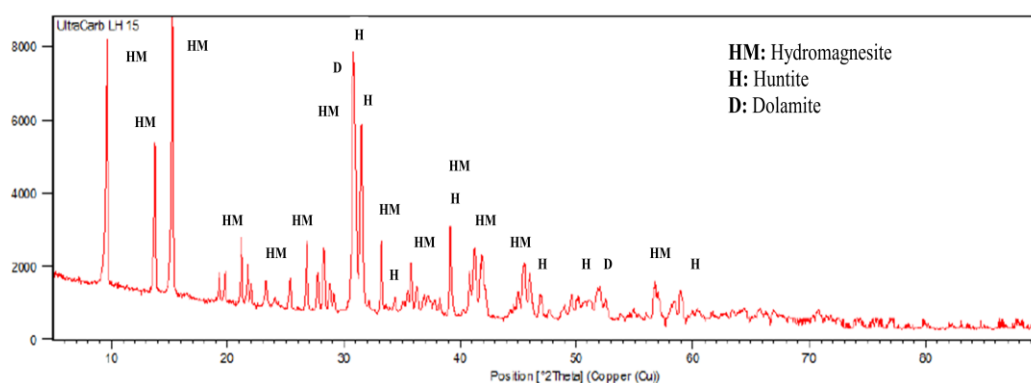


Figure 4.8 : XRD pattern of LH15 with higher hydromagnesite content.

4.1.1.4 Determination of melt flow index

Melt flow index (MFI) test was done as described in section 3.4.1.4. MFI test results indicated a steady decrease with increasing loading level. Neat polypropylene has MFI of 49.7 g/10 min. The highest loading of 60 wt% H/HM decreased MFI to approximately 0.6 g/10 min. By the entrance of huntite and hydromagnesite particles to the matrix the melt flow index values decreased due to decreased chain movements of polypropylene. In the same loading levels, there were no important differences for mixtures of H/HM filled polypropylene in terms of rheological properties. Higher huntite or hydromagnesite content in the mixtures did not have positive effect on MFI values. In addition, silicone-coated mixture of H/HM (U1253) and uncoated mixtures of H/HM (U1250, H2090, and LH15) had same MFI values with the increasing loading levels. The MFI test results of neat PP and mixtures of H/HM filled PP are given in the Table 4.2.

Table 4.2: Melt flow index test results of neat PP and mixtures of H/HM filled polypropylene.

Samples	H/HM loading levels (%)	MFI (g/10min)
Neat PP	0	49.7 ± 0.2
PP+U1250	30	13.4 ± 0.2
	40	7.5 ± 0.1
	50	4.2 ± 0.1
	60	0.7 ± 0.1
PP+U1253	30	12.5 ± 0.2
	40	8.7 ± 0.1
	50	5.8 ± 0.1
	60	0.7 ± 0.2
PP+H2090	30	13.3 ± 0.1
	40	7.3 ± 0.1
	50	3.2 ± 0.1
	60	0.6 ± 0.2
PP+LH15	30	13.5 ± 0.1
	40	7.4 ± 0.2
	50	3.5 ± 0.2
	60	0.6 ± 0.1

4.1.1.5 Scanning Electron Microscopy (SEM) analysis

Scanning electron microscopy analysis was carried out for H2090 (higher huntite content (75-80%)) and LH15 (higher hydromagnesite content (55-60%)) samples by the procedure given in Section 3.4.1.5. Figure 4.9 shows SEM micrographs of LH 15 and H2090. Figure 4.10 and Figure 4.11 indicate SEM micrographs of LH15 filled PP and H2090 filled PP at 30% and 60% loading levels respectively. Figure 4.12 shows EDS analysis of LH 15.

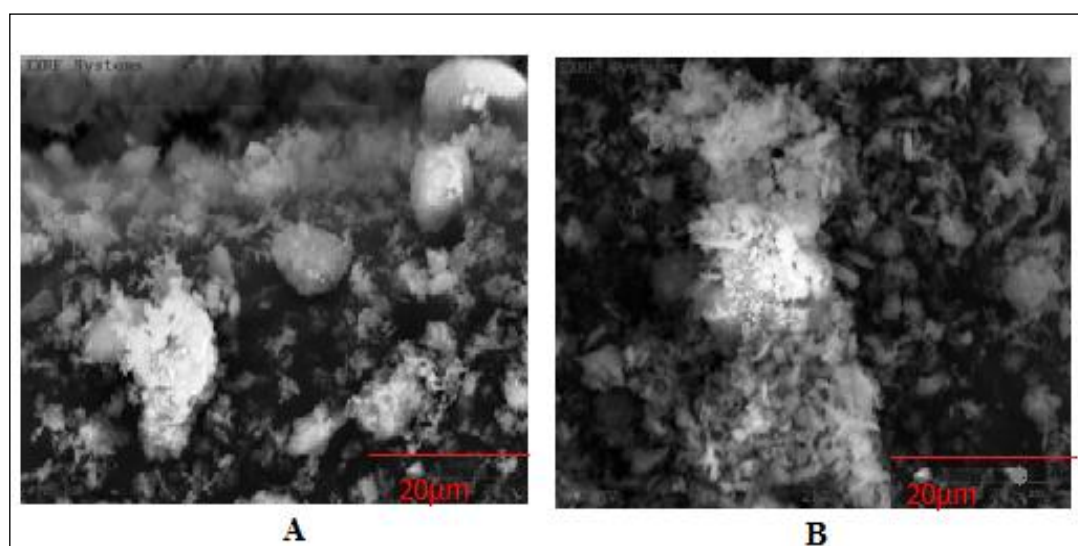


Figure 4.9 : SEM micrographs of A) H2090, B) LH 15.

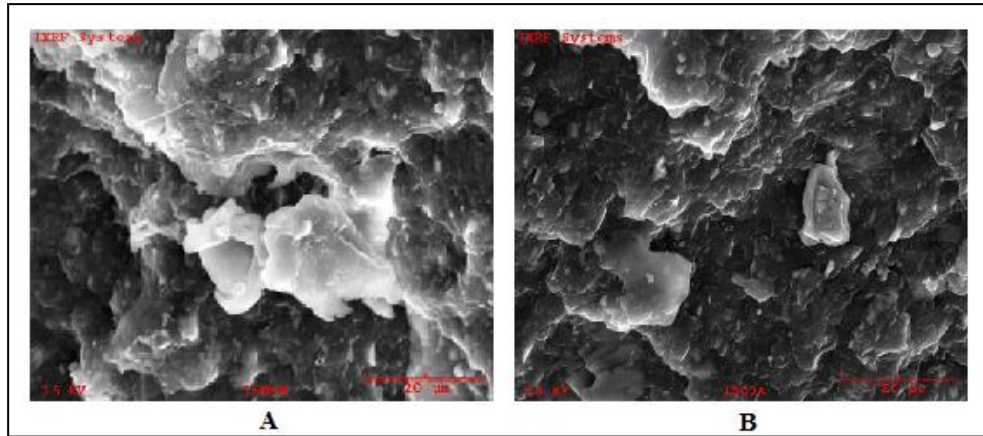


Figure 4.10 : SEM micrographs of A) H2090 filled PP, B) LH15 filled PP at %30 loading level.

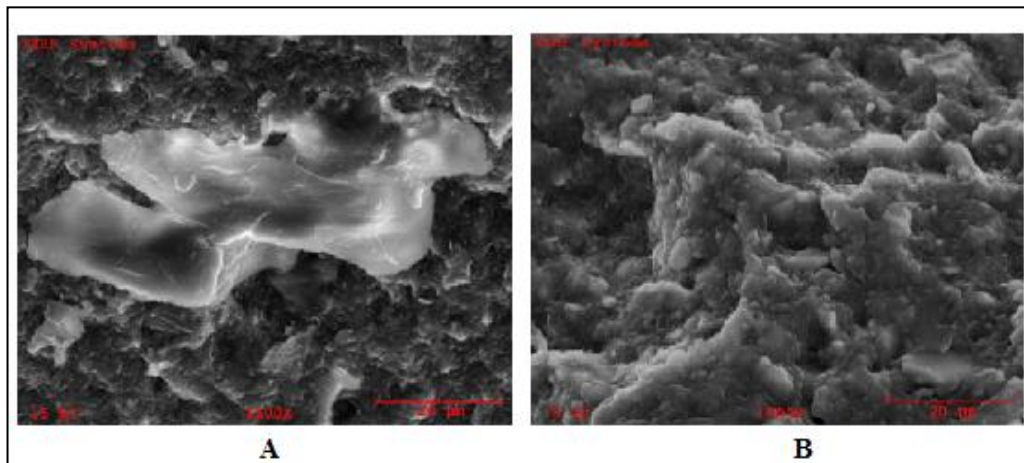


Figure 4.11 : SEM micrographs of A) H2090 filled PP, B) LH15 filled PP at %60 loading level.

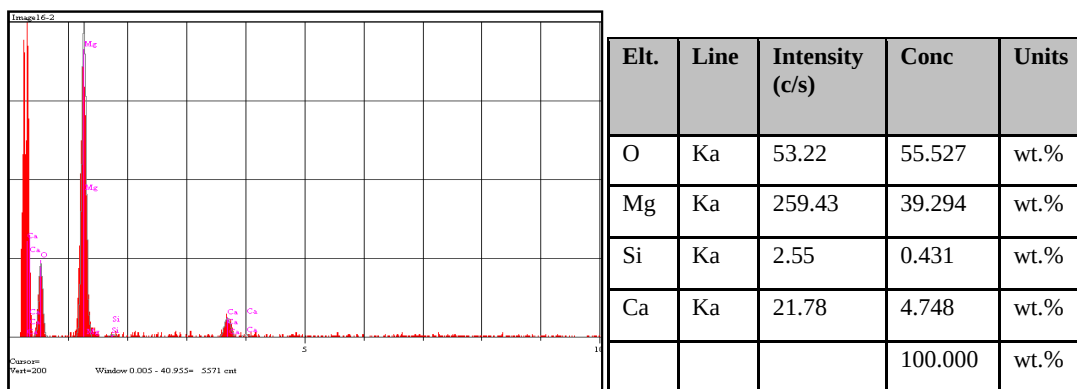


Figure 4.12 : EDS analysis of LH 15.

SEM observations showed that during extrusion hydromagnesite particles are well dispersed than huntite particles in polypropylene composites . There is no interaction between huntite/hydromagnesite and polypropylene except mechanical adhesion between filler and polypropylene.

4.1.2 Mechanical properties results

Mechanical properties of polypropylene composites were determined by using mechanical testing method.

4.1.2.1 Tensile properties

Tensile test was done according to the procedure explained in section 3.4.2.1. Experimental mechanical test results of all samples are shown in Table 4.3. Max. stress values of neat PP and H/HM (U1250, U1253, H2090 and LH15) filled PP composites were presented in Figure 4.13. Elastic modulus diagram of neat PP and H/HM filled PP composites was indicated in Figure 4.14. The effects of H to HM weight ratio in the H/HM grades and H/HM loading level on mechanical properties of PP composites were investigated. Influences of surface treatment of H/HM with silicone coating were also researched.

Table 4.3 : Average tensile test results of neat PP and mixtures of H/HM filled PP.

Samples	H/HM loading levels (%)	Elastic Mod. (MPa)	Max. Stress (MPa)	Strain (%)
Neat PP	0	1924 ± 30	36 ± 3	26.5 ± 3
PP+U1250	30	2542 ± 30	30 ± 1	3.1 ± 0.2
	40	3113 ± 65	29 ± 1	2.3 ± 0.4
	50	4282 ± 120	28 ± 1	1.2 ± 0.1
	60	5521 ± 85	25 ± 1	0.6 ± 0.1
PP+U1253	30	2837 ± 60	30 ± 1	5.8 ± 2.3
	40	3531 ± 80	27 ± 1	2.9 ± 0.3
	50	4360 ± 160	26 ± 1	1.5 ± 0.1
	60	5852 ± 75	25 ± 1	0.9 ± 0.1
PP+H2090	30	2749 ± 65	30 ± 1	3.4 ± 0.8
	40	3278 ± 107	29 ± 1	2.4 ± 0.2
	50	4406 ± 140	28 ± 1	1.3 ± 0.1
	60	6069 ± 155	25 ± 1	0.5 ± 0.1
PP+LH15	30	3005 ± 212	29 ± 1	5.9 ± 2.1
	40	3480 ± 146	27 ± 1	3.7 ± 0.6
	50	4414 ± 158	26 ± 1	1.3 ± 0.1
	60	5753 ± 155	23 ± 1	0.5 ± 0.1

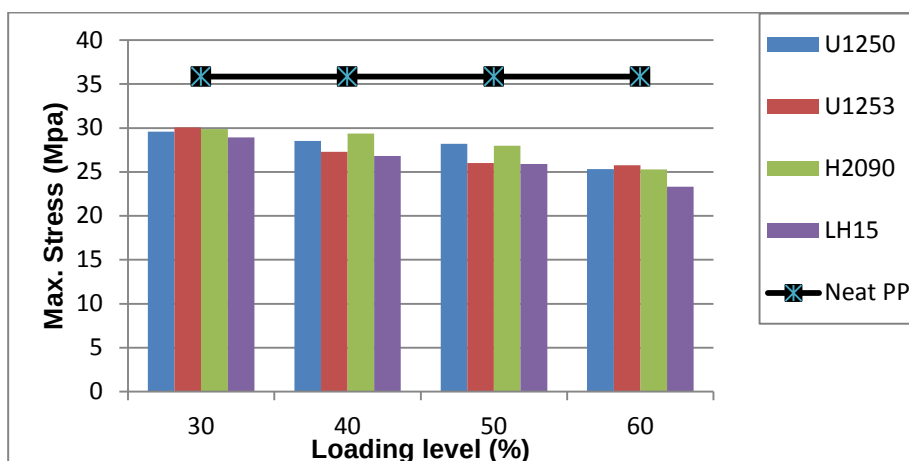


Figure 4.13 : Max. Stress (MPa) results of H/HM-PP composites.

Tensile tests were carried out for understanding influence of varying proportions of huntite and hydromagnesite at different loading levels on the mechanical properties of PP composites. Elastic modulus, strain and maximum stress are known as the most important mechanical properties of PP composites. The tensile strength of neat PP was around 36 MPa and this was much higher than loading levels of 30-40-50-60% by weight of H/HM filled PP. Tensile (Max.) stress properties of composites did not change with varying proportions of huntite and hydromagnesite and were close to each other at the same loading levels. Differences were not observed. In addition, silicone coated mixture of H/HM (U1253) did not modify tensile strength properties of PP composites.

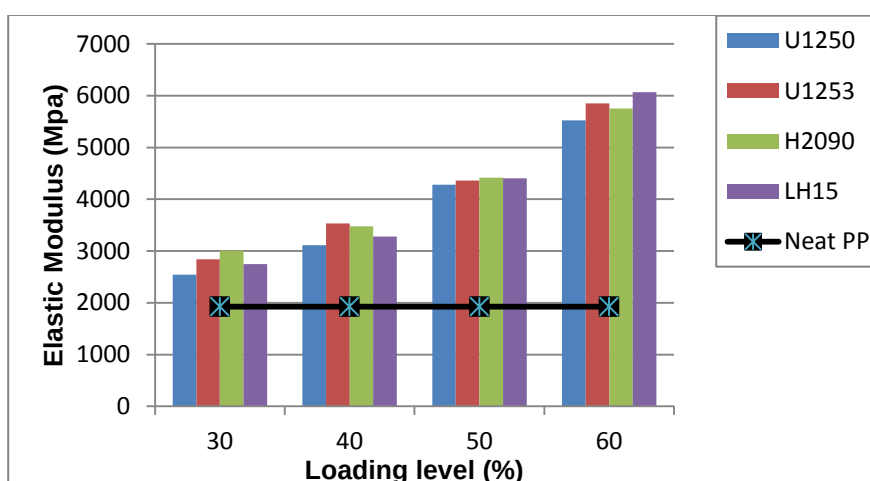


Figure 4.14 : Tensile-Elastic modulus (MPa) results of H/HM-PP composites.

Elastic modulus increased with increasing amounts of mixtures of H/HM in PP composite. Elastic modulus of neat PP was 1924 MPa and the highest loading of

60wt.% H/HM increased the elastic modulus up to 6069 MPa. Silicone coated mixture of H/HM (U1253) did not improve elastic modulus properties of PP composites.

Strain values of PP composites decreased with increasing amounts of mixtures of H/HM in PP composites. Elongation of neat PP was 27%. Filler addition almost decreased elongation of PP matrix to 5.8%. Silicone coated mixture of H/HM (U1253) did not develop the strain properties of PP composites. Strain values were close to each other at the same loading levels. Higher huntite or hydromagnesite content did not improve the strain properties of PP composites. Tensile properties of filled polymeric compounds depend on interaction between polymer and fillers. High loading levels, at least 60% by weight, mixtures of H/HM have negative effect on the mechanical properties of the compound. Higher levels of hydromagnesite (LH15) in the mixture showed better effect in elastic modulus and elongation at break compared to other samples.

4.1.2.2 Flexural properties

Flexural test was done as three point bending method according to the procedure explained in section 3.4.2.2. Test results are given in Table 4.4 and Figure 4.15 and Figure 4.16.

Table 4.4 : Flexural test results of neat PP and mixtures of H/HM filled PP.

Samples	H/HM loading levels (%)	Modulus (MPa)	Stress (MPa)	Strain (%)
Neat PP	0	1338 ± 50	45 ± 3	8.2 ± 0.4
PP+U1250	30	2398 ± 70	44 ± 4	4.8 ± 0.6
	40	3113 ± 45	43 ± 1	3.7 ± 0.2
	50	3405 ± 80	42 ± 1	2.9 ± 0.2
	60	4756 ± 65	40 ± 1	1.2 ± 0.1
PP+U1253	30	2500 ± 45	50 ± 2	4.8 ± 0.5
	40	3137 ± 60	48 ± 2	3.3 ± 0.2
	50	3786 ± 95	43 ± 1	2.2 ± 0.2
	60	4925 ± 82	41 ± 2	1.3 ± 0.1
PP+H2090	30	2458 ± 55	50 ± 3	4.3 ± 0.2
	40	3118 ± 45	49 ± 2	3.1 ± 0.2
	50	4067 ± 68	46 ± 3	1.8 ± 0.1
	60	4991 ± 105	43 ± 1	1.1 ± 0.1
PP+LH15	30	2590 ± 70	48 ± 1	4.6 ± 0.3
	40	3267 ± 85	47 ± 2	3.3 ± 0.3
	50	4032 ± 30	43 ± 2	1.8 ± 0.2
	60	5267 ± 80	40 ± 3	0.9 ± 0.1

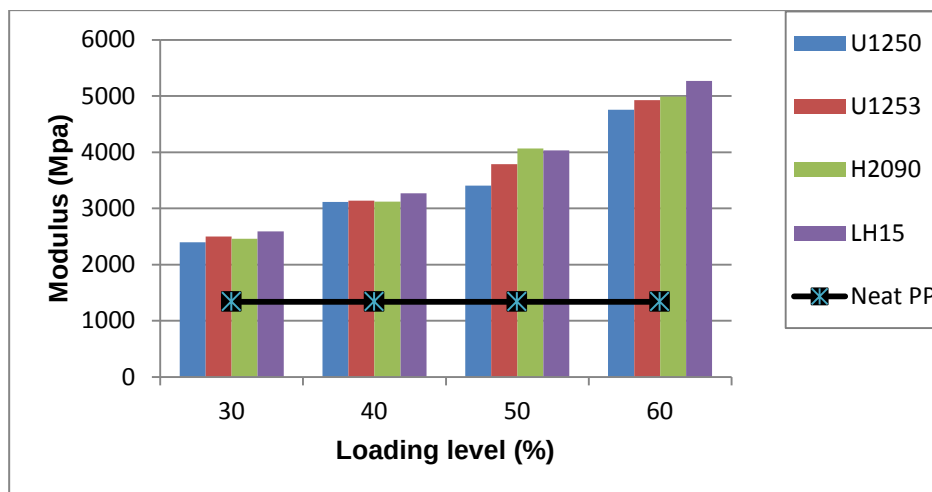


Figure 4.15 : Flexural modulus (MPa) results of H/HM-PP composites.

Three point bending test was carried out for understanding the effects of H to HM weight ratio in the H/HM grades and H/HM loading level on the mechanical properties of polymeric composites. Flexural modulus values of polymeric composites did not change with varying proportions of huntite and hydromagnesite and were close to each other at the same loading levels. Higher huntite content or higher hydromagnesite content in the samples did not improve flexural modulus values of polymeric composites. Flexural modulus values were increased with the addition of mixtures of H/HM into the polymeric matrix. In addition, silicone coated mixture of H/HM did not modify flexural modulus values of polymeric composites. The flexural modulus value of neat PP was around 1338 MPa and this was much lower than loading levels of 30-40-50-60% by weight of H/HM filled PP.

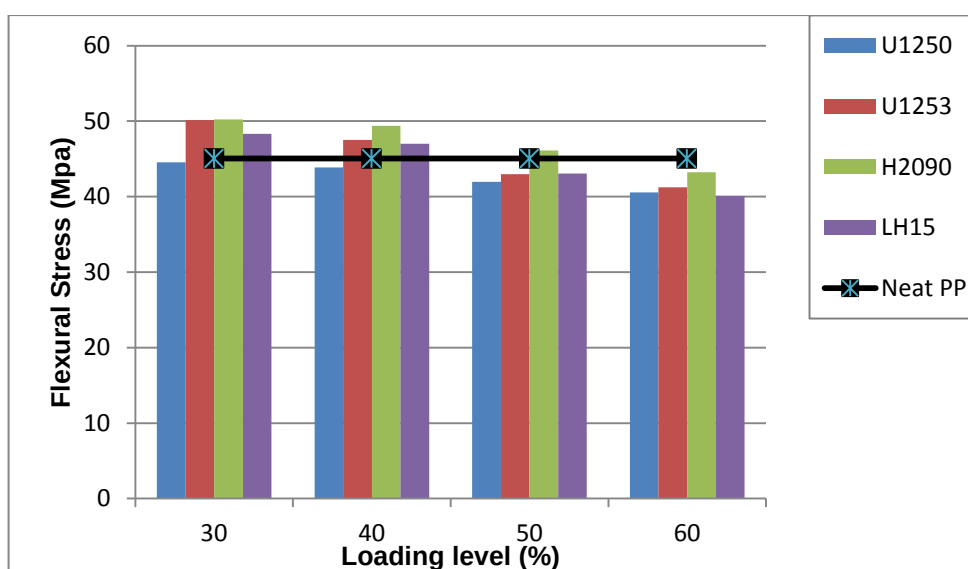


Figure 4.16 : Flexural stress (MPa) results of H/HM-PP composites.

The Flexural stress value of neat PP was around 45 MPa. Silicone coated mixture (U1253) filled PP and uncoated mixtures (U1250,H2090 and LH15) filled PP were great flexural stress values than neat PP at a 30% loading level. The highest loading level of 60wt.% H/HM decreased the flexural stress to 40 MPa. In addition, flexural stress values of polymeric composites were close to each other at the same loading levels.

The Flexural strain value of neat PP was around 8.24% and this was much higher than loading levels of 30-40-50-60% by weight of H/HM filled PP. The results showed a steady decrease with increasing loading level. Higher huntite content mixture (H2090) was much lower strain values compared to other samples. Silicone coated mixture (U1253) did not modify strain properties of polymeric composites.

4.1.2.3 Izod impact properties

Izod impact test was done according to the procedure explained in section 3.4.2.3. Izod impact test results are given in Table 4.5 and Figure 4.17.

Table 4.5 : Impact test results of neat PP and mixtures of H/HM filled PP.

Samples	H/HM loading levels (%)	Izod Impact Strength (kJ/m ²)
Neat PP	0	2.8 ± 0.1
PP+U1250	30	2.8 ± 0.1
	40	2.7 ± 0.1
	50	2.1 ± 0.1
	60	2.0 ± 0.1
PP+U1253	30	3.5 ± 0.2
	40	2.8 ± 0.1
	50	2.0 ± 0.1
	60	1.9 ± 0.1
PP+H2090	30	3.4 ± 0.2
	40	2.8 ± 0.2
	50	2.1 ± 0.1
	60	1.8 ± 0.1
PP+LH15	30	3.3 ± 0.1
	40	3.0 ± 0.3
	50	2.1 ± 0.1
	60	1.9 ± 0.2

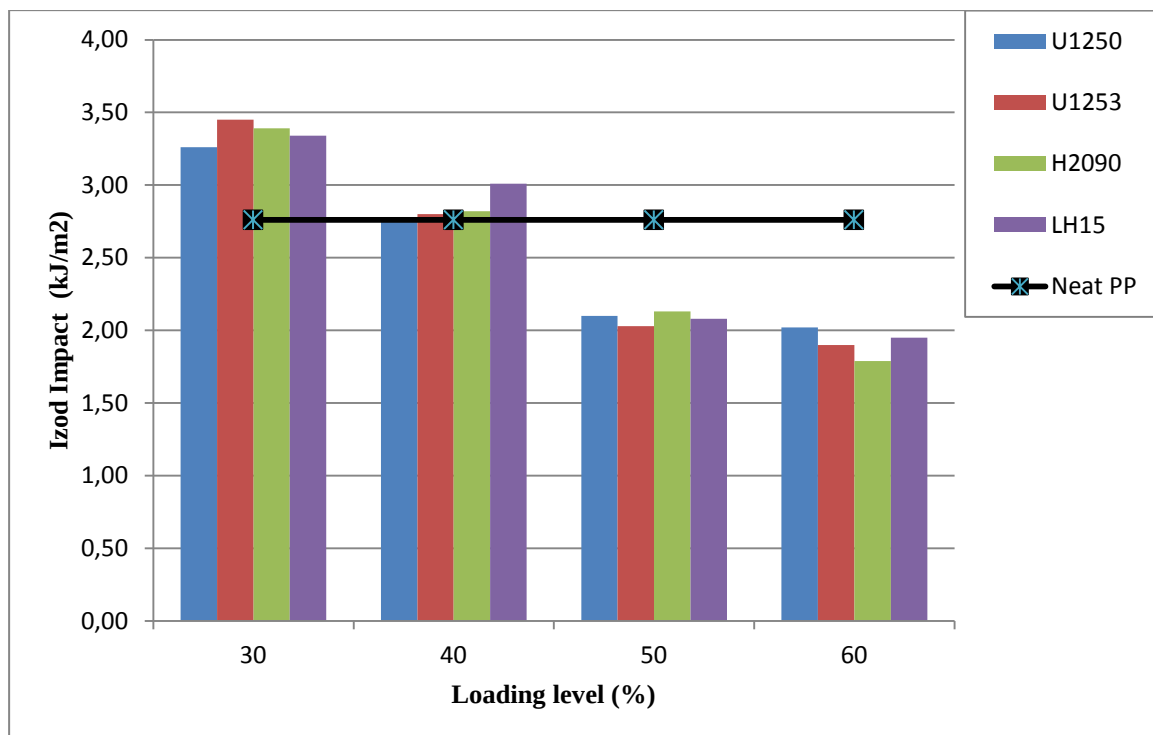


Figure 4.17 : Izod impact strength results of H/HM-PP composites.

The Izod impact strength value of neat PP was around 2.8 kJ/m² and this was much lower than other samples at 30% loading level of H/HM. At 40% loading level, neat PP and other samples were close to each other in terms of impact strength. At 50-60% loading levels of mixtures of H/HM showed negative effect on Izod impact strength. The reduction of Izod impact strength with mixtures of H/HM addition into PP could be explained by the restriction of chain mobility. The influence of H/HM ratio of natural mixtures was also important parameter to evaluate impact strength. And also, Clemens said that huntite was much more effective than hydromagnesite at nucleating crystallisation of polypropylene and this effect was observed to give compounds improved impact properties when a higher proportion of huntite was used [48]. U1250, U1253 and H2090 are the mixtures of H/HM (huntite content greater than 65). They had a positive effect on impact strength at 30% loading level.

4.1.3 Thermal properties results

4.1.3.1 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis (TGA) was done according to the procedure explained in section 3.4.3.1. The raw materials were analyzed individually as shown in Figure 4.18. According to the literature hydromagnesite has three decomposition steps while

huntite has two decomposition steps [71]. Mass losses of hydromagnesite are 15.45%, 19.31% and 57.08% respectively for three steps. Mass losses of huntite are 37.5% and 50% for two steps. Hydromagnesite starts to decompose at the temperature of 220°C. The loss of crystalline water from the hydromagnesite causes an initial mass loss between the temperatures of 220°C and 350°C. The loss of carbon dioxide from the hydromagnesite is second step in mass loss, is not complete until about 540°C. It overlaps with the initial mass related to loss of carbon dioxide from the huntite. The loss of the hydroxyl group from hydromagnesite as water occurs between the temperatures of 380°C and 450°C. This region also includes the temperature range of the loss of carbon dioxide from hydromagnesite. The mass loss from hydromagnesite continues up to about 700°C which is known slow degradation of the small amount of crystalline magnesium carbonate. Huntite starts to decompose at about 470°C. The initial loss of carbon dioxide from huntite occurs between the temperatures of 470°C and 610°C. Secondary loss of carbon dioxide from huntite resulting from the decomposition of the carbonate groups related to with the calcium ions. At 800°C, the decomposition product of hydromagnesite is magnesium oxide. Magnesium oxide and calcium oxide are also known as the decomposition products of huntite at this temperature.

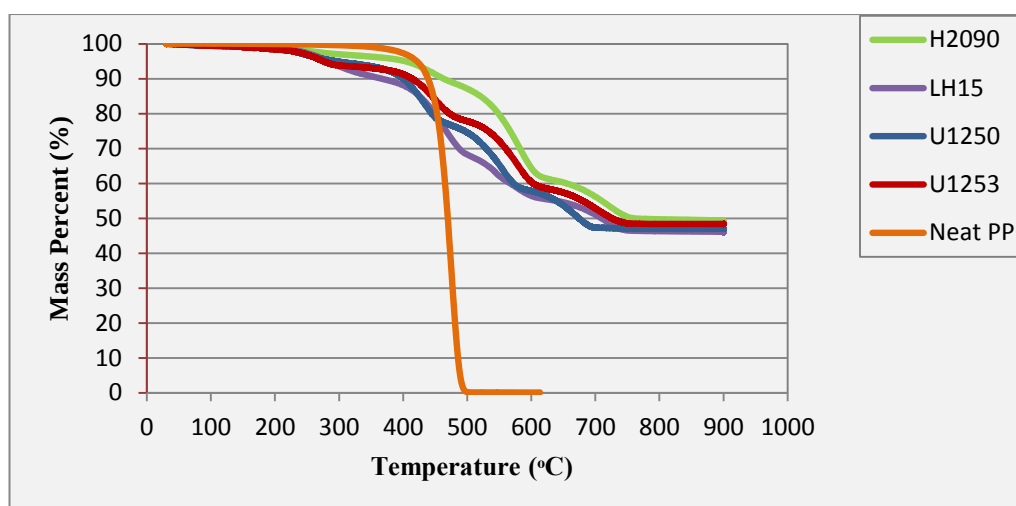


Figure 4.18 : Thermal degradation curves of raw materials.

The TGA curves of raw materials were given in Figure 4.18. Polypropylene began to decompose at 262°C and consumed completely at 500°C from this figure.

LH15 (higher hydromagnesite content (55-60%)) showed four steps in its thermal decomposition curve. First step started at 222°C and second step decomposition

began at 350°C. Third and fourth step decomposition began at 450°C and 620°C respectively. The weight loss of LH15 was 54% at 900°C.

U1250 (higher huntite content (65-70%)) showed four steps in its thermal decomposition curve. First step began at about 220°C and second step decomposition started at 350°C. Third and fourth steps began at 440°C and 620°C respectively. The weight loss of U1250 was 53% at 900°C.

U1253 (higher huntite content and silicone coated (65-70%)) showed four steps in its thermal decomposition curve First step began at about 211°C and second step decomposition started at 353°C. Third and fourth steps began at 440°C and 600°C respectively. The weight loss of U1253 was 52% at 900°C.

H2090 (higher huntite content and silicone coated (75-80%)) showed four steps in its thermal decomposition curve First step began at about 223°C and second step decomposition started at 350°C. Third and fourth steps began at 440°C and 625°C respectively. The weight loss of U1250 was 51% at 900°C.

The mass percent of H/HM-PP composites was illustrated with commercial grades of H/HM. The decomposition of PP and the mixture of H/HM were also measured individually. Then, these curves added together to predict the behavior of commercial grades filled PP composites.

At the hydromagnesite decomposition temperatures PP matrix may have become softened but not yet decomposed in Figure 4.19, Figure 4.20, Figure 4.21 and Figure 4.22. The decomposition of PP started at 262°C which was higher than the initial decomposition temperature of hydromagnesite so the compound containing higher hydromagnesite content did not begin to loss mass at the decomposition temperature of hydromagnesite. Hydromagnesite began to decompose endothermically giving off water and carbon dioxide between about 220°C and 500°C. The endothermic decomposition took heat from the solid phase slowing decomposition of the polymer and the release of water and carbon dioxide into the flame slowed the rate of burning. The decomposition of hydromagnesite obviously helped with putting out the flame, but platy huntite particles increased the viscosity of the molten polymer helping to prevent dripping. The decomposition of the remaining polymer was slowed down the accumulation of the inorganic residue. Huntite began to decompose at about between 440°C and 470°C where PP started to consume completely. Huntite and

hydromagnesite continued to decompose to inorganic residue. According to thermal gravimetric analysis curves, polypropylene composites containing higher hydromagnesite content were effective than samples containing higher huntite content.

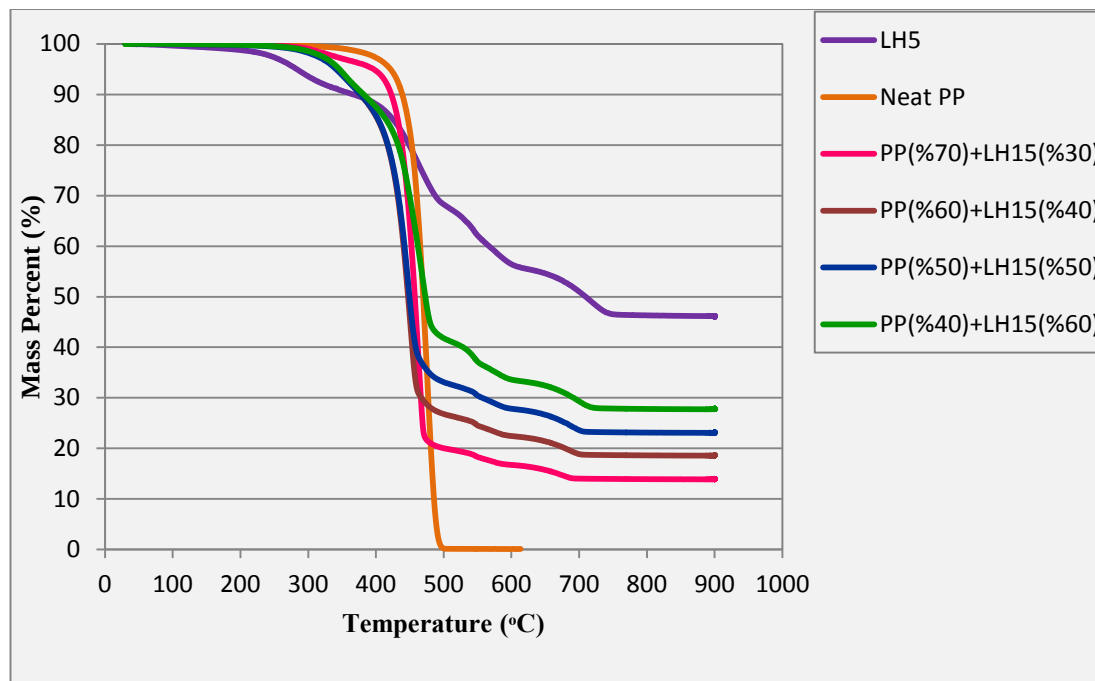


Figure 4.19 : TGA curves of PP, LH15 and LH15-PP composites with higher hydromagnesite content.

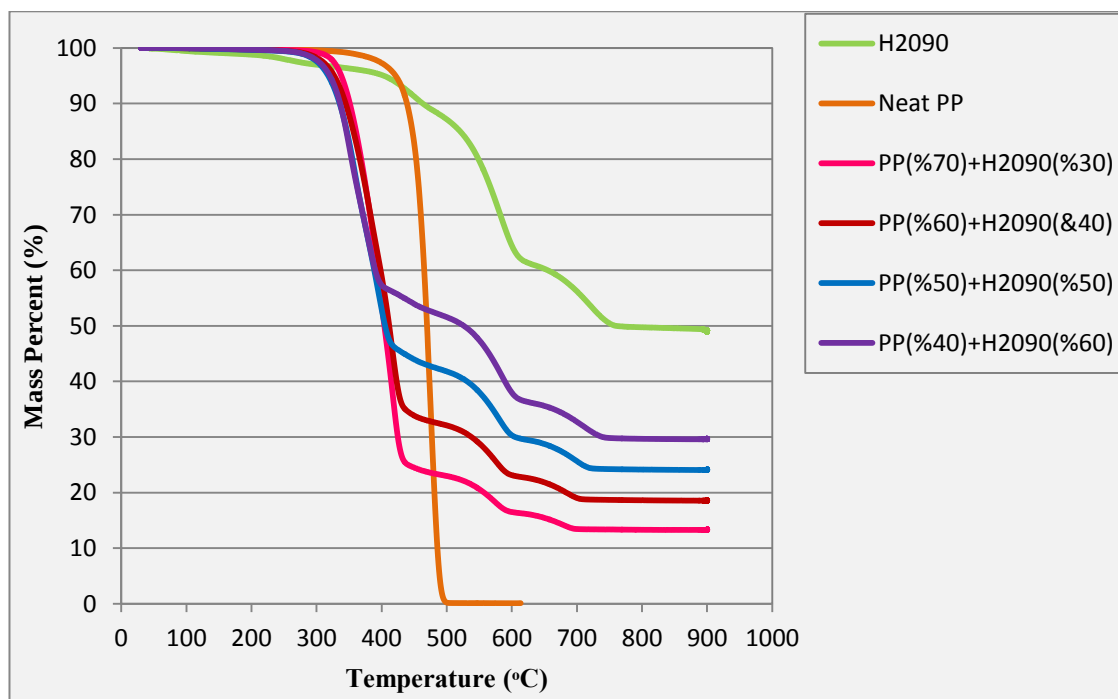


Figure 4.20 : TGA curves of PP, H2090 and H2090-PP composites with higher huntite content.

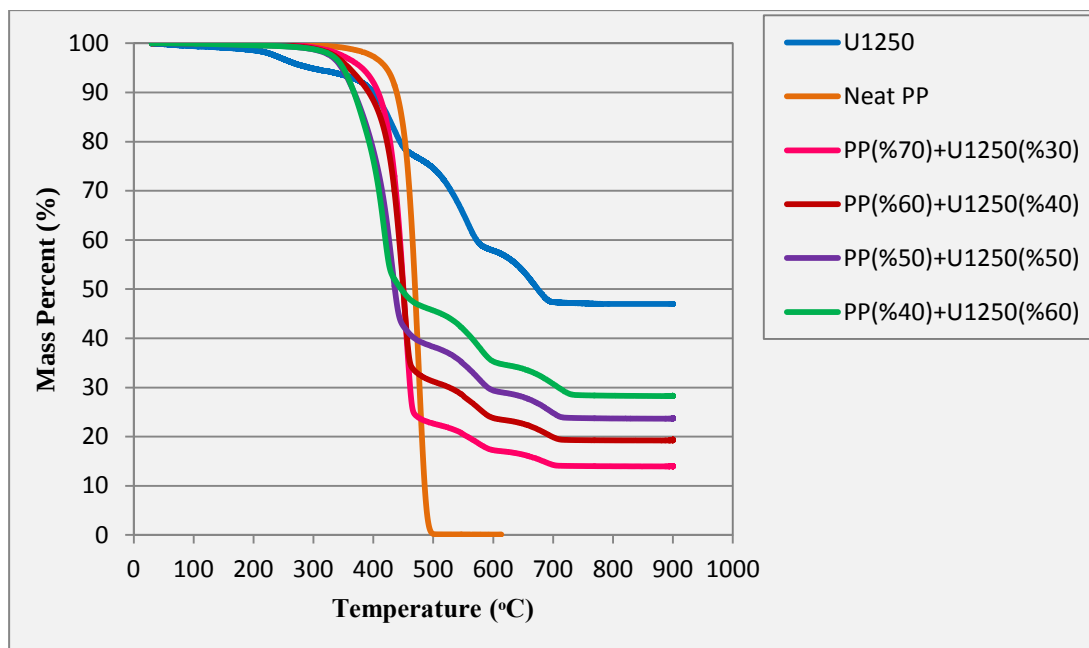


Figure 4.21 : TGA curves of PP, U1250 and U1250-PP composites with higher huntite content.

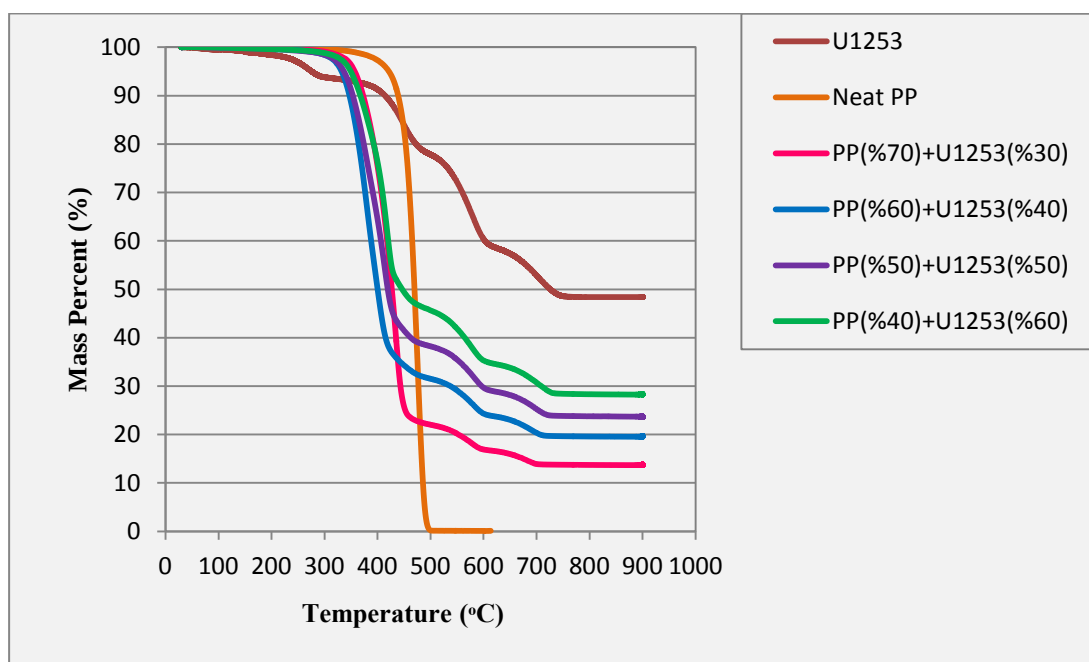


Figure 4.22 : TGA curves of PP, U1253 and U1253-PP composites with higher huntite content and silicone coated.

Formation of char residue, indicating thermal stability, was enhanced by adding the mixtures of H/HM. At the same loading level, char of H/HM-PP composites were higher than neat PP. In all cases, thermal stability of polypropylene was increased by adding the mixtures of H/HM as flame retardant materials. According to the ratio of H/HM in the mixtures and loading levels of the minerals, the mass loss of H/HM-PP

composites decreased with increasing amounts of H/HM in composites. The mass losses of natural mixtures, PP and the PP composites were illustrated at Table 4.6. And also experimental and calculated residue (%) at 900°C were estimated.

Table 4.6 : Max. rate mass loss temperature and inorganic residue of polymeric composites at 900°C.

Samples	H/HM loading levels (%)	Max. rate of mass loss temperature (°C)	Residue (%) at 900°C (experimental)	Residue(%) at 900°C (calculated)
Neat PP	0	475	-	
PP+U1250	30	450	13.96	14.10
	40	452	19.25	18.79
	50	431	23.67	23.49
	60	418	28.24	28.19
PP+U1253	30	434	13.70	14.52
	40	400	19.56	19.36
	50	416	23.68	24.20
	60	415	28.67	29.03
PP+H2090	30	418	13.28	14.68
	40	417	18.54	19.58
	50	400	24.08	24.47
	60	405	29.60	29.36
PP+LH15	30	463	13.90	13.81
	40	450	18.58	18.41
	50	447	23.08	23.02
	60	469	27.76	27.62

4.1.3.2 Measurement of Vicat softening point

Vicat softening temperature was determined according to the procedure explained in section 3.4.3.2. Test results are given in Table 4.7.

When we investigated the Vicat softening point by addition of H/HM particles Vicat A values were not affected too much. Vicat B values of polypropylene composites increased with addition of H/HM.

Table 4.7 : Vicat softening point test results of H/HM-PP composites.

Samples	H/HM loading levels (%)	Vicat Temperature (°C)	
		A	B
Neat PP	0	151 ± 2	94 ± 2
PP+U1250	30	153 ± 1	108 ± 3
	40	154 ± 1	111 ± 3
	50	154 ± 1	115 ± 3
	60	155 ± 1	120 ± 2
	30	154 ± 1	108 ± 3
PP+U1253	40	153 ± 1	110 ± 1
	50	155 ± 1	116 ± 2
	60	155 ± 1	122 ± 1
	30	153 ± 1	108 ± 1
PP+H2090	40	153 ± 1	115 ± 1
	50	154 ± 1	120 ± 2
	60	155 ± 2	123 ± 3
	30	153 ± 2	111 ± 1
PP+LH15	40	154 ± 1	115 ± 3
	50	155 ± 1	120 ± 2
	60	155 ± 1	127 ± 1
	30	153 ± 2	111 ± 1

4.1.4 Flame retardancy properties

Flame retardancy properties of polypropylene composites were investigated by limiting oxygen index (LOI), glow wire temperature (GWT) and UL 94 horizontal test methods.

4.1.4.1 Limiting oxygen index (LOI)

Limiting oxygen test was done according to the procedure explained in section 3.4.4.1. The limiting oxygen index test method provides to determine the minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that supports combustion of neat PP, mixtures of H/HM filled PP. LOI value of neat PP is around 18.2% and this is lower than loading levels of 30-40-50-60% by weight of H/HM filled PP. Polypropylene composites with increasing loading levels also increase the

LOI values. Table 4.8 and Figure 4.23 show effects of H/HM ratio in the mixtures and increasing loading level of mixtures of H/HM on flammability of PP.

Table 4.8 : LOI test results of H/HM-PP composites.

Samples	H/HM loading levels (%)	LOI (%)
Neat PP	0	18.0 ± 0.2
	30	19.6 ± 0.2
	40	20.2 ± 0.1
	50	20.7 ± 0.2
	60	21.8 ± 0.2
PP+U1250	30	20.0 ± 0.2
	40	20.6 ± 0.2
	50	21.9 ± 0.2
	60	22.8 ± 0.2
PP+U1253	30	19.8 ± 0.2
	40	20.3 ± 0.2
	50	21.6 ± 0.1
	60	22.5 ± 0.1
PP+H2090	30	20.2 ± 0.1
	40	21.5 ± 0.2
	50	22.9 ± 0.2
	60	24.3 ± 0.2

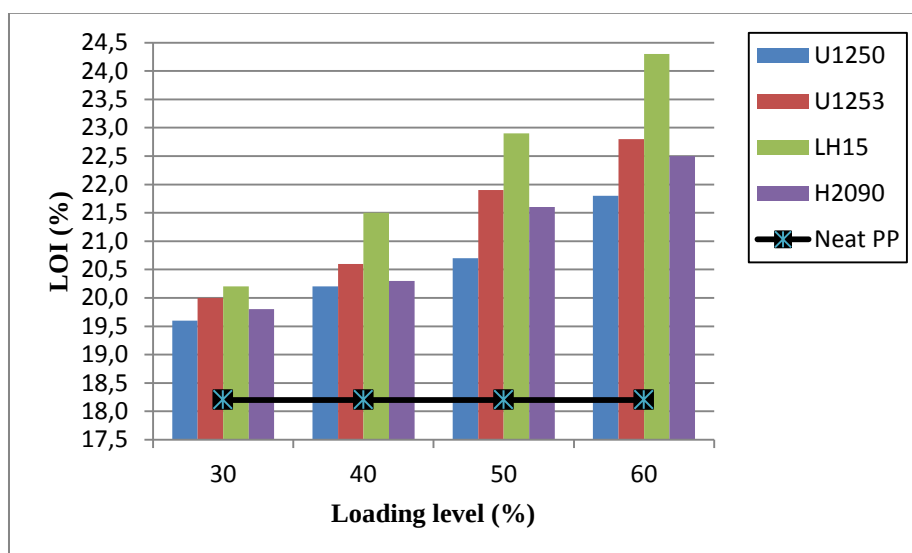


Figure 4.23 : LOI (%) test values of H/HM-PP composites.

The mixtures of H/HM increased limiting oxygen index (LOI) value significantly when loading levels in polypropylene were raised from 30% to 60%. In PP, mixtures of H/HM containing more than 50% hydromagnesite were shown to give an oxygen

index of 24.3% at a 60% loading level. Hydromagnesite is also known as active in the initial stages of the fire. It begins to decompose at about 220°C and releases water and carbon dioxide. Huntite starts to decompose at about 470°C so hydromagnesite is more effective than huntite.

The silicone coated mixture of H/HM with higher content gave an oxygen index 22.8% at a 60% loading level. It was higher than other samples containing between 66% and 77% huntite.

Consequently, these results showed that LOI values of the polymeric composites increased with increasing loading levels and increasing hydromagnesite content in the mixtures of H/HM.

4.1.4.2 Glow wire test (GWT)

Glow wire test was done according to the procedure explained in section 3.4.4.2. GWT test results provide a way of comparing the ability of materials to extinguish flames and their ability to not produce particles capable of spreading fire. Glow wire test results are given in Table 4.9, Table 4.10, Table 4.11, and Table 4.12.

Table 4.9 : Glow wire test results of U1250-PP composites.

Sample	H/HM loading levels (%)	Glow Wire Temperature (°C)	
		750	850
PP+U1250	30	There are flames and glowing of the sample.	Burning time (80) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	40	There is no flame and no glowing.	Burning time (74) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	50	There is no flame and no glowing.	Burning time (70) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	60	There is no flame and no glowing.	Burning time is less than 30 seconds after removal of the glow wire and the cotton does not ignite.

Table 4.10 : Glow wire test results of U1253-PP composites.

Sample	H/HM loading levels (%)	Glow wire temperature (°C)	
		750	850
PP+U1253	30	There are flames and glowing of the sample.	Burning time (83 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	40	There is no flame and no glowing.	Burning time (65 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	50	There is no flame and no glowing.	Burning time (62 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	60	There is no flame and no glowing.	Burning time is less than 30 seconds after removal of the glow wire and the cotton does not ignite.

Table 4.11 : Glow wire test results of H2090-PP composites.

Sample	H/HM loading levels (%)	Glow Wire Temperature (°C)	
		750	850
PP+H2090	30	There are flames and glowing of the sample.	Burning time (90 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	40	There is no flame and no glowing.	Burning time (70 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	50	There is no flame and no glowing.	Burning time (65 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	60	There is no flame and no glowing.	Burning time (55) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.

Table 4.12 : Glow wire test results of LH15-PP composites.

Sample	H/HM loading levels (%)	Glow wire temperature (°C)	
		750	850
PP+LH15	30	There is no flame and no glowing.	Burning time (70 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	40	There is no flame and no glowing.	Burning time (66 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	50	There is no flame and no glowing.	Burning time (62 s) is much more than 30 seconds after removal of the glow wire and the cotton does not ignite.
	60	There is no flame and no glowing.	Burning time is less than 30 seconds after removal of the glow wire and the cotton does not ignite.

The mixtures of H/HM decreased burning time of polypropylene composites significantly when loading levels in polypropylene were raised from 30% to 60%. The effects of H/HM ratio in mixtures of H/HM on flame retardancy properties of polymeric composites were investigated. The tests were done at temperatures of 750°C and 850°C. The glow wire test results showed that compounds containing higher hydromagnesite (LH15) content had positive effect on flame retardancy. Specimens (LH15, U1250, and U1253) achieved the test at temperature of 750°C and 850°C at 60% loading level. But compounds containing the highest huntite content (H2090) did not achieve the test at temperature of 850°C. Just compound containing LH15 at 30% loading level achieved the test at temperature of 750°C. Test results indicated that higher hydromagnesite content was much more effective than huntite.

4.1.4.3 UL 94 flammability test (horizontal)

UL 94 flammability test was done according to the procedure explained in section 3.4.4.3. Burning time, length and burning rate of polypropylene composites were indicated at Table 4.13. Most of polymeric composites did not burn in atmospheric conditions. Burning time and length should be taken account when burning rates of

polypropylene composites were compared to each other. Some polymeric composites burned completely in air but some of them burned only a part. All polypropylene composites having high hydromagnesite ratio (LH15) did not burn in atmospheric conditions. Polymeric composites having high huntite ratio except at 30% loading level of mixtures of H/HM also did not burn in horizontal burning tests. Flammability resistance of PP was enhanced with addition of the huntite and hydromagnesite in PP matrix.

At 30% loading level, composites containing high huntite content burned in atmospheric conditions as shown in Table 4.13. However, their horizontal burning rates were lower than neat PP. The test results showed that higher hydromagnesite content samples addition to PP increased flammability resistance of PP. And also higher huntite samples increased flammability resistance of PP at appropriate loading levels. Burning rate of polymeric composites changed according to the ratio of H/HM in the mixtures and loading levels of the minerals.

Table 4.13 : UL 94 test results of neat PP and mixtures of H/HM filled PP.

Sample	H/HM loading levels (%)	Burning Length (mm)	Burning Time (s)	Burning Rate (mm/s)
Neat PP	0	75	270	0.28
PP+U1250	30	75	510	0.15
	40	-	-	Not Burn
	50	-	-	Not Burn
	60	-	-	Not Burn
PP+U1253	30	70	525	0.13
	40	-	-	Not Burn
	50	-	-	Not Burn
	60	-	-	Not Burn
PP+H2090	30	75	349	0.22
	40	1	48	0.03
	50	-	-	Not Burn
	60	-	-	Not Burn
PP+LH15	30	-	-	Not Burn
	40	-	-	Not Burn
	50	-	-	Not Burn
	60	-	-	Not Burn

4.2. Polypropylene/Mixture of Huntite and Hydromagnesite/Zinc Borate Composite

In order to improve flame retardancy properties of polypropylene, zinc borate and LH 15 added to polypropylene to obtain polypropylene composite. Zinc borate is an important additive to help achieve excellent flame resistance in polymers. Zinc borate can be added to any flame retardant system and will improve flame test results with minimal effect on compound properties. Zinc borate will form a glassy char at high temperatures that prevents flame propagation. It also releases water of hydration similar to hydromagnesite.

4.2.1. Physical properties results

4.2.1.1. Measurement of density

Measurement of density was done as defined as in section 3.4.1.1. Zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) has density of approximately 2.70 g/cm^3 . Incorporation of LH 15 (H/HM) and zinc borate into the polypropylene matrix resulted in processing composites with higher density. The highest loading level of 10 wt.% ZnB and 50 wt.% LH 15 increased the density up to 1.5 g/cm^3 . The results indicated that there were no significant differences in the density values. Test results are given in Table 4.14.

Table 4.14 : Test results of density measurements of neat polypropylene, zinc borate and LH 15 filled polypropylene.

Samples	H/HM loading levels (%)	ZnB (%)	Density (g/cm^3)
Neat PP	0	-	0.903 ± 0.003
PP+LH 15	60	-	1.436 ± 0.002
PP+LH 15+ZnB	50	10	1.485 ± 0.005

4.2.1.2. Determination of melt of index

Melt flow index (MFI) test was done as described in section 3.4.1.4. MFI test results indicated that a steady decrease with adding zinc borate and LH 15 (H/HM). Neat polypropylene has MFI of 49.7 g/10 min. Zinc borate and LH 15 decreased MFI to approximately 2.8 g/10 min. By the entrance of H/HM and zinc borate particles to the matrix the melt flow index values decreased due to decreased chain movements

of polypropylene. The MFI test results of neat PP and zinc borate, LH 15 filled PP are given in the Table 4.15.

Table 4.15 : Melt flow index test results of neat PP, zinc borate and LH 15 filled polypropylene.

Samples	H/HM loading levels (%)	Zinc Borate (%)	MFI (g/10min)
Neat PP	0	-	49.7 ± 0.2
PP+LH 15	50	-	3.5 ± 0.2
	60	-	0.6 ± 0.1
PP+LH 15+ZnB	50	10	2.8 ± 0.2

4.2.2 Mechanical properties results

Mechanical properties of polypropylene composites were determined by using mechanical testing method.

4.2.2.1 Tensile properties

Tensile test was done according to the procedure explained in section 3.4.2.1. Experimental mechanical test results of all samples are shown in Table 4.16.

Table 4.16: Average tensile test results of neat PP and H/HM and zinc borate filled polypropylene.

Samples	H/HM loading levels (%)	ZnB (%)	Elastic Mod. (MPa)	Max. Stress (MPa)	Strain (%)
Neat PP	0	-	1924 ± 30	36 ± 3	26.5 ± 3
PP+ LH 15	50	-	4414 ± 158	26 ± 1	1.3 ± 0.1
	60	-	5753 ± 155	23 ± 1	0.5 ± 0.1
PP+LH 15+ZnB	50	10	5235 ± 170	25 ± 2	1.5 ± 0.1

Elastic modulus, strain and maximum stress are known as the most important mechanical properties of PP composites. The tensile strength of neat PP was around and this was much higher than LH 15 and zinc borate filled PP. Differences were not observed.

Elastic modulus increased with adding zinc borate and LH 15 into PP. Elastic modulus of neat PP was 1924 MPa and the loading of zinc borate and H/HM into PP increased the elastic modulus up to 5235 MPa.

Strain values of PP composites decreased with increasing amounts of mixtures of H/HM in PP composites. Strain values of PP composites decreased with adding zinc borate and LH 15 together. Elongation of neat PP was 27%. Zinc borate and LH 15 addition almost decreased elongation of PP matrix to 1.5%. This result was better than 60 wt.% LH 15 filled PP.

4.2.2.2 Flexural properties

Flexural test was done as three point bending method according to the procedure explained in section 3.4.2.2. Test results are given in Table 4.17.

Table 4.17 : Flexural test results of neat PP and H/HM and zinc borate filled polypropylene.

Samples	H/HM loading levels (%)	ZnB (%)	Modulus (MPa)	Stress (MPa)	Strain (%)
Neat PP	0	-	1338 ± 50	45 ± 3	8.2 ± 0.4
PP + LH 15	50	-	4032 ± 30	43 ± 2	1.8 ± 0.2
	60	-	5267 ± 80	40 ± 3	0.9 ± 0.1
PP + LH 15+ZnB	50	10	4978 ± 65	40 ± 3	1.3 ± 0.3

Flexural modulus values increased with the addition of zinc borate and LH 15 (H/HM) into polymeric matrix. Flexural stress value of neat PP was around 45 MPa. The loading level 50 wt.% LH 15 and %10 wt.% ZnB decreased the flexural stress to 40 MPa. In addition, flexural stress values of polymeric composites were close to each other. Flexural strain value of neat PP was around 8.24 % and this was much higher than LH 15 and ZnB filled PP composite.

4.2.2.3 Izod impact properties

Izod impact test was done according to the procedure explained in section 3.4.2.3. Izod impact test results are given in Table 4.18.

Table 4.18: Izod impact test results of neat PP and H/HM and zinc borate filled polypropylene.

Samples	H/HM loading levels (%)	ZnB (%)	Izod Impact Strength (kJ/m ²)
Neat PP	0	-	2.8 ± 0.1
PP + LH 15	50	-	2.1 ± 0.1
	60	-	1.9 ± 0.2
PP + LH 15 + ZnB	50	10	2.4 ± 0.2

Izod impact strength value of PP was around 2.8 kJ/m². At 50 wt.% LH 15 and 10 wt.% ZnB loading level, neat PP and other samples were close to each other in terms of impact strength.

4.2.3 Thermal properties results

Thermal gravimetric analysis (TGA) was done according to the procedure explained in section 3.4.3.1. The raw materials were analyzed individually as shown Figure 4.24.

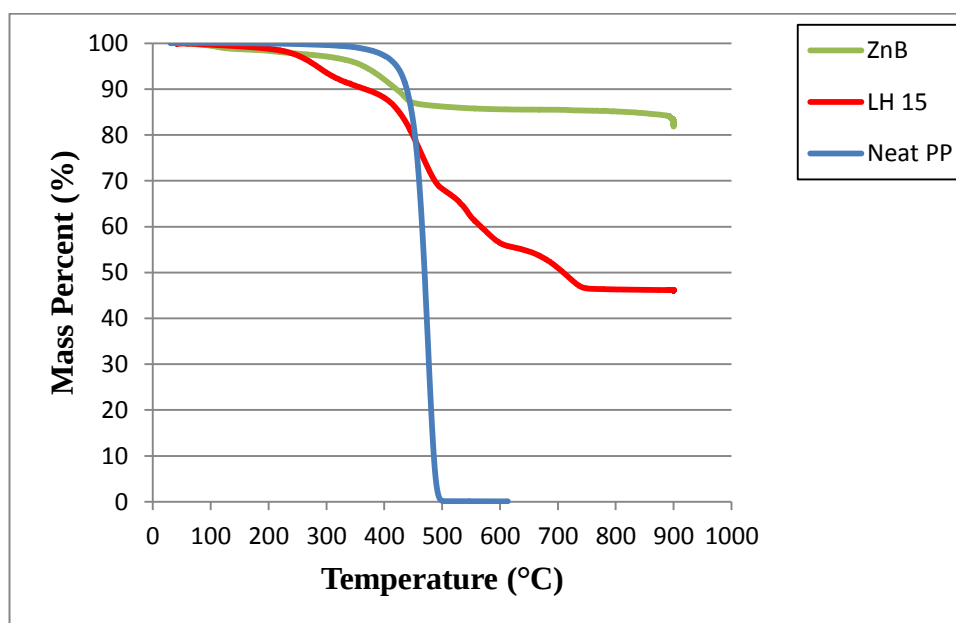


Figure 4.24 : Thermal degradation of raw materials.

TGA which is a good way in studying dehydration of water in the zinc borate was carried out to have an idea about thermal behaviour of the zinc borate particles. Low weight loss until 120°C (1%) was due to the physical water on the zinc borate particles. Then, zinc borate particles started to lose its crystal water at 120°C and loss continued until 450°C with a total mass loss of 13% between 120-450°C. The results were in agreement with theoretical values of zinc borate with chemical composition of $2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3\text{--}3.5\text{H}_2\text{O}$. (weight loss of zinc borate which has 3 mole water is 12.7% and the weight loss of zinc borate which has a 3.5 mole water is 14.5%) TG results showed that synthesized zinc borate had a 3-3.5 molecular crystal water.

Formation of char residue, indicating thermal stability, was enhanced by adding the zinc borate and LH 15 into the polypropylene matrix. TGA curves added together to predict the behaviour of LH 15 and zinc borate filled PP composite as shown in Figure 4.25.

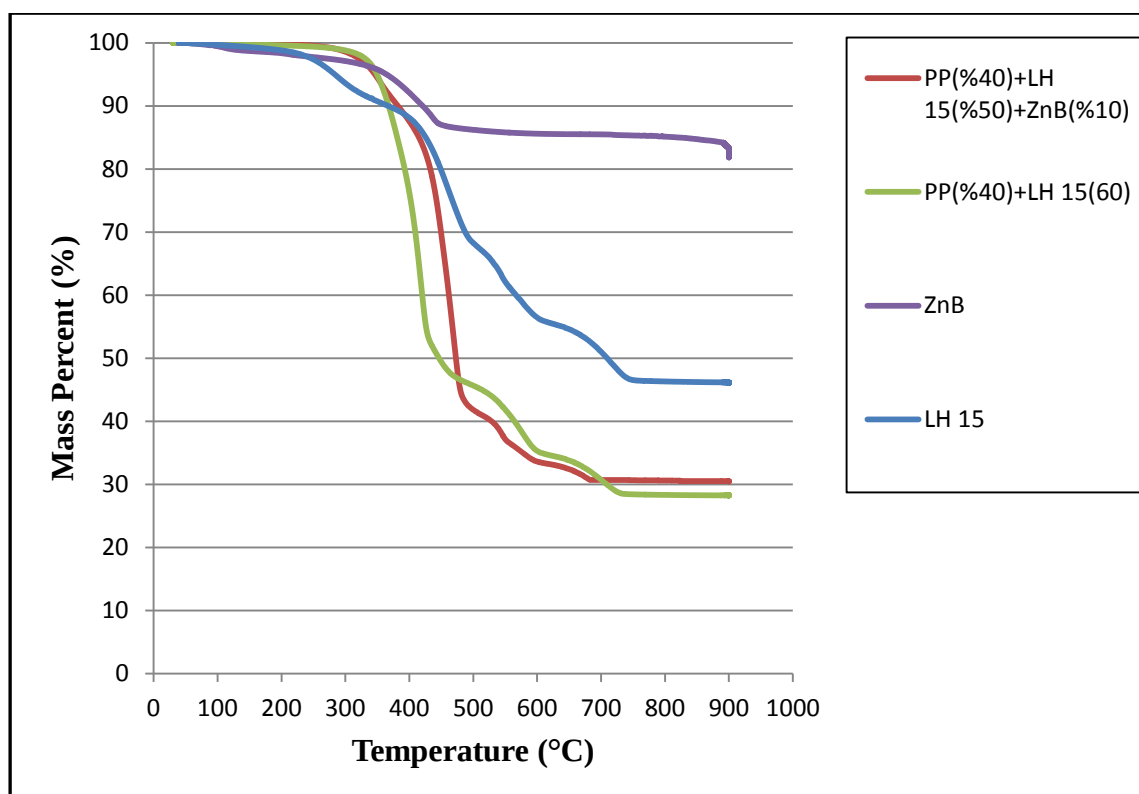


Figure 4.25 : TGA curves of LH15, zinc borate and LH 15 filled PP composites.

4.2.4 Flame retardancy properties

Flame retardancy properties of LH 15 and zinc borate filled PP composite were investigated glow wire temperature and UL 94 horizontal test methods.

4.2.4.1 Glow wire test (GWT)

Glow wire test was done according to the procedure explained in section 3.4.4.2. Glow wire test results are given in Table 4.19.

Table 4.10 : Glow wire test results of LH 15 and zinc borate filled PP composite.

Sample	H/HM loading levels (%)	ZnB (%)	Glow wire temperature (°C)	
			750	850
PP + LH 15 +ZnB	50	10	There is no flame and no glowing.	Burning time is less than 30 seconds after removal of the glow wire and the cotton does not ignite.

The glow wire test results showed that compounds containing zinc borate and LH 15 had positive effect on flame retardancy.

4.2.4.2 UL 94 Flammability Test (Horizontal)

UL 94 flammability test was done according to the procedure explained in section 3.4.4.3. Burning time, length and burning rate of polypropylene composites were indicated at Table 4.20. Burning time and length should be taken account when burning rates of polypropylene composites were compared to each other. All polypropylene composites having high hydromagnesite ratio (LH15) and zinc borate did not burn in atmospheric conditions.

Table 4.11 : UL 94 test results of neat PP and LH 15 and ZnB filled PP.

Sample	H/HM loading levels (%)	ZnB (%)	Burning Length (mm)	Burning Time (s)	Burning Rate (mm/s)
Neat PP	0	-	75	270	0.28
PP+LH 15	50	-	-	-	Not Burn
	60	-	-	-	Not Burn
PP+LH 15+ZnB	50	10	-	-	Not Burn

5. CONCLUSIONS

The objective of this study was to prepare flame retardant polypropylene composites. The mixtures of huntite/hydromagnesite (H/HM) comprising varied proportions of huntite and hydromagnesite (4 different grades; U1250, U1253, H2090, LH15) were processed with polypropylene by using a twin-screw extruder at 185°C and 100 rpm. Polypropylene composites were prepared varying the H/HM percentages (30, 40, 50, and 60 wt.%) in the formulation. The effects of H to HM weight ratio in the H/HM grades and H/HM loading level on the flame retardancy performance and mechanical properties of composites were investigated. In addition, H/HM filled polypropylene composites were compared with neat polypropylene.

Density measurements showed a steady increase with increasing H/HM loading level. H/HM is an inorganic mixture and has a higher density of 2.5 g/cm³ than that of polypropylene which is 0.9 g/cm³. Therefore, the incorporation of H/HM into the polypropylene matrix resulted in processing composites with higher density. The highest loading of 60 wt.% H/HM increased the density up to 1.5 g/cm³.

The ratios of huntite and hydromagnesite in the mixtures were determined based on XRD results. XRD analysis of the mixtures of H/HM showed characteristic peaks of huntite and hydromagnesite. H2090 consists of huntite and hydromagnesite with the higher huntite content. It is not surface treated. LH15 consists of huntite and hydromagnesite. This grade contains mainly hydromagnesite but does still contains a proportion of huntite. U1250 and U1253 contain huntite and hydromagnesite with higher huntite content. U1253 is surface treated with silicone.

FTIR results showed that, a very sharp band occurred at 3647 cm⁻¹ which must be due to an almost free O-H vibration. The pair of strong sharp bands occurred at 3515 and 3450 cm⁻¹ in the spectrum because of hydromagnesite (Mg₅(CO₃)(OH)₂·4H₂O). Magnesium carbonate indicates lower intensity absorptions at 550-700 cm⁻¹. In addition, polypropylene shows peaks at 2922 cm⁻¹ due to the methyl (–CH₃) groups.

Rheological properties were affected by the addition of H/HM mixtures into polypropylene matrix at different loading levels. The results indicated that the melt flow index (MFI) values decreased significantly with increasing loading level. Neat polypropylene has MFI of 50 g/10 min. The highest loading of 60 wt% H/HM decreased MFI up to 0.6 g/min. By the entrance of huntite and hydromagnesite particles to the matrix the melt flow index values decreased due to decreased chain movements of polypropylene.

SEM observations showed that during extrusion hydromagnesite particles are well dispersed than huntite particles in polypropylene composites. There is no interaction between huntite/hydromagnesite and polypropylene except mechanical adhesion between filler and polypropylene.

The effect of H/HM loading, H to HM ratio and surface treatment of mixture of minerals with silicone (U1253) on the mechanical properties of polypropylene composites were investigated. Tensile strength of polypropylene composites decreased with increasing loading level. The tensile strength of neat polypropylene was around 36MPa and this was much higher than loading levels of 30-40-50-60% by weight of H/HM filled polypropylene. The highest loading of 60 wt.% decreased the tensile strength to 23 MPa. At the same loading levels, tensile strength values of polypropylene composites were close to each other. Silicone coated mixture of H/HM did not improve elastic modulus properties of polypropylene composites. Elastic modulus increased with increasing amounts of H/HM in polypropylene composites. Elastic modulus of pure polypropylene was 1924 MPa and The highest loading of 60wt.% increased the elastic modulus to 6000 MPa. The silicone coated mixture of H/HM did not improve the elastic modulus values. The silicone coated mixture of H/HM did not improve the elongation at break (strain) values of polypropylene composites.

Flexural modulus values were increased with the addition of mixtures of H/HM into the polymeric matrix. In addition, silicone coated mixture of H/HM did not modify flexural modulus values of polymeric composites. The flexural modulus value of neat polypropylene was around 1338 MPa and this was much lower than loading levels of 30-40-50-60% by weight of H/HM filled polypropylene. The Flexural stress value of neat polypropylene was around 45 MPa. Silicone coated sample with higher huntite content (U1253) and uncoated higher huntite content sample (H2090) were

greater flexural stress values than other samples and neat polypropylene at a 30% loading level. The Flexural strain value of neat polypropylene was around 8.2% and this is much higher than loading levels of 30-40-50-60% by weight of mixtures of H/HM filled polypropylene. The results showed a steady decrease with increasing loading level. Higher huntite content sample (H2090) was much lower strain values compared to other samples. Silicone coated sample did not modify strain properties of polymeric composites.

The Izod impact strength value of neat polypropylene was around 2.8 kJ/m^2 and this was much lower than other samples at 30% loading level. At 40% loading level, neat polypropylene and other samples were close to each other in terms of impact strength. The highest loading of 60wt.% H/HM decreased the Izod impact strength to 1.9 kJ/m^2 .

The decomposition of polypropylene started at 262°C which was higher than the initial decomposition temperature of hydromagnesite so the compound containing higher hydromagnesite content did not begin to loss mass at the decomposition temperature of hydromagnesite (220°C). The endothermic decomposition took heat from the solid phase slowing decomposition of the polymer and the release of water and carbon dioxide into the flame slowed the rate of burning. The decomposition of hydromagnesite obviously helped with putting out the flame, but platy huntite particles increased the viscosity of the molten polymer helping to prevent dripping polypropylene. Formation of char residue, indicating thermal stability, was enhanced by adding H/HM. At the same loading level, char of H/HM- polypropylene composites were higher than neat polypropylene. In all cases, thermal stability of polypropylene was increased by adding H/HM as flame retardant materials. According to the ratio of H/HM in the mixtures and loading levels of the minerals, the mass loss of H/HM- polypropylene composites decreased with increasing amounts of H/HM in composites.

When we investigated the Vicat softening point by addition of H/HM particles Vicat A values were not affected too much. Vicat B values of polypropylene composites increased with addition of H/HM.

The glow wire test results showed that polypropylene composites containing higher hydromagnesite (LH15) content had positive effect on flame retardancy. Specimens

(LH15, U1250, and U1253) achieved the test at temperature of 750°C and 850°C at 60% loading level. But compounds containing the highest huntite content (H2090) did not achieve the test at temperature of 850°C. In addition, just compound containing LH15 at 30% loading level achieved the test at temperature of 750°C.

The results of this study showed that the addition of H/HM in polypropylene matrix increased flammability resistance of polypropylene. Most of polypropylene composites did not burn in atmospheric conditions. UL 94 horizontal test method should be used to relative burning characteristics of plastic materials. Polypropylene composites containing higher hydromagnesite content (LH15;55-60%) showed better burning characteristics than other samples at 30% loading level according to horizontal test method.

In order to improve flame retardancy properties of polypropylene, zinc borate and LH 15 (huntite/hydromagnesite mixture) were used together. %10 zinc borate and % 50 LH 15 filled polypropylene composite was prepared by the twin screw co-rotating extruder and injection molded test specimens were subjected to the mechanical, thermal, and flammability tests. Test results can explain as; the addition of zinc borate into the PP/LH 15 matrix caused an improvement in inflammability properties.

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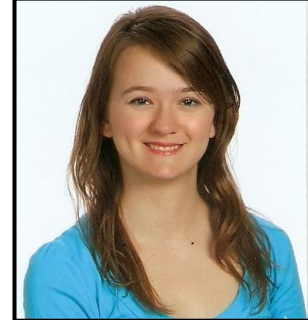
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