

ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

**INVESTIGATION OF MECHANICAL, PHYSICAL AND FLAME RETARDANT
PROPERTIES OF POLYPROPYLENE COMPOUNDS USING SYNERGISTIC
COMBINATION OF MINERALS AND INTUMESCENT FLAME RETARDANTS**



Ph.D. THESIS

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Department of Polymer Science and Technology

Polymer Science and Technology Programme

FEBRUARY 2022



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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

**POLİPROPİLEN BİLEŞİKLERİNİN MEKANİK, FİZİKSEL VE ALEV GECİKTİRİCİ
ÖZELLİKLERİNİN MİNERALLER VE KÖPÜREN ALEV GECİKTİRİCİLERİN
SİNERJİSTİK KOMBİNASYONUNUN KULLANILARAK İNCELENMESİ**

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To my lovely daughter,



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ABBREVIATIONS

ASTM	: American Society for Testing and Materials
APP	: Ammonium Polyphosphate
ATH	: Aluminium Tri Hydrate
BS	: British Standards
EG	: Expandable Graphite
EPDM	: Ethylene Propylene Diene Monomer
FR	: Flame Retardant
GWT	: Glow Wire Temperature
HB	: Horizontal Burning
HBCD	: Hexabromocyclododecane
HDPE	: High-Density Polyethylene
IFR	: Intumescent Flame Retardant
ISO	: International Organization for Standardization
LOI	: Limiting Oxygen Index
L/D	: Length/Diameter
MFI	: Melt Flow Index
MPa	: Mega Pascal
PER	: Pentaerythritol
PMMA	: Poly (methyl methacrylate)
PP	: Polypropylene
SEM	: Scanning Electron Microscopy
TGA	: Thermal Gravimetric Analysis
UL	: Underwriters Laboratory
ZS	: Zinc Stearate



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INVESTIGATION OF MECHANICAL, PHYSICAL AND FLAME RETARDANT PROPERTIES OF POLYPROPYLENE COMPOUNDS USING SYNERGISTIC COMBINATION OF MINERALS AND INTUMESCENT FLAME RETARDANTS

SUMMARY

In daily life, polymeric materials can be used in many different applications because of their low price, processability and also good features. Polypropylene is very important polymer of polyolefins. Especially, polypropylene material is used in home appliances and automotive sector due to its constructive properties. Beside good properties, polypropylene has also negative properties to use in industry therefore some additives need to be compounded with plastics depending on the application fields to achieve the desired features. In order not to lose desired functional properties, additive can be added to polymers at optimum quantity. Due to fires in the world, increasing the flame retardant properties of materials becomes even more important so the usage of flame retardant additives and smoke suppressants are increasing day by day in polymeric materials. These materials have important role on improving flame retardancy properties of polymeric materials but environmental friendly materials have to be used due to toxicological properties of halogenated flame retardant additives so environmental friendly systems like halogen free and mineral based flame retardant materials have to be used inside polymeric materials. Polypropylene has been chosen as main polymer due to usage of home appliances sector. The main goal of this study is to increase flame retardancy features of polypropylene and create synergistic effect with using intumescent flame retardant system, mica, colemanite and expandable graphite. Commercially available materials like IFR, mica, colemanite and expandable graphite have been chosen not to face any production restriction. IFR is environmental friendly and halogenated flame retardant additive. Mica and colemanite minerals are abundant materials on the earth and their price is lower compared to IFR system. Expandable graphite is promising flame retardant material to increase flame retardancy properties of polypropylene. In this research, concentration of flame retardant additives was adjusted at 30 wt% mass of overall volume of compound. Potential flame retardant additives were added with mass fractions of 2, 4, 6, 8, 15 wt.%. Flame retardant additives were also added to the polypropylene at a rate of 30 wt% and its effect also were observed. Flame retardant additives filled compounds were prepared in the co-rotating twin screw extrusion at 100 rpm screw speed and at 185 °C. After production of compounded materials, standard testing specimens were prepared in the injection molding machine. Density and melt flow index(MFI) tests were carried out to define physical properties of sampling parts. Mechanical testing were conducted to define mechanical features of sampling materials. Thermal gravimetric analysis(TGA) and heat deflection temperature(HDT) tests were used to measure thermal properties of compounds. Investigation of char layer was evaluated using scanning electron microscopy(SEM). Furthermore, limiting oxygen index(LOI), UL 94 vertical flammability test, and glow wire test were used to determine flame

retardancy performance of compounds. In the first stage of this thesis, IFR was added to polypropylene material at 20-25-30 wt% loading levels to evaluate the influence of the IFR system on polypropylene and to determine ideal formulation to catch desired mechanical, physical and flame retardancy properties. The blend compounds were designated as PP80/IFR20, PP75/IFR25, PP70/IFR30 respectively. In this terminology, the letters “PP” and “IFR” were used to indicate the plastic polypropylene and flame retardant additive intumescent flame retardant. The numbers following the sample same were used to represent the loading level of materials by weight percent. According to flame retardancy test results, IFR has an important effect on flame retardancy, LOI values reached to 37.9% with loading level of 30 wt% IFR. PP75/IFR25 and PP70/IFR30 passed to UL 94 vertical tests and all compounds passed glow wire tests both 750 and 850°C. TGA results showed that thermal stability of compounds enhanced by adding IFR to the polypropylene. In the second stage of thesis, IFR and mica were mixed with PP material in co-rotating twin screw extrusion to increase flame retardancy of PP. The blend compounds were designated PP70/IFR28/M2, PP70/IFR26/M4, PP70/IFR24/M6, PP70/IFR22/M8, PP70/IFR15/M15, PP70/IFR0/M30 respectively. In this terminology, the letters “PP”, “IFR” and “M” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and mineral mica. The LOI, UL 94 and glow wire test results represented that mica had a considerable effect on flammability and LOI rate which can reach to 37.5 % with loading level of 2 wt% mica at the overall quantity of flame retardant ingredients fixed constant at 30 wt.%. Additionally, the PP/IFR compounds passed UL 94 V0 rating and both 750 °C and 850 °C glow wire tests and with 2-8 wt% mica loading. According to TGA analyses, the results indicated that mica improved the thermal uniformity of PP/IFR compounds and also promoted formation of char layer. When mica mineral added to polypropylene without IFR system, it has no influence on flammability of polypropylene. Mica content can be used up to 8 wt.% in polypropylene compound with IFR material.

In the third stage of thesis, synergistic action between IFR and EG in PP compounds was observed. The blend compounds were designated PP70/IFR28/EG2, PP70/IFR26/EG4, PP70/IFR24/EG6, PP70/IFR22/EG8, PP70/IFR15/EG15, PP70/IFR0/EG30 respectively. In this terminology, the letters “PP”, “IFR” and “EG” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and additive expandable graphite. The LOI, UL 94 and glow wire test results represented that EG had prominent effect on flammability and LOI rate which can reach to 37.2 % with loading level of 4 wt.% EG at the overall quantity of flame retardant ingredients fixed constant at 30 wt.%. Additionally, the PP/IFR compounds passed UL 94 V0 grade and both 750 °C and 850 °C glow wire tests and with 2-6 wt.% EG loading. These tests demonstrated that the addition of EG into PP/IFR system improved the flame retardancy properties of PP compounds. It means that synergistic is available between IFR and EG additives. HDT values can be increased with addition of EG as a result, the load carrying ability will be increased during fire. Furthermore, it is difficult to process EG with PP material at 30 wt% loading level of EG. It is not suitable in terms of processability. In terms of mechanical properties, elastic modulus values increased with addition of EG to PP/IFR compound.

In the fourth stage of thesis, IFR and colemanite were mixed with PP material in co-rotating twin screw extrusion to create flame retardant system and increase flame retardancy of PP. The blend compounds were designated PP70/IFR28/C2, PP70/IFR26/C4, PP70/IFR24/C6, PP70/IFR22/C8, PP70/IFR15/C15, PP70/IFR0/C30 respectively. In this terminology, the letters “PP”, “IFR” and “C” were used to

indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and mineral colemanite. The LOI, UL 94 and glow wire test results represented that colemanite had a valuable influence on flammability and LOI grade which can reach to 37.6 % with loading level of 2 wt.% colemanite at the overall quantity of flame retardant ingredients fixed constant at 30 wt.%. Additionally, the PP/IFR compounds passed UL 94 V0 grade and both 750 °C and 850 °C glow wire tests and with 2-6 wt.% colemanite loading. Tensile strength value of polypropylene homopolymer decreased when IFR and colemanite added to polymeric system. The stiffness of PP70/IFR0/C30 sample was higher than PP70/IFR30/C0 sample when temperature increased. When all properties have been taken into consideration, colemanite can be used up to 4 wt% in IFR filled PP compound.

In the fifth stage of thesis, IFR, colemanite, mica and expandable graphite were compounded with PP material in the different combinations and loading levels to create synergistic flame retardant system and increase flame retardancy properties of final compound. Combinations and loading levels were determined according to test results of binary mixtures of IFR and other potential flame retardant materials. The blend compounds were designated PP70/IFR20/M8/C2, PP70/IFR22/M6/C2, PP70/IFR22/M4/C4, PP70/IFR22/EG6/C2, PP70/IFR22/EG4/C4, PP70/IFR22/EG6/M2, PP70/IFR22/EG4/M4, PP70/IFR22/EG2/M6, PP70/IFR20/EG2/M8 respectively. In this terminology, the letters “PP”, “IFR”, “C”, “EG”, “M” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant, mineral colemanite, expandable graphite and mica. The LOI, UL 94 and glow wire test results indicated that mica and colemanite created synergistic effect with IFR in PP compound when they used at reasonable amount. The LOI achieved up to 33%, and UL 94 test attained V0 rate for PP/IFR/mica/colemanite samples at the total amount of flame retardant additives kept constant at 30 wt.%. Additionally the PP/IFR/mica/colemanite compounds passed UL 94 V0 rating and both 750 °C and 850 °C glow wire tests. According to TGA analyses, it is obvious that the char residue increased by the increasing loading of mica. Colemanite gives their structure water to the system and they create cooling effect on the surface. PP70/IFR30 and PP70/IFR20/M8/C2 samples indicated the same mechanical properties in terms of elastic module value. Increasing of mica content increased elastic module but decreased tensile strength and strain values. PP70/IFR20/EG2/M8 and PP70/IFR20/M8/C2 showed the same tensile strength and strain values but the formula containing expandable graphite indicated lower elastic modulus. Consequently, it is observed that the usage of colemanite, mica and expandable graphite in certain proportions instead of IFR into the PP compound doesn't adversely affect the mechanical properties of final compound. Flame retardant additives don't improve impact resistance and also don't create a synergistic effect in terms of izod impact properties. In the mica, colemanite and IFR mixtures, when mica used at 8 wt% loading level, HDT value reached to 94.5°C. When colemanite amount started to increase in the compound with mica and IFR, HDT values decreased. In the expandable graphite mixtures, expandable graphite filled flame retardant compound reached to 96.2 °C. According to all test results, mica and colemanite materials can show synergistic effect when they used with IFR in PP compound at reasonable amount. Especially, colemanite is abundant and commercial available material in Turkey. Usage of this material with reduction of IFR amount in the final compound will bring cost reduction and national resource will be used.



POLİPROPİLEN BİLEŞİKLERİNİN MEKANİK, FİZİKSEL VE ALEV GECİKTİRİCİ ÖZELLİKLERİNİN MİNERALLER VE KÖPÜREN ALEV GECİKTİRİCİLERİN SİNERJİSTİK KOMBİNASYONUNUN KULLANILARAK İNCELENMESİ

ÖZET

Polimerik malzemeler uygun maliyetleri, proses edilebilirlikleri ve iyi özellikleri nedeniyle günlük hayatta farklı uygulamada kullanılabilirler. Polipropilen, poliolefinlerin en önemli polimeridir. Polipropilen özellikle yapıcı özelliklerinden dolayı beyaz eşya ve otomotiv sektöründe kullanılmaktadır. Polipropilen iyi özelliklerinin yanı sıra, endüstride kullanmak için uygun olmayan özelliklere de sahiptir bu nedenle gerekli özellikleri yakalayabilmek için kullanım alanına bağlı olarak, bazı katkı maddeleri polimere eklenmelidir. İstenen fonksiyonel özelliklerinin kaybedilmemesi adına, katkı maddeleri polimere optimum oranlarda eklenmelidir. Önemli katkı maddelerinden biri de plastik malzemelerin neden olduğu yangınları azaltan alev geciktirici malzemelerdir. Plastik, metal ve ahşap malzemelerin alev geciktirici özelliklerinin araştırılması için birçok çalışma yapılmıştır. Dünyadaki yangınlar nedeniyle malzemelerin alev geciktirici özelliklerinin artırılması daha da önemli hale gelmekte ve polimerik malzemelerde alev geciktirici katkı maddeleri ve duman bastırıcıların kullanımı da her geçen gün artmaktadır. Bu katkı maddelerinin polimerik malzemelerin alev geciktirici özelliklerinin geliştirilmesinde önemli bir rolü vardır fakat halojenli alev geciktirici katkı maddelerinin toksikolojik özelliklerinden dolayı polimerik malzemelerin içerisinde halojensiz ve mineral bazlı alev geciktiriciler gibi çevre dostu sistemler kullanılmalıdır. Bu çalışmada, beyaz eşya sektöründe yoğun olarak kullanımından dolayı ana polimer olarak polipropilen seçilmiştir. Bu çalışmanın amacı, potansiyel alev geciktirici katkı maddeleri olan köpüren alev geciktirici sistem, mika, kolemanit ve genişleyebilen grafit arasında sinerjik bir etkinin yaratılması ile birlikte polipropilenin alev geciktirici özelliklerinin artırılmasıdır. Üretimde herhangi bir kısıt ile karşılaşılması adına ticari olarak da mevcut olan köpüren alev geciktirici sistem, mika, kolemanite ve genişleyebilen grafit alev geciktirici katkı maddeleri olarak seçilmiştir. Köpüren alev geciktirici sistemler çevre dostudur ve halojen içermezler. Mika ve kolemanit mineralleri doğada yaygın olarak bulunurlar ve köpüren alev geciktirici sistemlere göre fiyatları daha uygundur. Genişleyebilen grafit, polipropilenin alev geciktirici özelliğini arttırmak amacıyla kullanılan gelecek vaadeden bir alev geciktirici malzemedir. Bu çalışmada, alev geciktirici hammaddelerin compound içerisindeki miktarı %30 olarak ayarlanmıştır. Potansiyel alev geciktirici katkı maddeleri de %2-4-6-8-15 oranlarında eklenmiştir. Alev geciktirici katkı hammaddeleri ayrıca polimer içerisine %30 oranında eklenerek, polimer ile tek başına gösterdiği etki de değerlendirilmiştir. Alev geciktirici katkı maddeleri eklenmiş olan compoundlar 100 rpm vida hızında ve 185 °C sıcaklıkta çift vidalı ekstruderde eriyik proses metodu kullanılarak üretilmiştir. Compoundların üretilmesinin ardından, test numuneleri enjeksiyon makinesinde uluslararası test standartlarına göre hazırlanmıştır. Yoğunluk ve eriyik akış indeks testi, test

numunelerinin fiziksel özelliklerinin belirlenmesi amacıyla yürütülmüştür. Çekme ve darbe dayanımı testi de komponentlerin mekanik özelliklerinin belirlenmesi amacıyla yapılmıştır. Termal gravimetrik analiz ve ısı sapma sıcaklığı testi, komponentlerin ısısal özelliklerinin tespit edilmesi amacıyla kullanılmıştır. Yanık tabakanın araştırılması taramalı elektron mikroskopi yöntemiyle yapılmıştır. Bununla birlikte, limit oksijen indeks testi, UL 94 dikey yanmazlık testi ve kızgın tel testi de komponentlerin alev geciktirici performanslarının ölçülmesi amacıyla yapılmıştır.

Tezin birinci aşamasında, istenen mekanik, fiziksel ve alev geciktirici özelliklerin yakalanması ideal formülasyonun belirlenebilmesi amacıyla köpüren alev geciktirici sistem polipropilen içerisine %20-25-30 oranında eklenmiştir. Karışım komponentleri sırasıyla PP80/IFR20, PP75/IFR25, PP70/IFR30 olarak dizayn edilmiştir. Bu terminolojide, PP ve IFR, plastik malzemenin polipropilen, alev geciktirici katkı maddesinin de köpüren alev geciktirici sistem olduğunu göstermek amacıyla kullanılmıştır. İsimleri takip eden sayılar da malzemelerin formülasyon içerisindeki yüzdesel oranlarını ifade etmektedir. Alev geciktirici test sonuçlarına göre, köpüren alev geciktirici katkı maddesi alev geciktirici özelliğın geliştirilmesi üzerinde önemli bir etkiye sahiptir ve 30% oranında köpüren alev geciktirici madde polipropilene eklendiğinde limit oksijen indeks değeri %37,9'a çıkmaktadır. PP75/IFR25 ve PP70/IFR30 numuneleri de UL 94 dikey yanmazlık testini geçebilmektedir ve bütün komponentler kızgın test testini hem 750 °C hem de 850 °C için başarıyla tamamlamıştır. Termal gravimetrik analiz sonucu da, polipropilene köpüren alev geciktirici eklenmesiyle birlikte komponentlerin ısısal kararlılığı artmıştır.

Tezin ikinci aşamasında, polipropilenin alev geciktirici özelliklerinin artırılması amacıyla, IFR ve mika, polipropilen ile birlikte çift vidalı ekstruderde karıştırılmıştır. Karışım komponentleri PP70/IFR28/M2, PP70/IFR26/M4, PP70/IFR24/M6, PP70/IFR22/M8, PP70/IFR15/M15, PP70/IFR0/M30 olarak sırasıyla dizayn edilmiştir. Bu formüllerde, "PP", polipropileni, "IFR" köpüren alev geciktirici katkı maddesini "M" de mikayı temsil etmektedir. LOI, UL 94 ve kızgın testi sonuçları, toplam %30 alev geciktirici katkı madde miktarından %2'sinin ağırlıkça mika olması durumunda LOI değerinin 37.5% olarak elde edildiğini buna bağılı olarak da mikanın alev geciktirici özelliğının artırılması yönünde etkisi olduğunu gösterdi. Sisteme IFR yerine ağırlıkça 2-8% oranında IFR eklenmesiyle birlikte UL 94 testinde V0 değeri yakalanmaktadır ve kızgın testi de hem 750 °C hem de 850 °C için başarılı olmaktadır. TGA sonuçlarına göre de, mika ve IFR birlikte kullanıldığında ısısal kararlılık atmakta ve karbon tabakanın oluşumu desteklenmektedir. Sisteme yalnızca mika katılması durumunda da, polipropilenin alev geciktirici özelliklerinin üzerinde etkisi olmadığı tespit edilmiştir. Sonuç olarak da mikanın polipropilen compound içerisinde IFR ile birlikte kullanıldığında etki sağladığı ve sisteme ağırlıkça %8 oranında mika yüklenebileceği tespit edilmiştir.

Tezin üçüncü aşamasında, PP komponent içinde IFR ve genişleyebilen grafitin sinerjistik etkisi gözlemlenmiştir. Karışım komponentleri PP70/IFR28/EG2, PP70/IFR26/EG4, PP70/IFR24/EG6, PP70/IFR22/EG8, PP70/IFR15/EG15, PP70/IFR0/EG30 olarak sırasıyla dizayn edilmiştir. Bu formüllerde, "PP", polipropileni, "IFR" köpüren alev geciktirici katkı maddesini "EG" de genişleyebilen grafiti temsil etmektedir. LOI, UL 94 ve kızgın tel sonuçlarına göre, toplamda %30 alev geciktirici katkı maddesinin %4'ünün genişleyebilen grafit olması durumunda LOI değerinin %37.2'ye ulaştığı ve genişleyebilen grafitin polipropilenin alev geciktirici özelliklerinin iyileştirilmesi yönünde etkisi olduğu tespit edilmiştir. Ek olarak, PP/IFR komponentleri %2-6 oranında genişleyebilen grafit eklenmesiyle

birlikte hem UL 94 dikey hem de kızgın tel testini geçmiştir. IFR ve EG katkı maddelerinin arasında sinerjik bir etki olduğu tespit edilmiştir. Isısal sapma sıcaklığı verileri de EG'nin sisteme eklenmesiyle birlikte yükselmiştir bu da yangın sırasında ortama ekstra bir güvenlik sağlanacağını göstermektedir. Bununla birlikte, %30 oranında EG'nin polipropilene eklenmesi de proses edilebilmesi açısından oldukça güçtür. Mekanik özellikler açısından, PP/IFR compound içerisine EG eklenmesi durumunda elastik modül değerlerinin yükseldiği gözlemlenmiştir.

Tezin dördüncü aşamasında, IFR ve kolemanit polipropilenin alev geciktirici özelliklerinin artırılması amacıyla beraber kullanılmıştır. Karışım komponentleri PP70/IFR28/C2, PP70/IFR26/C4, PP70/IFR24/C6, PP70/IFR22/C8, PP70/IFR15/C15, PP70/IFR0/C30 olarak sırasıyla dizayn edilmiştir. Bu formüllerde, "PP", polipropileni, "IFR" köpüren alev geciktirici katkı maddesini "C" de kolemaniti temsil etmektedir. LOI, UL 94 dikey ve kızgın tel sonuçlarına göre, kolemanit alev geciktirici özellik açısından sinerjik etkiye sahiptir ve toplam alev geciktirici katkı maddesinin %30 olarak sabitlendiğinde, bunun %2 'sinin kolemanit olması LOI değerini %37.6'ya çıkarmaktadır. %2-6 oranında kolemanit içeren PP/IFR komponentleri hem UL 94 dikey testini hem de kızgın tel testini başarıyla geçmiştir. Mekanik özellikler açısından bakıldığında kolemanit sisteme eklendiğinde akma noktasında çekme dayanım değerleri düşmüştür. Tüm özellikler göz önünde bulundurulduğunda, IFR katkılı polipropilen komponent içerisine %4 oranına kadar eklenen kolemanitin IFR ile sinerjik etki yaratacağı saptanmıştır.

Tezin beşinci aşamasında, IFR, kolemanit, mika ve genişleyebilen grafit farklı kombinasyon ve yükleme seviyelerinde komponent edilerek sinerjik etki yaratılması planlanmıştır. Komponentta kullanılacak malzemelerin minimum ve maksimum miktarlarına diğer raporlardaki test sonuçlarına bakılarak karar verilmiştir. Karışım komponentleri PP70/IFR20/M8/C2, PP70/IFR22/M6/C2, PP70/IFR22/M4/C4, PP70/IFR22/EG6/C2, PP70/IFR22/EG4/C4, PP70/IFR22/EG6/M2, PP70/IFR22/EG4/M4, PP70/IFR22/EG2/M6, PP70/IFR20/EG2/M8 olarak sırasıyla dizayn edilmiştir. Bu formüllerde, "PP", polipropileni, "IFR" köpüren alev geciktirici katkı maddesini "C" de kolemaniti, "M" mikayı, "EG" de genişleyebilen grafiti temsil etmektedir. LOI, UL 94 ve kızgın tel sonuçları, mika ve kolemanitin IFR ile birlikte PP içerisinde belirli oranlarda kullanıldığında sinerjik etki yarattığını göstermiştir. Toplam alev geciktirici katkı maddesi miktarı %30 oranında tutulduğunda PP/IFR/Mika/kolemanite numuneleri UL 94 testinde V0 seviyesi yakalanmıştır ve LOI değerinde %33 değerine ulaşılmıştır. Buna ek olarak kızgın tel testinde de 750°C ve 850 °C sıcaklıklarında başarı sağlanmıştır. Termal gravimetrik analiz sonuçlarına göre, mikanın yükleme seviyesinin artırılmasıyla birlikte karbon tabaka artmıştır. Kolemanit ise, sıcaklığın artmasıyla birlikte yapısındaki su kristallerinin uzaklaşmasıyla birlikte yüzey üzerinde soğutucu etki yaratmaktadır. PP70/IFR30 ve PP70/IFR20/M8/C2 numuneleri elastik modül değerleri açısından aynı mekanik özellikleri göstermiştir. Artan mika içeriği elastik modülü arttırmıştır fakat çekme dayanımı ve uzamasını da azaltmıştır. PP70/IFR20/EG2/M8 ve PP70/IFR20/M8/C2 aynı çekme dayanımı ve uzama değerlerini göstermiştir fakat genişleyebilen grafit içeren formülasyon düşük elastik modül değeri göstermiştir. Sonuç olarak, polipropilen içerisinde IFR yerine belirli miktarlarda mika, kolemanit ve genişleyebilen grafit kullanımı, final komponentlerin mekanik özelliklerini olumsuz yönde etkilememektedir. Alev geciktirici katkı maddeleri, darbe dayanımı değerlerini iyileştirmemektedir ve bu açıdan sinerjik bir etki yaratmamaktadır. Mika, kolemanit ve IFR karışımlarında, mika 8% yükleme seviyesinde kullanıldığında HDT değeri 94.5°C değerine ulaştığı tespit edilmiştir.

Mika ve IFR ile birlikte compound içerisinde kolemanit miktarı arttırıldığında, HDT değerleri düşmüştür. Genişleyebilen grafit karışımlarında HDT değeri 96.2°C değerine ulaşmıştır. Tüm sonuçlar değerlendirildiğinde, mika, kolemanit ve IFR, PP içerisinde belirli oranlarda kullanıldığında sinerjik etki göstermiştir. Özellikle kolemanit Türkiye’de ticari olarak üretilebilen ve yaygın olarak bulunabilen bir malzemedir. Formülasyon içerisinde IFR kullanımının azaltılarak, kolemanit malzemesinin kullanılması hem maliyet avantajı yaratacaktır hem de doğal kaynakların kullanımına yardımcı olacaktır.



1. INTRODUCTION

Polymeric material is called as a high molecular weight compound made from many repeating monomeric units and they linked together with covalent bonds throughout the polymeric chains [1]. The meaning of the polymer is generated from Greek poly and meros, meaning many and parts. Sometimes it is called as macromolecule by some scientist. Most materials are polymeric and it is possible to see polymers in every field in today's technology so it is called as polymer age [1]. Detailed researches were carried out during 20th century so polymeric materials started to use as engineering material. Bakelite is also known as the first synthetic resin which was found in 1907. Bakelite can be used more commonly especially in electronic industry. Staudinger worked on thermoplastic materials in 1926. Plastic materials are divided into the following groups according to their industrial usage; plastics, rubber, synthetic fibers, plastic coatings and plastic additives. Plastics consist of two main groups; main plastics are polyolefines, acrylonitrile butadiene, polyvinyl chloride plastics which are used in industrial sector. Another group is high performance engineering plastics which are called as polyamides, polyimides, polycarbonate, acetals, polysulfones, fluoropolymers etc. Lately, plastic materials are used as commodity materials instead of traditional parts such as metal parts, wooden etc. In particular, plastic materials are used in many implementations such as household appliances and also automotive industry, consumer and sport sector, architecture [2].

The most commonly used thermoplastic material is polypropylene which can be used in many different type of fields. It is very suitable with many processing procedures. Additionally, it is the one of the growing thermoplastic material with 6-7% market share in the world. This growth rate is related to its usability, processability and good features. Fibers, films, filaments, packaging, household and automobiles parts, electronic parts, consumer goods can be produced with using polypropylene material due to its favorable properties.

Due to its poor flame retardancy property, its usage field is also limited. For example, LOI value of PP is around 18% so flammability of PP must be improved by the use of

flame retardant ingredients for fields in the consumer, automotive, appliances, and electronics industries [3].

Fire is damaging force for the nature. It is also known as important physical and chemical event. In the first stage, the flame and fuel interacted together the fire starts [4].

Fires are common on the earth. Fire are initiated by streak of lightning or accidentally by people. Smoke pollution, harmful gases are created by fire and It also has negative effect on our ecosystem. Main goal is to create protection from flames and enhancement of escape time when flame occurs therefore it is main point to increase flame retardancy properties of commercial plastic materials. Plastics are generally flammable so it is necessary to add flame retardant additives to meet required standards. Flame retardants are added to plastic material and other materials to inhibit, smoke suppress or delay combustion. The main tasks of flame retardants added to plastics are as follows:

- Enhancement the ignition temperature
- Decreasing of the grade of burning
- Decreasing of the fire spread
- Decreasing of the smoke production

Lately, halogenated flame retardant materials can't be used commonly because they release harmful gases to the media so halogen free flame retardants can be used in the system. Halogenated flame retardants have important disadvantages such as the production of smoke, harmful gasses and degradation products. In addition them, The EU industry needs to discover help to substitute the halogenated ingredients employed in the production of flame retardant plastic materials, used in a extensive series of commodity products, and markets such as household appliances, electronic sector. Unlike halogenated flame retardants, mineral type flame retardants provide extremely low smoke values. They also show environmental friendly profile [4]. Minerals used as fire retardant additive in plastic fields for long years. They have low toxicity, ready availability and low cost. Halogen free flame retardant alternatives are commercially available but due to the high filler content between 40-60% needed to provide the same FR properties than conventional halogenated flame retardant [4].

Intumescent flame retardant ingredients are used to improve flammability efficiency of plastic materials therefore they can commonly used inside polymeric formulations [5]. Expandable graphite acts as intumescent. Expandable graphite can develop the ignition time and also decreasing heat release, mass loss smoke and fire spread. Mica will increase thermal properties of polypropylene material because it can be stable up to 600 °C. Layer will be occurred and this layer will protect polymeric material and improve flame retardancy properties of polymeric compound. Colemanite is known as a natural hydrated calcium borate It can release water from their structure under endothermic process. The mechanism is ended with water and inorganic residue formation. It provides a protective layer on the polymer surface [6].

The synergistic influence is very important parameter between fire retardant additives to improve flammability properties of plastic materials. Low cost additives and high efficiency flame retardant combinations are used together in the system to create synergistic effect in the polymeric system [5-6].



2. THEORETICAL PART

2.1 Polymeric Materials and Classification

Polymeric materials play a complementary role in daily life. Annual consumption volume is over 150 million tones. They can be used in production of commodity products. Polymeric materials are also used as a replacement of metals [1]. Polypropylene (PP), Polyethylene (PE), Polystyrene (PS) are very well known commodity polymers. These commodity polymers can be used over 10 million tonnes annually. They are also known as structural components for packaging, bottles and container sectors [1]. Engineering polymers are often used as replacement of metals and woods. Polyamides (PA), often called as nylon, polyester both saturated and unsaturated, polycarbonates, polyoxymethylenes (POMs), styrene / acrylonitrile (SAN) and acrylonitrile/butadiene/styrene (ABS) are known as engineering polymers. These type of products can be used in home appliances and automotive sector especially [1]. The polymers are divided into two main groups in terms of thermal processing behaviour as thermoplastics and thermosets. Thermosets don't melt when they exposed to heat but under sufficient high temperature they start to decompose irreversibly. Thermoplastics melt when they exposed to heat, then resolidify. Polymer classification is shown in Figure 2.1 [2].

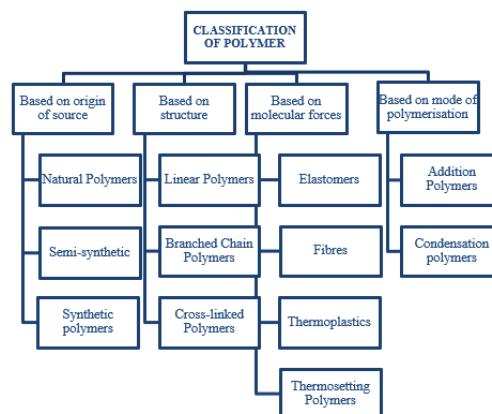


Figure 2.1 : Polymer Classification [2].

2.2 Combustion of Polymers

Fire dynamic is called as the scientific explanation of fire phenomena in quantitative terms. Combustion is also described as fast oxidation of material which is achieved by fast release of energy. Another explanation of fire is known as physical and chemical phenomena which include chemical reactions between degradation products and oxygen from the air. Oxidizer is an important factor of ignition to take place. If there is pressure and heat in the system at the same time, there will be a release of oxygen that supports combustion. For ignition to occur, three substances must be present, then fire triangle will form. It is also indicated in Figure 2.2. If any one of the components remove from the system, fire can be prevented and extinguished [6].

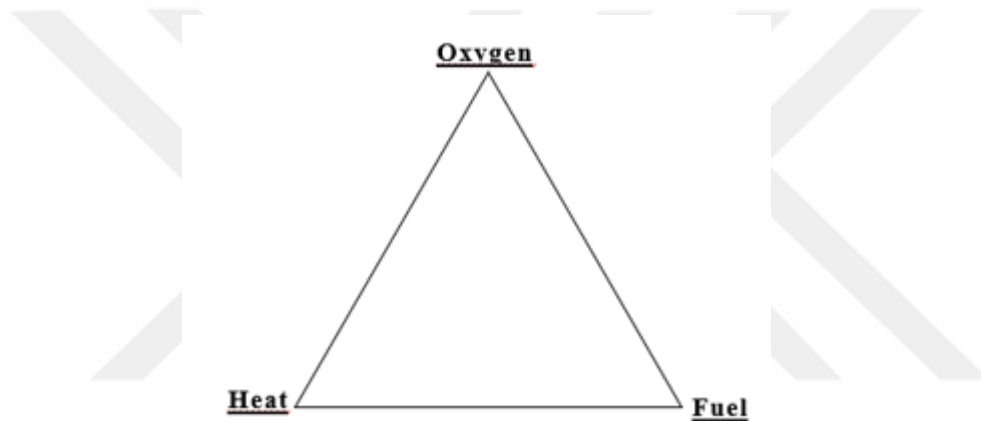


Figure 2.2 : Flame Triangle.

The Fuel, an oxidize and energy are brought into the same environment at the suitable amounts according to flame triangle theory, then fire will take place. The most basic component is oxygen to initiate fire and it must be available in the system. The second basic component is fuel. Plasticizers, plastics, process oils are can be fuel components. If there is gas in the environment, it will attack it directly and start burning [6].

Combustion is known as an exothermic process that can progress rapidly on its own, depending on the type of initiation and propagation. The fire retardancy features of natural and synthetic plastic materials are examined by the capability of such materials to set on fire and spread and ignition process [6].

If plastic materials are exposed to some suitable ignition sources, the combustion will occur in the presence of oxygen and air. Burning plastic material forms highly complex

ignition system. Gas phase, condensed phase, and gas-condensend phase are important regions which chemical reactions take place [6].

Polymer combustion is special process and period of polymer combustion is related to heating of the polymer, degradation, ignition and combustion. The plastic material is exposed to heat, it will be heated up to specific temperature at which it begins to decompose and releases products but these products are generally flammable so flame can't go bottom side of polymer. If the ignition source is present in the system, combustion will take place in the gas phase and release more heat to the system. As a result of these conditions, polymer surface will face with more heat due to this reason. Combustion process will be sustained with more volatile plastic sources [6].

When natural and synthetic plastic materials are exposed to heat, they will start to degrade with giving volatiles to the environment. If the heat of environment is high enough to initiate ignition, plastic combustion process can be occurred as given in Figure 1.3.

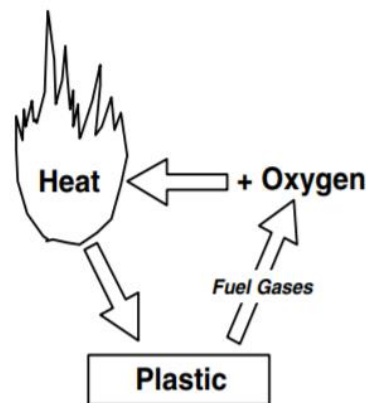


Figure 2.3 : Plastic ignition process.

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 [6].

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 [6].

2.3 Thermal Decomposition of Polymers

Rigid plastics can stand both physical and chemical changes when they exposed to heat. Undesirable changes are observed in properties of the polymeric materials. The main difference between thermal decomposition and thermal degradation was explained by the American Society for Testing and Materials' (ASTM). Thermal decomposition is a phenomena of widespread chemical types change caused by heat while thermal degradation is also known as a process whereby the action of heat or elevated temperature on a material. Thermal degradation causes a loss of main properties of materials [8].

Plastic degradation contains all the varies in the chemical structure, physical and other important properties of plastic materials because of exterior chemical stresses originated from serious chemical reactions. The polymer degradation can be defined in broader terms as biodegradation, pyrolysis, oxidation and mechanical, photo and catalytic degradation [8-10].

Two different mechanisms of degradation of plastics are depolymerisation and statistical fragmentation of chains. Polymer has many different bonds which can break during depolymerisation. The weakest link in chain tend to break in the first stage. Thermal degradation of plastics have three major trails which are side-group elimination, random scission and depolymerisation [8-10].

The side groups elimination occurs in two main stages which linked to backbone of polymer is the first stage. For instance, generation of hydrogen chloride is made by the first step of thermal degradation of PVC. A polyoene macromolecule remains when the side groups removed from polymer [8-10].

The monomer of comonomers degraded with free radical mechanism reaction which produce the copolymer is explained as depolymerisation. For instance, polymethacrylate and polystyrene can behave according to this structure. Free radical on the polymer backbone can be generated to produce unsaturated small molecules and then propagation will continue to the free radical on the polymer structure. Statistical fragmentation has similar conditions with depolymerisation. The

mechanism of depolymerisation is directly related to relations between monomer and polymer at the required temperature in the closed reaction system. This temperature level is important to see depolymerisation mechanism. Thermal stability and flammability of polymers are indicated in Table 2.1 [1-8-9].

Table 2.1 : Thermal Stability and flammability properties of polymers.

Polymer	Td ^a (K)	T1% ^b (K)	LOI ^c (-)	Pk RHR ^d (KW/m ²)
Polyacetal	503	548	15.7	360
Polymethyl methacrylate	528	555	17.3	670
Polypropylene	531	588	17.4	1500
Polyethylene (LDPE)				
Polyethylene (HDPE)	506	548	17.4	1400
Polystyrene	436	603	17.8	1100
ABS copolymer	440	557	18.0	950

aTd: Minimum thermal decomposition temperature from Thermal gravimetric analysis.

bT1%: Temperature for 1% thermal decomposition.

cLOI: Limiting oxygen index

dPk RHR: Peak rate of heat release in the cone calorimeter, at 40-kW/m² incident flux, at a thickness of 6 mm, all under same conditions.

2.4 Properties and Decomposition of Polypropylene

Polyolefins are the most properly used commodity plastics on the earth. They are produced with a variety processes. The most well known of polyolefins is polypropylene (PP). In thesis, fire retardancy features of PP are searched so mechanical, physical and thermal decomposition properties of PP are indicated in this level with details. Especially, PP uses in many different type of commodity fields like household appliances, automotive applications, white goods sector etc. PP has high market share growth of 6-7% / year amongst polyolefines. It means that PP is the one the fastest growing classes of commodity plastic materials [3].

PP can be in three form as atactic, isotactic and syndiotactic. If all methyl groups are attached to the one side of c-c backbone, it means that it is isotactic form. Syndiotactic form can be explained that methyl groups are designed at regular intervals and on the either side of backbone. Maximum crystallinity is observed in isotactic form of PP. The molecular figure of PP is indicated in Figure 2.4 [3].

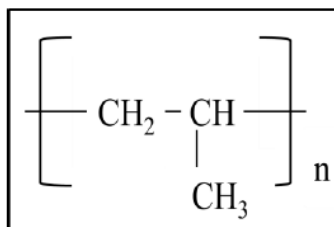


Figure 2.4: Molecular structure of PP.

Polypropylene is a plastic material with many useful properties as outstanding and good properties like physical, thermal, mechanical and electrical properties. When crosschecked with low and high density polyethylene, Impact strength values are low. Different type of properties are indicated in below [3].

Glass transition temperature: -10 °C

Melting temperature: 165 °C

Amorphous density at 25 °C: 0.85 g/cm³

Crystalline density at 25 °C: 0.95 g/cm³

Molecular weight of repeat unit: 42.08 g/mol

PP is the one of the most used plastics in the consumer sectors in furniture, household appliances, automotive sector, luggage, toys, battery cases etc. PP has oxidatively unstable structure. It means that it is very vulnerable to oxidative degradation under the effect of required temperature and sunlight due to the presence of tertiary atoms. Every carbon atom in the main chain of polypropylene is tertiary carbon that is thus prone attack. Uniformity of polypropylene is less than polyethylene due to this reason. Chain scission and transfer are important steps during decomposition as with polyethylene. In additon to them, secondary radicals are more important than primary radicals [3].

When PP is exposed to heat, it can easily burn and form molten droplets during burning process and it releases a large amount of heat and toxic fumes. This reason limits its wider application areas. So, it is important to increase fire retardancy features of PP with flame retardant additives. The combustion process of PP can be explained with following steps; heating step, degradation stage, decomposition step, ignition step and finally combustion step [3].

2.5 Mechanisms and Theories of Flame Retardancy

Flame retardants should prevent or delay the ignition process by physical or chemical action in the solid, liquid or gas phase. There are two possible mode of actions for a flame retardant additive [9-11].

Chemical action: General target of this method is to interfere with free radical reactions which occur during burning (gas phase) and proposes to preserve materials from heating along char formation (solid phase) [9-11].

Physical action: Aim of this procedure is depend on decreasing the temperature by endothermic reactions with reduction the fire spread by discharging oxygen with non-combustible gases and enhancemenet the creation of a safety char layer on the surface [9-11].

Many theories are also proposed to explain the mechanisms of flame retardants because different types of flame retardants have different fire reactions and corresponding basic theories of these fire protective mechanisms have been investigated and they are summarized as follows [11]:

- 1) Protective barrier theories: In this theory, flame retardant additive form glassy layer which inhibits the release of gases and prevent oxygen reaching the material and protecting the surface from the effect of elevated temperatures. Char generation can be obtained with two possible mechanisms: redi-reaction of the chemical reactions included in decomposition in reactions yielding carbon rather than CO and CO₂ and generation of protective layer on the material surface. For instance, intumescent flame retardant systems start to swelling when exposed to heat and flame and they form porous carbon structure which behaves as a barrier and protects from air, heat and pyrolysis products. A carbonisation material, acidic source and blowing agent are key

components of intumescent systems. The carbonisation agent is known as a char creating compound [11].

- 2) Thermal Theories: the thermal conductivity of the organic material is increased by flame retardant additives. These materials can adsorb energy, because as endothermic reaction is initiated along their thermal decomposition. For instance, aluminium trihydroxide (ATH), magnesium dihydroxide (MDH), huntite and hydromagnesite work according to this theory [11].
- 3) Theory on noncombustible gases: the flame retardant additive decompose and spread out nonflammable gases that are blended with the pyrolysis products and generate a noncombustible mixture of gases [11].
- 4) Free radical theories: Halogenated flame retardants works according to this theory. These type of compounds work in the vapour phase as inhibitors. Inhibitors interrupt the chain propagation reactions with giving free radicals to the system [11].
- 5) Theory on char increasing and volatile reduction: In this theory, flame retardant additives can reduce temperature required for pyrolysis so more char and fewer volatile gases are produced.
- 6) Reduction heat content of combustible volatiles: the number of volatiles is reduced and the quantity of char is enhanced so reduction of the heat content occurs [11].

Most flame retardant additives behave via several of the explained mechanisms. Some materials can be used together to create synergistic effect in the system. For instance, the combination of aluminium or magnesium hydroxides with zinc borate, and the mixture of intumescent flame retardants with zinc borate can be used as synergistic systems [11].

2.6 General Flame Retardant Additives for Polymeric Materials

The basic mission of fire retardant additive is to increase the combustion resistance of polymeric materials. They can decrease flame spread rates and quantity of harmful and combustion products in the event of burning. The most fire retardant additives have significant effect on the some desired properties of polymeric materials. For this

reason, an appropriate link must be established between the minimum fire safety expected of the product and other technical properties. The required properties for fire retardants are shown in the following [12]:

- Compatibility with polymer and other additives,
- High efficiency to decrease negative influences on properties and prices,
- Thermal stability at processing temperature,
- Stability of UV has to be protected,
- Fire retardant Colour and odourless is important,
- Resistance to ageing and hydrolysis,
- No corrosion effect on equipments,
- Environmental safety and no toxicity,
- Regulations and recycleable.

2.6.1. Halogenated flame retardants

Halogenated flame retardants which can reduce combustibility of polymeric materials. Halogenated flame retardants are known as aliphatic, cycloaliphatic and aromatic structures. Halogens contain five chemically-related, highly reactive non-metallic elements found in group 17 of the periodic table. Fluorine, chlorine, bromine, iodine and astatine are highly reactive elements. They are classified as halogens. All halogens find many uses in everyday life [12].

Although fluorine and iodine are not used as flame retardant materials, they are quite effective in the combustion process. If halogenated flame retardant material contains chlorine, they release hydrogen chloride (HCl) over a wide temperature range therefore fire retardant amount is decreased and is thus less active. Among the halogenated flame retardants, brominated ones are the most active halogenated flame retardant because linking to carbon structure make possible it to interfere at a more convenient point in the combustion process. Hydrogen bromide is used as effective halogenated flame retardant and released over a narrow temperature range therefore it is present at a high quantity in the flame zone. Bromine breaks down to generate a bromine radical that reacts with the hydrocarbon to produce HBr. The high energy H and OH radicals are removed from the system with reaction by the HBr. Low-energy bromine radicals are

replaced with high energy radicals. The mechanism for brominated based flame retardant is indicate in below [12].



The consumed HBr is reformed with the reaction of hydrocarbon.



2.6.2 Antimony trioxide (Sb_2O_3)

Antimony trioxide has no flame retardancy effect during combustion process when it is used alone in the system. It has synergistic effect when it used with brominated fire retardants. Thanks to working as a catalyst and starts the breakdown of halogenated flame retardants to produce active molecules. Antimony trioxide and halogens react each other during combustion then volatile antimony halogen compounds obtained, which are directly influence on eliminating the high energy $\text{H}\cdot$ and $\text{OH}\cdot$ radicals which feed the flame phase of the fire. One of the most important synergistic fire retardant combinations is mixtures of antimony trioxide and halogenated flame retardant. It is significant parameter to obtain a greater impact of mixture of polymer additives than supposed from individual contribution. This is achieved by creating a synergistic effect in the system [13].

2.6.3 Phosphorus based flame retardants

These ingredients is working in the condensed phase where varied degrees of melting are included at fire temperatures. This type of flame retardants provide two char forming mechanisms; one of both is redirection of the chemical reactions and other is the generation of protective layer on the surface [9-14].

Phosphorus based flame retardant systems have effective and significant role on generation of low flammability polymeric materials. They can be used commonly in the plastic compounds but it is not deeply studied for plastic combustion and ignition process in all steps. On the other hand, they can be used also with some halogens. The most important reason for this is to create a synergistic effect in the system. The harmful effects of halogens on the environment can be minimized with creating synergistic effect [9-14].

2.6.4 Melamine based flame retardants

Melamine is a white crystalline powder and it has a melting point of approximately 354 °C and density of melamine is 1.573 gr/cm³. Melamine indicates good fire retardant features due to its capability to hinder combustion process in all steps. Melamine based flame retardants can also indicate effective contribution to the generation of a char layer in the intumescent system. The char layer behaves as a barrier between oxygen and plastic decomposition gases. Melamine and phosphorous based flame retardants can be used together to create synergistic effect and they enhance char stability during generation nitrogen-phosphorous materials [15].

Melamine can be used in polyurethane and also melamine cyanurate can be used in polyamides but melamine derivatives fire retardants are used in limited applications in plastic materials. Melamine contains 67 wt.% nitrogen in the structure with high thermal capability. Stable salts are formed with the reaction of melamine and strong acids. Commercially available melamine based flame retardants like melamine cyanurate, melamine phosphate, melamine pyrophosphate are used in various flame retardant applications [15].

2.6.5 Silicone based flame retardants

Silicone based flame retardants generate protective layer during fire, caused by a low value of heat released. This makes silicone based flame retardants potentially prominent. The use of low amount of silicone based flame retardants in polymeric systems enhances UL-94 and LOI properties of final product. In the 1-3% loading level, silicone based flame retardants indicated that good performance in terms of flame retardant properties, especially in PS. They decreased the rate of heat released by 30 to 50 %. The same improvements can be observed in different types of polymeric systems like High impact polystyrene (HIPS), PP, PS blends, PP and EVA. While burning, they create silicone dioxide layer on the material surface which behave as a thermal insulator and prohibit the feedback of energy to the substrate by re-radiating the external heat flux [15].

2.6.6 Boron based flame retardants

These type of flame retardants have impact and effect both in condensed phase and gas phase as well. They can work by endothermic, first decomposition step is release

of water and second stage is formation of a glassy coating protecting the substrate. Boric acid indicates dehydrating and charring action with oxygen substrates. This behaviour has similarity with polyphosphoric acid resulting from phosphate esters. Protective layer and glassy coating are generated successfully and they work against to oxygen attack and heat [16].

Borates (such as colemanite, ulexite, kernite, etc.) take place a variety of fields in the market including glass, ceramics and detergents. Colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) has 5 mol crystal water in its structure therefore it is the most significant calcium and boron containing commercial borate mineral. High tensile strength glass fiber and also other high strength required products are also produced using borates. Especially, heat resistance glasses are produced with using boron mineral. Due to low thermal expansion of boron compounds, they are used as flame retardants. They create good protective layer on the surface with hindering the passage of oxygen to the surface. Boron types have different application area for example; cellulose materials are produced using sodium borates and boric acid. Fire retardant fibreboard can be produced using anhydrous borax [16].

Colemanite gives its structural water to the environment with endothermic reaction. The mechanism is ended with water and inorganic residue formation. It provides a preservative layer for material surface. The share of colemanite reserves is approx. 73.9% when compared to tincal (24.5%) and ulexite (1.6%) [16-17].

The use of boron based flame retardants was also evaluated to enhance to increase flame retardant performance of wood plastic composites in compared with commercially available flame retardants. For example, when colemanite and ulexite added to wood plastic composites limited oxygen values increased approximately 13% [16-17].

2.6.7 Metal hydrate based flame retardants

Some inorganic types materials are used as flame retardants in plastic materials since they are operative within the range of decomposition temperature of the plastic materials. This decomposition temperature range is mainly between 150-400°C. Aluminium trihydrate, magnesium hydroxide, mica, huntite and hydromagnesite are the most widely used inorganic flame retardants which affect the combustion process with physically. On the contrary, halogenated flame retardants has an effect on the

ignition process chemically in the plastic material compounds. When these type of inorganic compounds start to decompose, they can't release toxic gases to the system. They give non-flammable gases like water, carbon dioxide etc. They also create shielding on the plastic material when oxygen attack occurred [16-18].

Especially, ATH, MDH, mica, huntite and hydromagnesite are the most common inorganic flame retardant that can be used to extinguish combustion in polymeric system. ATH is very important flame retardant material and also it has smoke suppression capability on polymeric systems. It releases 34.6% water during endothermic dehydration in temperature range between 220-250 °C. This material can be effective with high loading level but processing temperature shouldn't exceed 180 °C. Compared to halogenated flame retardant, ATH has low price, environmentally friendly and easy to incorporate into plastic compound. Flame retardant properties can be achieved high loading levels at between 40-60% weight. ATH is commercially available flame retardant which can be used in wire industry, plastic compounds, elastomeric products etc [18].

Magnesium hydroxide works as a good smoke suppressant material in the plastic compounds and protect them from the fire. This material also release water at superior temperature. Heat and other ingredients are absorbed by water during combustion process. Compared to ATH, decomposition temperature of magnesium hydroxide is high. It means that it can be processed at higher temperatures. This flame retardant is also used at high loading levels. Due to high decomposition temperatures, it can be used in engineering plastics and polyolefins. It needs to be added to plastic compounds at high loading levels to achieve flame retardancy performance but it adversely affects its mechanical properties [18].

Huntite and hydromagnesite mixtures are used as a flame retardant in plastic compounds. This mixture can be alternative to ATH and MD in some plastic compounds like Polyvinyl chloride and rubber usages. Huntite is mixed calcium magnesium carbonate and hydromagnesite is called as basic magnesium carbonate. Huntite and hydromagnesite are added to system at high loading levels to enhance flame retardancy properties of final product [19].

Another important flame retardant is mica which belongs to a group of aluminosilicate minerals characterized by a layered structure. Muscovite and phlogopite are classified

as important derivatives of mica. Mica is chemically inert and thermally stable up to 600 °C where dehydroxylation occurs. It works as flame retardant and char promoter [20].

2.6.8 Intumescent flame retardants (IFR)

Nowadays, the usage of halogenated flame retardants are restricted due to their high toxic effects. Intumescent flame retardant is good alternative to halogenated flame retardant. This type of flame retardant form char on the surface that provides protective layer from heat and oxidative degradation. Intumescent systems comprise three components as carbon source, acid source and blowing agent [21-22].

Intumescent flame retardant systems is used to develop flammability performance of plastic materials. This type of flame retardant ingredients started to use in plastic science due to its effective features in plastic compounds. IFR compound includes ammonium polyphosphate (APP) as an acid material and blowing agent, pentaerythritol (PER) as a carbonific material and as a synergistic material is utilized to enhance flammability of polypropylene [21-22].

Intumescence is explained as flame retardant technology that creates a protective barrier on the combustible material and causes foam formation when the material exposed to heat. When the intumescent flame retardant system is exposed to heat, there is a chemical interaction between them. Intumescent coating are used also flame retardant systems. They also protect structures for example plastics and wood from dangerous fire. Protection can be provided for steel and other materials from high temperatures. Intumescent coatings are formed by a mixture of various flame retardant additives. Various phosphate-pentaerythritol systems are being searched and developed as intumescent additives [21-22].

The intumescent flame retardant system is occurred by foaming and carbonizing composition on the burning polymer surface. Physical barrier is created by carbon structure which reduces transfer between phases. Intumescent flame retardant system is formed by acid type, carbon type and also blowing agent. This system is indicated in Figure 2.5. Components for intumescent flame retardant system are shown in Table 2.2 [21-22].

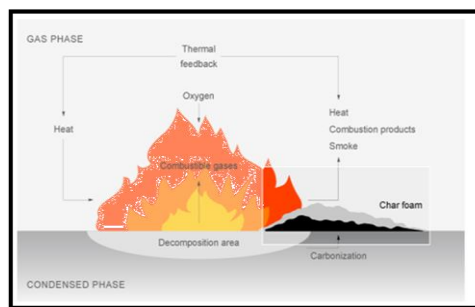


Figure 2.5 : Working mechanism of intumescent flame retardant system.

Table 2.2 : Components for intumescent flame retardant system.

<u>Acid Types</u>	<u>Carbon Types</u>
<u>Inorganic acid types</u>	-Starch
-Phosphoric	-Dextrin
-Sulphuric	-Sorbitol, mannitol
-Boric	-Pentaerythritol
<u>Ammonium salts</u>	-Phenol formaldehyde resin
-Phosphates, polyphosphates	-Methylol melamine
-Borates, polyborates	-Carbon layer forming polymers(Polyamide, polyamide 6)
-Sulfates	<u>Blowing Agents</u>
-Halogen Salts	-Urea
<u>Amide</u>	-Urea formaldehyde resin

2.6.9 Expandable graphite:

Expandable graphite has layered structure therefore atoms or small molecules can be intercalated between the carbon layers. Intercalation agents are usually sulphur or nitrogen compounds. When expandable graphite exposes to heat, layers start to separate like an accordion and its flakes expand. According to grade of material, expansion starts as low as 180 °C. Expansion can occur rapidly and easily. The final volume of graphite can be several hundred times greater than initial volume. Initial expansion temperature, degree of expansion are related to quality of proportion of intercalated layers and intercalation agent [23]. All expandable graphite doesn't act as a flame retardant, only low temperature expandable graphite shows flame retardant properties. The critical temperature is important for expansion and exothermal reaction and ignition occur spontaneously. Expansion of expandable graphite is represented in Figure 2.6 [23].

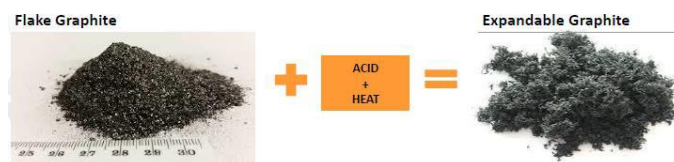


Figure 2.6 : Expansion of expandable graphite by heat.

2.2 Literature Review on Flame Retardancy

Literature search on general fire retardant systems and intumescent flame retardants is investigated. Plastic usage of the world increased from 86 million tons in 2000 to 230 million tonnes in 2010. The world plastics production almost reached 360 million tonnes in 2018. In Europe, this consumption was approx. 62 million tonnes. Polypropylene is very well known commodity plastic material which can be used in automotive, construction and other industries but its flame retardancy property is not good so it is needed to develop flammability performance of polypropylene for many types of applications. Flame retardant additives are commercially available in the market. Commercially available flame retardant materials are indicated in Table 2.3 [16].

Table 2.3 : Commercially available flame retardant materials in market.

Product	Commercial Name	Supplier
Ammonium Polyphosphate	AP 420 series	Clariant(Germany)
Coated ammonium Polyphosphate	AP 760 series	
Aluminium phosphinate salt	OP1230/1240 series	
Aluminium phosphinate salt +melamine polyphosphate	OP1310 series	
Zinc phosphinate salt	OP950	Budenheim(Germany)
Ammonium Polyphosphate (crystal form)	FR CROS480 series	
Melamine phosphate	Budit 310 series (310-312)	

Flame retardancy behaviour of polypropylene with magnesium hydroxide-clay compounds of different structures is investigated by Marosfori and co-workers. As they informed that mixture of montmorillonite and sepiolite types clays enhanced time to ignition and they reduced rate of heat release of final compound. By the way,

nanofillers-nanofillers interaction has a significant role on flame retardant structure of polypropylene [24].

At all times of flame retardant additives and usage in various sectors have been investigated in details by Green and co-workers. Flame retardant additives are also evaluated investigated in terms of specialities in the industry. Green reported that Aluminium trihydrate was developing day by day with 5% growth per year and it was also the largest growing flame retardant material [25].

Camino and co workers determined that ammonium polyphosphate (APP) and pentaerythritol (PER) increased flame retardancy properties of polypropylene by condensed phase mechanism. Limiting oxygen index (LOI) and thermal degradation tests showed that amount of carbon layer was very high at above 500 °C. APP: PER ratio into the flame retardant formulation should be (3:1) by weight to increase LOI and to prevent dripping during combustion process [26].

Wang and Chiu carried out LOI, smoke emission, tensile strength and dynamic combustion evaluation system tests together to evaluate flammability performance of system that includes APP, PER, melamine and polypropylene. As a result, they have observed that flame retardant additives show superior flammability performance in the system. And also, mechanical properties of flame retardant compound was suitable. They developed that dynamic combustion evaluation system using ISO 5660 and ASTM E1354 standards. Ignition time, loss of weight, heat release rate, flash over index and carbon monoxide (CO) concentration can be observed with dynamic combustion evaluation system. It has been determined through the dynamic combustion evaluation system that intumescent flame retardant materials reduce heat release rate of material. When large amounts of APP were added into the compound, mechanical tensile strength started to reduce [27].

Bourbigot and Bras searched the changes that can occur when kaoline was put to IFR system. APP:PER ratio was 3:1 by weight in the system. The flame retardancy effect of kaoline in the system was measured with LOI and UL 94 tests. Clays added to system according to their physical and chemical characteristics so they increased or reduced the flammability properties somewhere. Adding of different types of clays and increase in LOI values don't cause to good UL 94 classification. Kaolinit has good performance to increase flammability performance of polypropylene compound [28].

Bourbigot and coworkers investigated flame retardancy performance of APP and zinc borate when added to system 50/50% by weight. Thermal gravimetric analysis was used for explanation of thermal behaviour of these two components. Decomposition products of APP were polyphosphoric acid and ammonia at 250°C. Polyphosphoric acid reacted with carbon source between 360-460°C and phosphocarbon based products obtained. It is aimed to obtain carbon char layer on the material surface. Thermal decomposition of zinc borate occurred in 2 steps. In the first stage, mass loss was around 5% by weight during 300-360°C while second step occurred between 360-430°C. Reaction was observed between APP and zinc borate at 300-415 °C. Boronphosphate and zinc phosphate compounds were detected in the system. When zinc borate was added to polypropylene/APP compounds, they created synergistic effect each other [29].

Bourbigot and coworkers searched flame retardancy performance of PP/APP/Polyamide-6 when talc and calcium carbonate were added to system. Talc increased mechanical strength of compound but elongation at break values of compound decreased. In addition to them, calcium carbonate also reduced elongation at break values. Flame retardancy property of talc is high but when it reacted with APP, flame retardancy performance of compound reduced. Heat release rate, total radiated heat, carbon monoxide/ carbon dioxide development and residue were investigated. In the mechanical tests, commercial PP talc compounds indicated better properties than calcium carbonate reinforced PP compounds. Calcium carbonate reacts with APP and acid source left from flame retardant system therefore flame retardancy performance of compound reduced. There is no reaction between talc and APP due to this reason talc increased flame retardancy performance of final compound compared to calcium carbonate [30].

Wang and others searched fire retardancy effect of IFR system on polypropylene system. Pentaerythritol is widely used hydrophilic and carbonizer material. Melamine phosphate (MP), pentaerythritol, di-pentaerythritol (DPER), tri-pentaerythritol were used into the system to create synergistic effect between materials. LOI values increased when MP loading level increased in the system but it couldn't pass UL 94 test. It observed that it is not enough to increase MP ratio into the system. According to cone calorimeter test results, heat release rates reduced with the increase of

melamine content. Although prepared compositions created protective layer on the material surface, samples didn't pass the UL-94 tests [31].

Jiang and others conducted their research on the possibility of obtaining new systems by adding expandable graphite to intumescent flame retardant system. Flame retardant additive ratio fixed as 30% by weight into the formulation. However, the ratio between APP and PER was given as 3:1 and graphite was added to the system in certain proportions. It was observed that graphite acted as thermal barrier at high temperatures and graphite systems created more carbon char layer in the system [32].

Bourbigot and coworkers carried out search on APP and PER flame retardants with zeolit. 4A zeolite has important effect on flame retardancy performance of final compound when it was used with classical flame retardants. They conducted XPS test to observe protective layer on the material surface. In addition, it was determined that zeolites added to the system to delay the oxidation of the carbonized layer [33].

Wang and Chiu investigated synergistic effect between intumescent flame retardants and magnesium hydroxide. It has been determined that magnesium hydroxide added to the system was well compatible with the intumescent flame retardants. According to search, amount of carbon monoxide and smoke density was quite high. Amount of magnesium hydroxide had to be increased to reduce smoke density in the system. According to LOI test results, APP showed better performance than magnesium hydroxide [34].

Bayramli and others searched flame retardancy performance of calcium carbonate and intumescent flame retardant system together. In the presence of calcium carbonate, flame retardancy performance of final compounds reduced. LOI values of compounds containing calcium carbonate decreased from 29,3% to 19,7%. The test results showed that calcium carbonate is not suitable to use with intumescent flame retardant system [35].

Wang and Chen investigated flame retardancy effect between melamine phosphate and PER. It was detected that melamine phosphate and PER mixture were suitable flame retardant system for polyamide, polyethylene and also polypropylene system. Dipentaerythritol and tripentaerythritol can be used in the compounds instead of pentaerythritol. Melamine phosphate and PER mixture created effective flame retardancy effect with polypropylene at 35% loading level by weight [36].

Lan-Lan Ge and co-workers worked on expandable graphite and intumescent flame retardant materials. These materials were compounded acrylonitrile butadiene styrene polymer. Intumescent flame retardant system is composed of ammonium polyphosphate and expandable graphite. This system is applied to ABS material to increase its flame retardancy properties. Typical IFR system is applied in ABS at 30% loading level it shows low flame retardancy properties. To overcome this problem, synergistic effect has to be created between flame retardant additives. low efficiency, high loading, high cost. The aim of this work was to study the effects of APP and EG, whether or not they can enhance the fire-retardant features of ABS. EG to APP is 3 : 1 [37].

Lei Ye and co-workers studied on fumed silica and intumescent flame retardants for polypropylene material. In this research, Fumed silica material compounded with polypropylene material and Intumescent flame retardant system. IFR additive also includes nitrogen-phosphorus compound. When <1 wt % fumed silica added for the IFR additive NP can rise 2 to 4% LOI values of the PP compounds and keep the rating V0. TGA results indicated that required amount of fumed silica can enhance thermal capability and residue of the PP/IFR/SiO₂ blends after 500°C. According to SEM results, intumescent char layers occurred and this layer protects the polymer from burning. High loading level fumed silica restricts char layer formation and P-O-P and P-O-C complexes are occurred [37].

Xiaolang Chen and co-workers studied on flame retardancy properties of magnesium hydroxide and expandable graphite on polypropylene material. In this paper, expandable graphite and magnesium hydroxide were blended together to measure flammability properties. Particle size of expandable graphite has positive effect on PP/MH/EG compounds. The EG2 with smaller particle size enhance the LOI value and UL 94 test results [38].

Mengqi Tang and co-workers studied on ammonium polyphosphate, red phosphorus and expandable graphite. These materials compounded with high density polyethylene and ethylene vinyl acetate polymeric materials. In this work, high density polyethylene/ethylene vinyl acetate copolymer composites were prepared by using expandable graphite and ammonium polyphosphate and red phosphorus masterbatch. APP and red phosphorus can show synergistic effect [38].

Ribeiro and co-workers studied on different type of clay minerals to measure fire retardancy performance of ethylene based polymer materials with and without IFR

formulations. Clay types also tested and flame retardancy properties investigated. The intumescent formulation consists of ammonium polyphosphate and pentaerythritol. UL 94 test, LOI and cone calorimeter tests were carried out during study. Adding of Pal to IFR led to the greatest LOI grade and heat release (RHR) close to zero, it is indicated that synergistic effect occurred from the interaction of this clay mineral crystalline structure between materials. The K-Fsp didn't indicate the good efficiency. Structure of clays appears to affect the synergy with APP/PER. Availability of the tetrahedral SiO₄ sheets on both sides of the interlayer space seems to lead to a good synergistic position. Particle size (D (V, 0.5) (μm)) of mica is 210,69 μm [39].

Sheng and coworkers studied on interaction mechanism of ammonium polyphosphate (APP) mixed with muscovite. TG, XRD and SEM were used for testing studies. APP started to decompose at 295°C. The main thermal decomposition products are polyphosphoric acid and NH₄H₂PO₄ at 300 °C. The decomposition product of APP, polyphosphoric acid can interact with muscovite chemically and produce Al₂O₃.2SiO₂.α-SiO₂ and phosphates (AlPO₄ and K₅P₃O₁₀) compounds during 400-800 °C [40].

2.3 Significant of Study

Intumescent flame retardant additives are used to increase flame retardancy performance of polymers. IFR formulations takes place in plastic technology and market with providing good flammability performance to plastic materials. Expandable graphite act as intumescent. Expandable graphite enhances the ignition time of plastic materials and also reduce heat release, mass loss smoke and flame spread. Mica will increase thermal properties of polypropylene material because it can be stable up to 600 °C. Layer will be occurred and this layer will protect polymeric material and improve flame retardancy properties of polymeric compound. Colemanite is a natural hydrated calcium borate able to release structural water according to an endothermic degradation. The mechanism is ended with water and inorganic residue formation. It provides a protective layer on the polymer surface [10].

Mixtures of mineral type and IFR type flame retardant additive can generate synergistic effect to enhance flammability performance of compounds. If specific flame retardant use together in the formulation, it is possible to observe synergistic effect between different type of flame retardants. It brings advantage to producer

because they can use cheaper ingredients inside formulation to obtain desired and required flammability performance from end product. Recently, it is very significant to use abundant mineral and ingredients to create cost efficiency.

In this study, polypropylene will be compounded intumescent flame retardants, expandable graphite, colemanite, mica in twin screw extrusion to observe synergistic effect of materials between each other. Main objectives of this study to fulfil the fire safety standards will be;

-Reduction of FR content: A maximum 30% w/w flame retardant content compounds will be produced thanks to the usage of different species of non-halogenated flame retardants. The synergy is achieved by a combination of intumescent flame retardants with mica and expandable graphite. This reduction of FR needs will be also achieved by creating synergistic effect between materials.

-Increase mechanical and thermal properties in comparison with halogenated flame retardant for polypropylene material. The target properties in the case of polypropylene are summarized in below table.

-Technical, performance, health, environmental and economic factors must be considered in the justification of the optimum novel flame retardant material for household applications.

The thesis is focused on developing new flame retardant compounds with creating synergistic effect between IFR material, mica and expandable graphite that can replace halogen flame retardant compounds increasing their thermal and mechanical properties. Flame Retardants are based on the highly innovative combination with different effects against fire.

Polymeric materials bring many advantages to all sectors in everyday life, however most them can burn quickly and easily in the presence of heat source and oxygen. In this thesis, developed formulations will be used in household appliances to measure performance of flame retardant compounds. The needs and requirements of different applications in the field of household applications. Properties of potential flame retardant additives are indicated in Table 2.4.

Table 2.4 : The materials used in thesis and their properties.

Polymer	IFR	Filler 1	Filler 2	Filler 3
Polypropylene	Hlogen-free, phosphorus&nitrogenous-containing	Mica Mineral	Colemanite Mineral	Expandable graphite
Cost reduction, processability, different series of good features	Highly flame retardancy, halogen free, excellent processability and dispersibility in polyolefin resins	Chemically inert, thermally stable up to 600°C.	Stepwise release of water and generation of glazed coating to protect structure.	Expands to several hundred times its original size, synergistic effect with intumescent flame retardants



3. EXPERIMENTAL PART

3.1 Materials

The polypropylene homopolymer (PPH) was PP 578 L with MFI 25 g/10 min at 230 °C/2.16 kg and density 0.905 g/cm³. This material was supplied by Sabic, Netherlands. Intumescent fire retardant additives (IFR) consisting of ammonium polyphosphate (APP) and synergist was supplied by JLS, China with JLS PNP2D commercial name, properties indicated in Table 3.1. Mica mineral was supplied by Mikron's Company, Turkey, properties indicated in Table 3.2. Colemanite mineral was supplied by Eti Maden, Turkey, properties indicated in Table 3.4. Expandable graphite (EG) was supplied by GK Kropfmuhl, Germany, properties indicated in Table 3.3. All chemicals were used without further purification and the raw materials used in the experiment were not chemically treated before experiment.

Table 3.1 : Main composition and basic properties of IFR PNP2D.

Appearance and Compositions	Basic Properties
Aspect	White, free-flowing powder
Content of phosphorus (%)	21 ± 1
Nitrogen content (%)	18 ± 1
Average particle size (µm)	Approx. 15
Moisture Content (%)	0.50
Density at 25°C (g/cm ³)	Approx. 1.8
Thermal decomposition (°C)	≥250

Table 3.2 : Properties of Mica Mineral.

Properties	Results
Average particle size (d ₅₀) µm	19.52
D ₉₇ µm	78.55
D ₂ µm	8.35

Table 3.3 : Properties of expandable graphite

Material	Carbon Ratio (%)	Expansion rate (cm ³ /g)	Onset Temperature (°C)	Particulate Size
ES 350 F5	98	350	250	80%>300µm

Table 3.4 : Main composition and Basic Properties of Colemanite

Component	Content
B ₂ O ₃	40.00 ± 0.50 %
CaO	27.00 ± 1.00 %
SiO ₂	4.00 ± 6.50 %
SO ₄	0.60% max.
As	35 ppm max.
Fe ₂ O ₃	0.08% max
Al ₂ O ₃	0.40% max
MgO	3.00% max
SrO	1.50% max
Na ₂ O	0.50% max
L.O.I	25.00% max

3.2 Equipments-Compounding in Twin Screw Extruder and Sample Preparation by Injection Molding

3.2.1 Twin screw extruder

The twin screw extruder was an co-rotating type extruder. The brand name of extruder is PRISM TSE24 IIC modular system, with 28:1 L/D. The extruder has two Brabender DSR28 volumetric feeder, degassing port, water bath, pelletizer and also chopper. It is also equipped with seven modular barrel segments; 96 mm of length and L/D ratio is 28:1. Properties of twin screw extruder is indicated in Table 3.5 [41-43].

Table 3.5 : Properties of twin screw extruder.

	Key factors	PRISM TSE24
Diameter of screw	mm	24
Screw speed at maximum level	rpm	1000
Length of shaft and diameter of screw	-	28:1
Shaft center line distance	mm	
Depth of channel	mm	5.15
Overall volume	cm ³	511
Independent volume	cm ³	228
Peripheral surface area for barrel	cm ²	830

Required and good melting, mixing of polymers are achieved by high shear effect, enhanced residence time in extruder therefore screw profile of in the equipment was designed accordingly. Six zones are available in the extruder. The names of the zones are shown below.

- Entrance of plastic material and transferring to solid zone
- Zone for Plasticizing operations
- Zone for plastic melt
- Providing of extra homogenize mixture
- Release of gases-Zone
- Setting up pressure

After the polymer comes out of the extruder, it goes to the water bath. When it comes to the water bath, the molten polymer is cooled in this section. During this section, polymer spaghetti are available inside water. Water temperature of water bath is directly related polymer type. The polymer spaghetti coming into the water bath are cut in the pelletizer unit. At the end of this process, polymer granules can be obtained by pelletizer unit.

3.2.2 Injection molding machine

Sampling part were manufactured by using Arburg Allrounder 320C injection molding machine to measure the physical and mechanical properties of compounded materials and composites as per ISO standards. Specifications of injection molding machine are indicated in Table 3.6 [44].

Table 3.6 : Injection molding machine properties

	Key factors	Arburg Allrounder 320C
Diameter for screw	mm	30
Applied max. pressure	Bar	1068
Max.shot weight	Gr	70
Screw speed at max. level	Rpm	115
Back pressure at max. level	Bar	25

Compounded materials were dried at 90°C for at least 4 hours to eliminate water content from the materials. Barrel temperatures, injection time and speed, back pressure for screw, speed of screw, holding time and time of cooling were kept

constant to produce test specimens for testing. Sampling parts are manufactured according to international standards to eliminate deviation which can come from sampling parts difference. After production of sampling parts, measurement and control were checked to see quality control performance of sampling parts. After this type of controls, required tests have been carried out.

3.2.3 Measurement of density

Density values were measured with Mettler Toledo density test equipment according to the procedure explained in ISO 1183-1 Plastics-Methods for determining the density of non-cellular plastics-Part 1: Immersion Method [45].

3.2.4 Determination of melt flow index

Melt flow index (MFI) or melt flow rate (MFR) was measured by using Zwick testing machine according to reference standard. In this testing device, flow properties of polymers are determined under a certain temperature. Test temperature and weight is set to 230 °C and 2.16 kg, respectively [46].

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

According to this test, temperature profile of extruder are adjusted. Otherwise, final features of compounds can be effected.

3.2.5 Mechanical properties - tensile testing

Sampling parts were waited in special laboratory room at a temperature of 23 ± 2 °C and 50 % humidity for at least 24 hours. This operation is very beneficial to eliminate the post crystallization or physical aging effects from sampling parts.

Polymeric compounds were tested by using Zwick – Z020 testing equipment to measure tensile properties of end product according to ISO 527-1/2 1A Plastics-Determination of Tensile Properties- Part 2: Test Conditions for Molding and extrusion plastics. At least 5 specimens were tested for each plastic compounds [47].

3.2.6 Izod notched impact testing

Izod notched impact strength values of sampling parts were determined with using Zwick – HIT – 50 P test equipment according to ISO 180/A Plastics-Determination of Izod Impact Strength [48].

3.2.7 Heat deflection temperature (HDT)

The heat deflection temperature (HDT) values of pure PP and IFR filled PP compounds were evaluated using Heat deflection tester according to ISO 75 standard [49]. This test is very significant to determine performance of compounds for fire safety as well.

3.2.8 Thermal gravimetric analysis (TGA)

Thermogravimetric analysis (TGA) carried out on a Q500 thermal gravimetric analyzer. Plastic granules weighted 20.0 mg of material. Testing device is heated from room temperature to 800 °C at a heating rate of 20 °C/min in a dynamic nitrogen atmosphere. 50 ml/min of nitrogen flow has been chosen also.

3.2.9 Limiting oxygen index (LOI)

Limiting oxygen index test was performed using fire testing technology device according to ASTM D2863-10 standard. This device has test chimney, plastic specimen holder and gas controlling equipment [50]. Plastic sampling part puts to specimen holder then fire apply to polymer under gas supplies. Oxygen level can be changed during test to observe ignition time of plastic material.

3.2.10 Glow wire flammability test

Glow wire flammability index test was performed by using PTL Glow – wire test apparatus. Test plates use as sampling material. The fire resistance of sampling plastic materials can be measured and described using this test method. It is very important to know fire hazard and risk assessment of produced samples. Glow wire, thermocouple, temperature shower and chamber are available in the glow wire test apparatus. During test, sampling parts replaced to specimen holder then glow wire is touched to sampling parts at fixed temperature at 30 second. After this time, wire is removed from sampling parts. 30 seconds can be waited to see fire situation [51].

3.2.11 UL 94 flammability testing-vertical

UL 94 test use to determine burning rate and time of plastic compounds by using CEAST flammability tester. According to fire performance of the plastic materials this test can be applied both vertical and horizontal position. UL 94 flammability test results categorized by burning grades V-0, V-1 or V-2 depending on the total burning

time and dripping behaviours as described in the standard. The best flame retardancy property of plastic materials classified as V-0 grade [52].

3.2.12 Scanning electron microscopy (SEM) analysis

Morphology analysis of intumescent char of compounds was checked by Jeol JSM 6400 device.

3.3 Flow Chart of the Thesis

The Figure 3.1 indicates the flow chart of this thesis according to objective achievements.

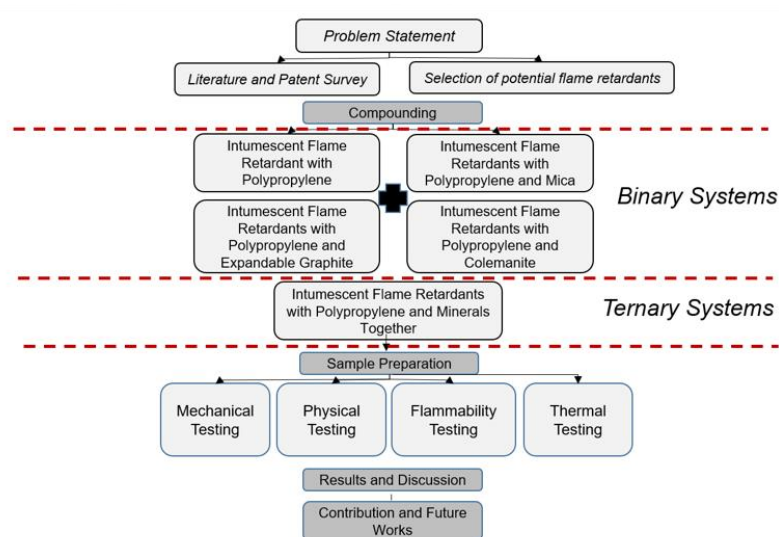


Figure 3.1 : The flow chart of this study.

3.4 Compounding Recipes

PP and IFR were compounded in twin screw extrusion at the different loading levels to obtain three different polymeric compound samples. IFR were loaded to PP at 20-25-30% loading levels to increase flame retardancy properties of PP. IFR and PP were fed separately into extruder from the inlet port of the extruder with the help of gravimetric feeders. Compounds were produced by twin screw extruder at a temperature profile of 180, 180, 180, 185, 190, 190, 195 °C, and granulator used to manufacture to pellets. To obtain good and homogenize mixed plastic compounds twin screw extruder used. Type of extruder is intermeshing and co-rotating; Coperion ZSK 26Mc with three Brabender feeders, with diameter of screw of 25.5 mm and ratio of

L/D 44:1. Sampling parts were produced in Arburg 370 S 800-150 injection machine with using ISO 20753:2018. Prepared compositions were indicated in table 3.7. The following nomenclature was used; Compositions of polypropylene compounds having 0, 20, 25, 30 percent by weight intumescent flame retardant additives were designated as PP100, PP80/IFR20, PP75/IFR25, PP70/IFR30 respectively. In this nomenclature, the letters “PP and IFR” were used to represent polypropylene and the intumescent flame retardant additive respectively.

Table 3.7 : Experimental design of IFR filled polypropylene compounds.

Sample name	PP (wt%)	IFR (wt%)
PP100	100	0
PP80/IFR20	80	20
PP75/IFR25	75	25
PP70/IFR30	70	30

To identify the combined effect of IFR and mica filling on mechanical, physical and flame retardancy properties and morphology of PP compounds, blends were prepared as indicated in Table 3.8. Before compounding procedure and getting the mica sampling was heated up to 100°C for 4h then sample cooled slowly. PP, IFR and mica mineral were mixed in twin screw extrusion at the different loading levels to obtain seven different polymeric compounds. Loading level amount of IFR and mica was kept at 30 wt% overall quantity of compound. Mica was put to system with following quantities 2, 4, 6, 8 and 15 wt%. In this terminology, the letters “PP”, “IFR” and “M” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and mineral mica.

Table 3.8 : Experimental design of mica and IFR filled polypropylene compounds.

Samples Name	PP (wt. %)	Mica Mineral (wt. %)	IFR (wt. %)
Neat PP	100	0	0
PP70/IFR30/M0	70	0	30
PP70/IFR28/M2	70	2	28
PP70/IFR26/M4	70	4	26
PP70/IFR24/M6	70	6	24
PP70/IFR22/M8	70	8	22
PP70/IFR15/M15	70	15	15
PP70/IFR0/M30	70	30	0

PP and EG compounded together at 20-25-30 wt% expandable graphite (EG) loading levels to observe flame retardancy performance of EG. Then, PP, IFR and expandable graphite were mixed in twin screw extrusion at the different loading levels to obtain

flame retardant additive filled polymeric compounds. Loading level amount of IFR and EG was kept at 30 wt% mass of overall quantity of compound. EG was put to system with following quantities 2, 4, 6, 10, 15 and 20 wt%. The detailed formulation is indicated in Table 3.9. In this terminology, the letters “PP”, “IFR” and “EG” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and additive expandable graphite.

Table 3.9 : Experimental design of EG and IFR filled polypropylene compounds.

Samples Name	PP (wt. %)	Expandable graphite (wt. %)	IFR (wt. %)
Neat PP	100	0	0
PP80/EG20	80	20	0
PP75/EG25	75	25	0
PP70/EG30	70	30	0
PP70/IFR28/EG2	70	2	28
PP70/IFR26/EG4	70	4	26
PP70/IFR24/EG6	70	6	24
PP70/IFR20/EG10	70	10	20
PP70/IFR15/EG15	70	15	15
PP70/IFR10/EG20	70	20	10

PP, IFR and colemanite were mixed in twin screw extrusion at the different loading levels to obtain seven different polymeric compounds. Total loading level amount of IFR and colemanite was kept at 30 wt% mass of overall quantity of compound. Colemanite was put to system with following quantities 2, 4, 6, 8 and 15 wt%. In this terminology, the letters “PP”, “IFR” and “C” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant and mineral colemanite. Prepared compounds are indicated in Table 3.10.

Table 3.10 : Experimental design of colemanite and IFR filled polypropylene compounds.

Samples Name	PP (wt. %)	Colemanite (wt. %)	IFR (wt. %)
Neat PP	100	0	0
PP70/IFR30/C0	70	0	30
PP70/IFR28/C2	70	2	28
PP70/IFR26/C4	70	4	26
PP70/IFR24/C6	70	6	24
PP70/IFR22/C8	70	8	22
PP70/IFR15/C15	70	15	15
PP70/IFR0/C30	70	30	0

In similar way, PP, IFR, colemanite, mica and expandable graphite were compounded in twin screw extrusion at the reasonable loading levels to obtain nine different

polymeric compounds. Total loading level quantity of flame retardant ingredients was kept at 30 wt% mass of total amounts of compound. All formulations are presented in Table 3.11. In this terminology, the letters “PP”, “IFR”, “C”, “EG”, “M” were used to indicate the plastic polypropylene, flame retardant additive intumescent flame retardant, mineral colemanite, expandable graphite and mica.

Table 3.11 : Experimental design of flame retardant additives filled polypropylene compounds.

Samples Name	PP (wt. %)	IFR (wt.%)	Colemanite (wt.%)	Mica (wt.%)	Expandable graphite (wt.%)
Neat PP	100	0	0	0	0
PP70/IFR20/M8/C2	70	20	2	8	0
PP70/IFR22/M6/C2	70	22	2	6	0
PP70/IFR22/M4/C4	70	22	4	4	0
PP70/IFR22/EG6/C2	70	22	2	0	6
PP70/IFR22/EG4/C4	70	22	4	0	4
PP70/IFR22/EG6/M2	70	22	0	2	6
PP70/IFR22/EG4/M4	70	22	0	4	4
PP70/IFR22/EG2/M6	70	22	0	6	2
PP70/IFR20/EG2/M8	70	20	0	8	2



4. RESULTS AND DISCUSSION

4.1 Compounding of Intumescent Flame Retardant with Polypropylene

4.1.1 Measurement of density

Density results represented a steady increase with rising IFR quantity. IFR has a density of 1.8 g/cm^3 . It is higher than polypropylene, which is 0.90 g/cm^3 . So addition of IFR into plastic material concluded in compounds with superior density. Significant difference couldn't be observed in density values at same loading levels as indicated in test results. Density test outcomes are displayed in Table 4.1.

Table 4.1 : Density value of neat PP, IFR filled PP compounds

Sample name	Density (g/cm^3)
PP100	0.9069 ± 0.0005
PP80/IFR20	0.9830 ± 0.0030
PP75/IFR25	1.0405 ± 0.0049
PP70/IFR20	1.0578 ± 0.0011

4.1.2 Melt flow index (MFI) test results

When IFR added to polypropylene, MFI value started to decrease from 22.35 to 14.88 g/10 min at 230°C and 2.16 kg loading. MFI values represented a steady reduction with rising IFR amount. One of the key parameters which has effect on the development of intumescent char layer is melt viscosity of polymeric materials. Melt viscosity could be described with MFI test [53]. MFI values have also effect on dripping behaviour of the pyrolysing polymer. Well specified melt flow and dripping are usually helpful to pass UL 94 vertical test and also glow wire test. The flame retardant materials can change the melt behaviour of polymeric materials critically. Test outcomes of neat PP and combinations of IFR filled PP compounds are represented in the Table 4.2.

Table 4.2 : MFI test results of neat PPs and mixtures of IFR filled PP.

Sample name	MFI (g/10 min)
PP100	22.35 ± 0.3
PP80/IFR20	18.25 ± 0.2
PP75/IFR25	17.65 ± 0.3
PP70/IFR30	14.88 ± 0.5

4.1.3 Mechanical Properties Tensile Test Results

Mechanical test results of polypropylene and fire retardant filled compounds with different amount level of IFR are showed in Table 4.3. Putting of IFR by high quantity to PP material decreases the tensile strength and elongation at yield point values due to effect of mineral like reinforcing effect. There is a correlation between tensile strength and strain at yield point for IFR filled PP compounds. When the IFR loading level is 20wt.%, there is no big difference between it and unfilled PP in terms of tensile strain at yield point values and then this difference started to increase with increasing IFR content into the formulation. Furthermore, tensile strength at yield point values started to decrease with the increase of the IFR content.

Elastic modulus values of IFR filled PP compounds increased nonlinearly with increasing of the IFR loading level. Elastic module values reached its highest point at 30wt.% IFR loading level. It is indicated that there is hardening effect of the IFR on PP matrix. IFR particles started to block the movement of the long chains of the polypropylene material therefore improvement of the stiffness of IFR filled compounds obtained [30].

Tensile strength at yield point values started to decrease with the addition of the IFR into the formulation. In the literature, interfacial adhesion between particles and polymer matrix and it was observed that tensile strength increases with the improvement of the interfacial adhesion. According to test results, tensile strength values reduced slightly therefor interfacial adhesion between IFR and polypropylene matrix was suitable in this situation.

Elongation values of PP compounds reduced with rising quantities of IFR content in PP compounds. Higher IFR content didn't develop elongation properties of PP compounds. Interaction between plastic and fillers has influence on tensile properties of filled PP compounds. At least 30 % by weight, IFR content has unfavorable influence on the mechanical properties of PP composite. That situation explained in

the literature as tensile strain properties of PP compound decreased and weakened due to the filling of filler particles. In addition to them plastic deformation can be created by the matrix around inclusions due to high level stress concentration. Test results were showed in Table 4.3.

Table 4.3 : Mechanical test results of neat PP and IFR filled PP compounds

Sample name	Elastic Mod.(MPa)	Tensile Strength @ Yield Point (MPa)	Tensile Strain @ Yield Point (MPa)
PP100	1578 ± 10	35.7 ± 0.23	9.43 ± 0.06
PP80/IFR20	2020 ± 25	32.8 ± 0.23	8.20 ± 0.15
PP75/IFR25	2435 ± 38	29.7 ± 0.3	6.1 ± 0.08
PP70/IFR30	2760 ± 102	26.4 ± 1	4.05 ± 0.12

4.1.4 Izod impact test results-notched

Izod impact notched testing outcomes of neat PPs and IFR filled PP compounds were indicated in Table 4.4. When the IFR loading level is 20%, Izod impact strength values of compounds are the maximum. The lowest impact strength values were observed when the IFR loading level reached to 30% in the PP compound. IFR and polymer matrix show poor interfacial interaction between each other so it has also negative effect on mechanical properties of compounds.

Table 4.4 : Izod impact properties of pure PP and IFR filled PP compounds.

Sample name	Izod Impact Strength (kJ/m ²)
PP100	3.21 ± 0.14
PP80/IFR20	2.80 ± 0.14
PP75/IFR25	2.45 ± 0.10
PP70/IFR30	1.76 ± 0.14

4.1.5 Heat deflection temperature testing results

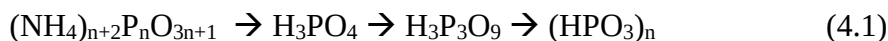
Heat deflection temperature (HDT) was performed as per method explained in characterization techniques part. This test is utilized to define short period heat durability of polymeric materials and to separate between materials that are capable to maintain light loads at elevated temperatures and losing stiffness over a tight temperature sequences. According to results, HDT values were increased essentially by the addition of intumescent flame retardant additive. It was observed that various amounts of intumescent flame retardant had effect on HDT of PP compounds. This property will provide extra safety to PP compounds during the fire HDT values of sampling materials are displayed in Table 4.5.

Table 4.5 : HDT testing results of pure PP and IFR filled PP compounds.

Sample name	Heat Deflection Temperature °C
PP100	87
PP80/IFR20	90.5
PP75/IFR25	90.9
PP70/IFR30	91.2

4.1.6 Thermal gravimetric analysis (TGA)

Thermal gravimetric analysis can be utilized to search thermal decomposition behaviour and also flame retardancy mechanism of compounds. According to Figure 4.1, neat polypropylene displayed only one-step thermal decomposition under nitrogen atmosphere, it initiated decomposition at 262 °C and it used up at 420 °C completely. It was consumed at 500 °C without leaving any ash. The initial decomposition temperature of IFR filled PP compound was at around 200 °C. The loss of quantity has relations with the volatilization of small molecules inside and fractional decomposition of ammonium polyphosphate (APP). According to literature, APP starts to decompose at 180 °C. It gives phosphoric acid, ammonia and also water to the medium. Then this acid reacts with pentaerythritol to create phosphate ester. Decomposition reactions of APP are in given below. The maximum weight loss was observed between 335°C-500°C. Then, approx. 20 wt% char residues at 500°C were obtained due to good char forming capability of IFR compound [54]. It was clear that the addition of IFR to PP material increased thermal features of PP. Approx. 20°C, it has been enhanced comparison with neat PP. At the beginning of heating, produced char layer has an inhibition effect on PP material. According to chart, IFR filled PP compound is more thermally stable than pure PP.



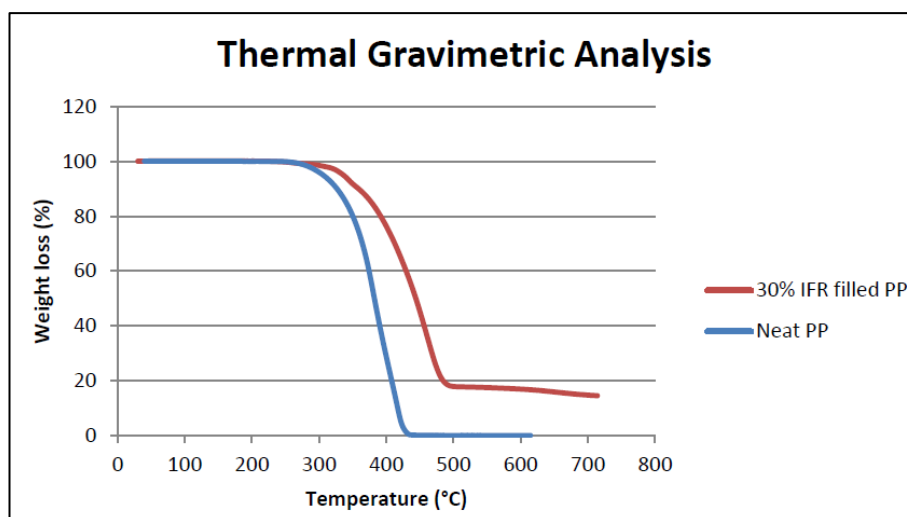


Figure 4.1 : Thermal gravimetric analysis of neat PP and 30wt% IFR filled PP compound.

4.1.7 Limiting oxygen index

LOI testing procedure helps to determine required concentration of oxygen in a following combination of oxygen and nitrogen that supports ignition of PP and IFR filled PP. The LOI of pure PP is approx. 18.2 %. It was observed that the LOI of the PP/IFR compound including 20 wt% IFR rises quickly to 31.7 from 18.2% of PP, specifying that IFR consumed at 20 wt% loading level considerably enhance flammability performance of PP. The LOI results of compounds (P100 to PP70/IFR30) rise 37.9 % with 30 wt% loading level of IFR in the final compound. LOI values are shown in Table 4.6.

Table 4.6 : LOI test results of pure PP and IFR filled PP compounds.

Sample name	LOI (%)
PP100	18.0 ± 0.23
PP80/IFR20	31.7 ± 0.18
PP75/IFR25	34.5 ± 0.20
PP70/IFR30	37.9 ± 0.15

4.1.8 UL 94 flammability test (vertical)

UL 94 flammability testing is utilized to observe ignition performance and fire spread of polymeric parts. Flammability ratings are categorized as V0, V1, or V2 with UL 94 flammability testing. The best flammability property is obtained by V0 rating.

V-0: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 10 seconds. Flaming drips can't be allowed.

V-1: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips can't be allowed.

V-2: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips are allowed.

Horizontal Burning HB: HB classification on a 3mm of thick specimen with a burning rate is less than 3"/min or stops burning before the 5" mark. HB classified materials are defined "self-extinguishing".

Flame retardants show different mechanisms which are connected with their influence on the dripping behaviour in the UL 94 vertical flammability test. Especially dripping is managed by viscosity of melt. Desired flammability classification can be obtained with controlling in the UL 94 test. Melt dripping behaviour has effect UL 94 flammability classification directly. UL 94 test results of IFR filled PP compounds are indicated in Table 4.7. When the amount of IFR was adjusted in between 25 and 30 wt% in compound, and testing specimens of PP/IFR compounds can achieve the V0 grade. Additionally, when putting of IFR to PP compound is less than 25%, testing samples only passed the V2 rating. Dripping also observed at 20wt% loading level so samples classified as V2 rating. These results indicated that V0 classification can be achieved with adding a suitable amount of IFR to PP material.

Table 4.7 : UL 94 test results of IFR filled PP compounds.

Samples	UL 94 Test-Vertical				
	T1	T2	T3	Dripping	Flame Rating
PP80/IFR20	26	51	0	Yes,drip particles that ignite	V2
PP75/IFR25	2	6	0	No	V0
PP70/IFR30	0	2	0	No	V0

4.1.9 Glow wire flammability test

Glow wire flammability results ensure to evaluate the capability of testing parts to remove fires and their capability not to obtain volatiles capable of spreading flame. The effects of IFR on flammability features of PP compounds were searched. The test was carried out at 750 and 850°C of temperatures. Burning time of polypropylene compounds significantly decreased when amounts in polypropylene were increased from 20% to 30%. The effectiveness of IFR on flammability features of plastic compounds were examined. Glow wire tests were performed at temperatures of 750°C

and 850°C. Test results represented that compounds including IFR had affirmative influence on flammability. Outcomes are indicated in Table 4.8.

Table 4.8 : Glow wire test results of IFR filled PP compounds.

Samples	Glow Wire Flammability Temperature (°C)	
	750	850
PP80/IFR20	There is no burning and flashing.	Cotton doesn't ignite and burning time less than 28 seconds after lifting over glow wire from the system.
PP75/IFR25	There is no burning and flashing.	There is no burning and flashing.
PP70/IFR30	There is no burning and flashing.	There is no burning and flashing.

4.1.10 Morphology analysis of IFR filled PP compounds

The char residue was obtained after ash content test. The morphology analysis of ash residue was done by SEM. Figure 4.2 indicates the state before ash testing. Figure 4.3 represents the SEM picture of ash residue of PP/IFR compound. It is observed that the structure of char residue of PP/IFR compound is loose and it has porous structure which is needed to be improved to form good flame shield for plastic material.



Figure 4.2 : Char residue picture after ash testing.

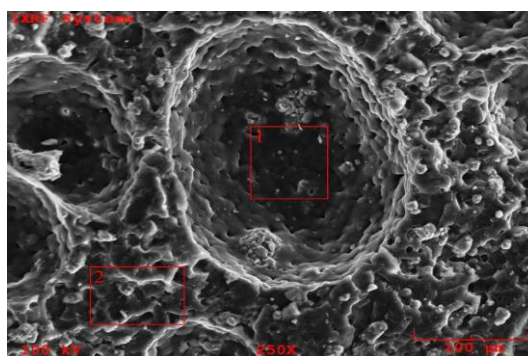


Figure 4.3 : SEM micrograph of PP/IFR char residue.

4.2 Compounding of Intumescent Flame Retardants with Polypropylene and Mica

4.2.1 Measurement of density

Density test results of compounds indicated stable rising with rising mica amount. Mica and IFR have higher density of 2,83 g/cm³ and 1,8 g/cm³ respectively. They have higher density value than polypropylene, which is 0.906 g/cm³. Thereof, the addition of Mica and IFR to polypropylene outcomed in compounds with superior density results as obeying the rule mixture. Moreover, even though total FR ratios were fixed due to higher density of mica, increased mica content increased the density of compounds slightly. Outcomes are given in Table 4.9.

Table 4.9 : Density results of neat PPs, IFR, Mica and IFR/Mica filled PP compounds.

Samples Name	Density (gr/cm ³)
Neat PP	0.9069 ± 0.002
PP70/IFR30/M0	1.0578 ± 0.002
PP70/IFR28/M2	1.0611 ± 0.004
PP70/IFR26/M4	1.0629 ± 0.004
PP70/IFR24/M6	1.0702 ± 0.002
PP70/IFR22/M8	1.0823 ± 0.002
PP70/IFR15/M15	1.0947 ± 0.003
PP70/IFR0/M30	1.1326 ± 0.002

4.2.2 Melt flow index (MFI) test results

When IFR added to polypropylene, MFI value started to decrease from 22.35 to 14.88 g/10 min at 230 °C and 2.16 kg loading. When mica mineral added to polypropylene with IFR, MFI values began to increase around 15.3 %. At 8 wt% mica loading level, MFI values decreased from 19.35 g/10 min to 17.64 g/10 min. Because the addition of filler content into the PP/IFR compounds will improve flexibility of compound because of plastic deformation thanks to stress concentration. One of the key parameters which has effect on the development of intumescent char layer is melt viscosity of polymeric materials. Melt viscosity could be described with MFI test [53]. MFI values have also effect on dripping behaviour of the pyrolysing polymer. Well specified melf flow and dripping are usually helpful to pass UL 94 vertical test and also glow wire test. The flame retardant materials can change the melt behaviour of polymeric materials critically. The MFI testing outcomes were given in Table 4.10.

Table 4.10 : MFI graph of IFR, Mica and IFR/Mica filled PP compounds.

Samples Name	MFI (gr/10 min.)
Neat PP	22.35
PP70/IFR30/M0	14.88
PP70/IFR28/M2	17.16
PP70/IFR26/M4	18.33
PP70/IFR24/M6	19.35
PP70/IFR22/M8	17.64
PP70/IFR15/M15	18.03
PP70/IFR0/M30	19.05

4.2.3 Mechanical properties tensile test results

Tensile features of polypropylene and fire retardant compounds with various amount of mica mineral are indicated in Table 4.11. Putting of IFR by high quantity in PP material decreases strain and tensile strength values due to effect of mineral like reinforcing effect. Increasing the amount of mica mineral content in polypropylene compounds increases elastic modulus. Tensile strength value of polypropylene homopolymer decreased when IFR and mica mineral added to system. No selective difference is observed on tensile strength values of only IFR and IFR/mica filled PP compounds. 30 wt% mica filled PP compound showed better tensile strength properties compared to IFR/mica filled PP compounds at different loading levels each other which might be related with higher particle size with aspect ratio as explained in Verbeek study [55]. Strain value of neat polypropylene homopolymer decreased with increasing amounts of mica mineral content in PP/IFR/Mica compounds. No selective difference is observed on tensile strain values of 30 wt% IFR and 30 wt% mica mineral in PP compounds. In addition to them, when the mica content is less than 8 wt%, the tensile strength values decreases, and it reaches up to at mica content of 8 wt%, and then it started to rise with rising of the mica amount in PP compound. This shows that tensile strength values of the compound improved because of high filler concentration. It is generally believed that the polymer matrix around the inclusions can produce plastic deformation thanks to stress concentration. Liang, Li and Feng observed that elastic modules nonlinearly increased when the amount of IFR content in polypropylene compound increases. IFR material has stiffening effect on the final compound. This effect is related to the movement of the big chains of the matrix material is blocked by IFR particles. Stiffness of filled PP compounds can be improved by adding IFR content to the PP compound. However, increasing IFR content leads to a decrease tensile strength of PP compound. It is related to interfacial adhesion

between inorganic materials and polymer matrix. If interfacial adhesion improves, tensile yield strength values can start to increase [56].

Mechanical features of filled PP composites are related to interaction between polymer and fillers. Decrease in strain at yield and break point may be the formation of some voids because of debonding operation of mica from plastic structure upon failure. Mica has good shape stability, high elasticity, high shear and compressive strength, perfect cleavability and incompressible in terms of mechanical properties. According to literature, when mica added to polymer matrix, some physical features of polymer matrix as mechanical endurance, modulus, and heat distortion temperature can be improved. The size, shape, and distribution of mica particles in the polymer compound have effect on mechanical properties of final compound. Interfacial adhesion effected from these properties directly. Liang and Yang have compounded with high density polyethylene and surface treated mica in twin screw extrusion. When they added to surface treated mica to HDPE during compounding, they searched that tensile endurance of the compounds increases slightly with an rise of weight fraction of the particles. As they explained that the interfacial adhesion between the filler and matrix for compounds has impact on tensile strength especially, so after the surface of mica particles treated by a silane-coupling agent, the interfacial adhesion between mica and HDPE matrix is improved [57].

Table 4.11 : Mechanical properties of mica and IFR filled PP compounds.

Samples Name	Elastic Mod. (MPa)	Tensile Strength at Yield Point (MPa)	Tensile Strain at Yield Point (MPa)
Neat PP	1578 ± 10.69	35.7 ± 0.23	9.43 ± 0.06
PP70/IFR30/M0	2760 ± 102.71	26.4 ± 1.00	4.05 ± 0.12
PP70/IFR28/M2	2622 ± 50.13	25.5 ± 0.10	3.77 ± 0.05
PP70/IFR26/M4	2561 ± 54.51	25.0 ± 0.19	3.84 ± 0.05
PP70/IFR24/M6	2667 ± 58.50	25.0 ± 0.13	3.68 ± 0.02
PP70/IFR22/M8	2734 ± 35.96	26.3 ± 0.13	3.61 ± 0.05
PP70/IFR15/M15	2798 ± 42.73	26.9 ± 0.08	3.75 ± 0.01
PP70/IFR0/M30	3045 ± 36.43	29.1 ± 0.15	3.98 ± 0.04

4.2.4 Izod impact test results-notched

Izod impact test outcomes of neat PPs, mica, IFR filled PP compounds were indicated in Table 4.12. It has been tested that izod impact value of PP homopolymer is around 3.22 kJ/m². Mica and IFR filled PP compounds showed negative effect on izod impact

strength values at different loading levels. No selective difference is observed on izod impact values at 2, 4, 6, 8 and 15 wt% mica loading level in PP compounds. The reduction of Izod impact strength with IFR and mica corporation to PP could be examined by the hindering of chain mobility.

Table 4.12 : Izod impact test results of IFR and mica filled PP compounds

Samples Name	Izod Impact Strength kJ/m ²
Neat PP	3.21 ± 0.14
PP70/IFR30/M0	1.76 ± 0.14
PP70/IFR28/M2	1.83 ± 0.08
PP70/IFR26/M4	1.81 ± 0.09
PP70/IFR24/M6	1.80 ± 0.07
PP70/IFR22/M8	1.74 ± 0.08
PP70/IFR15/M15	1.80 ± 0.10
PP70/IFR0/M30	2.03 ± 0.03

4.2.5 Heat deflection temperature testing results

Heat deflection temperature (HDT) was performed according to technique explained in characterization techniques section. This test is utilized to define short period heat defiance of polymeric materials and to separate between materials that are capable to maintain light loads at evalated temperatures and those that lose stiffness over a tight temperature. According to test results, HDT values were increased essentially by the addition of intumescent flame retardan additive. It was observed that various amounts of intumescent flame retardant additives had effect on HDT of PP compounds. This property will provide extra safety to PP compounds during the fire HDT values of sampling materials are indicated in Table 4.13.

Table 4.13 : Heat deflection test results of mica and IFR filled PP compounds.

Samples Name	Heat Deflection Temperature °C
Neat PP	87
PP70/IFR30/M0	90.2
PP70/IFR28/M2	90.6
PP70/IFR26/M4	92.1
PP70/IFR24/M6	93.2
PP70/IFR22/M8	93.8
PP70/IFR15/M15	96.3
PP70/IFR0/M30	97.9

4.2.6 Thermal gravimetric analysis

TGA is beneficial technique to see decomposition behaviours and to calculate char residue. The TGA graphs of neat PP, IFR/Mica filled PP compounds were shown in Figure 4.4, 4.5, 4.6, 4.7, 4.8, 4.9, 4.10, 4.11. Polypropylene started to decomposition at 250 °C and used up at 500 °C. It is observed that initial degradation temperature increased from 250 °C in PP to between 260 °C – 270 °C in PP compounds. According to literature, mica presented a mass loss around to 700 °C related to dehydroxylations process [7]. Addition of mica gave minimal effect on TGA curves. However, char residue was increased from 8.46 % to 10.25 %, 11.55 %, 15.74 %, 20.88 % and 28.42 % at 2, 4, 6, 8, 15 and 30 wt% mica content respectively. It is obvious that the char residue increased by the increasing loading of mica.

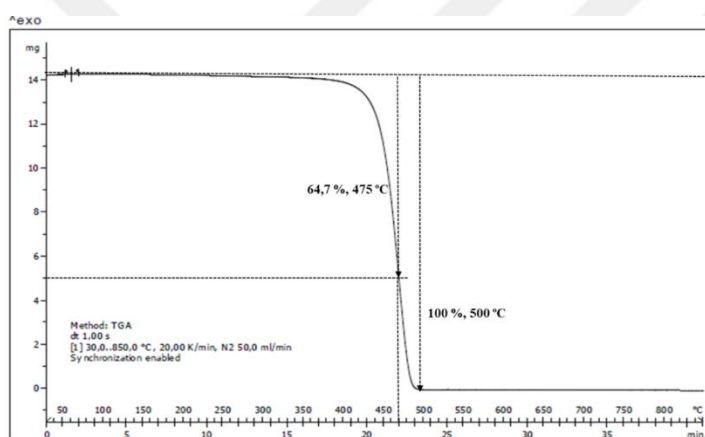


Figure 4.4 : TGA graph of neat polypropylene.

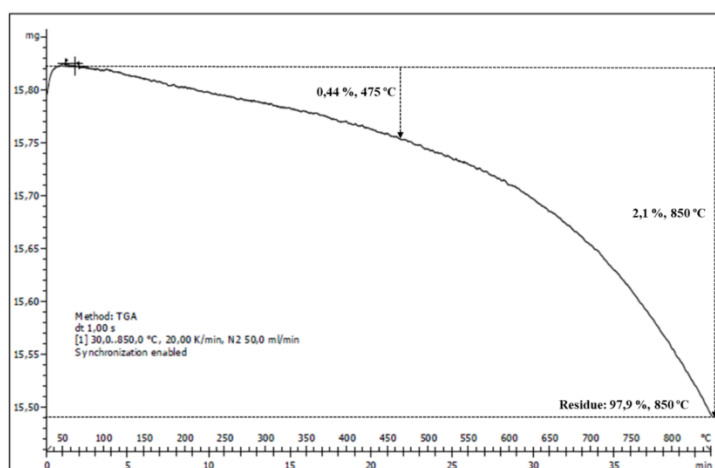


Figure 4.5 : TGA graph of pure mica mineral.

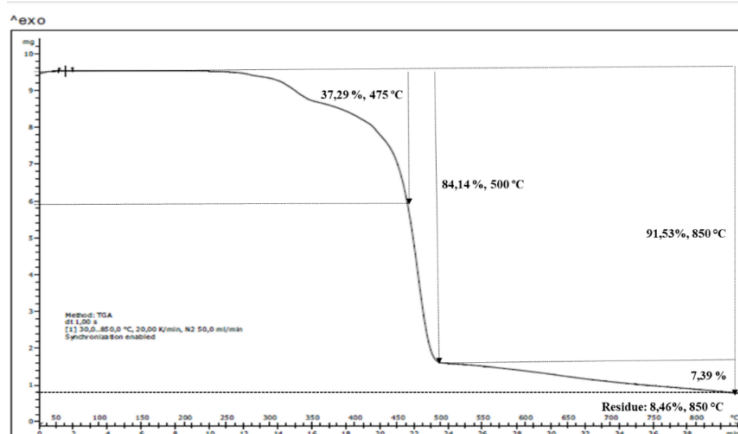


Figure 4.6 : TGA graph of PP/IFR30/M0 sample.

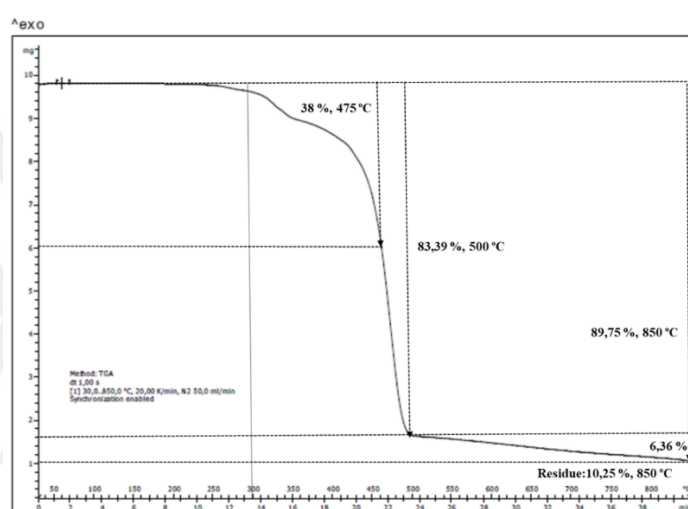


Figure 4.7 : TGA graph of PP/IFR28/M2 sample.

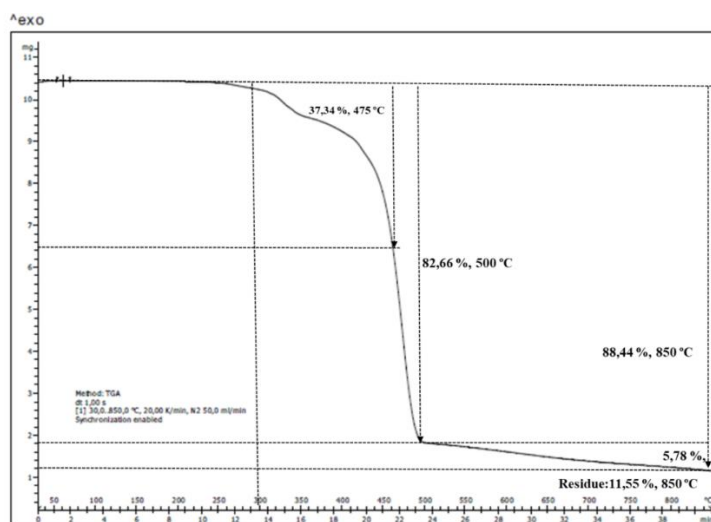


Figure 4.8 : TGA graph of PP/IFR26/M4 sample.

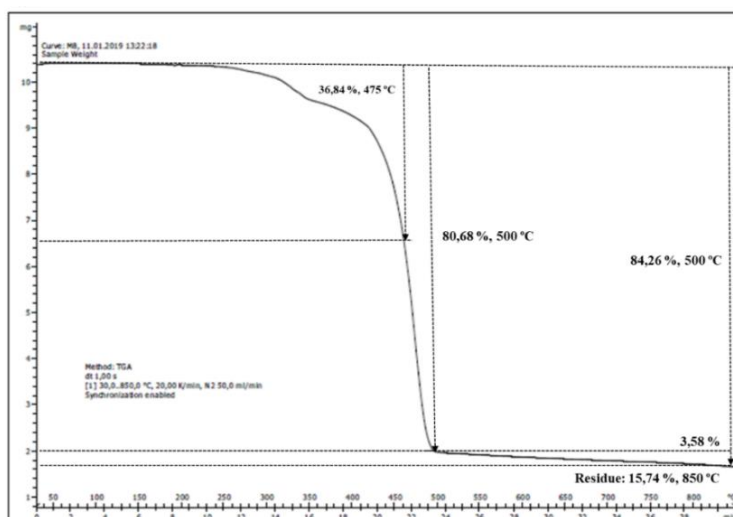


Figure 4.9 : TGA graph of PP/IFR22/M8 sample.

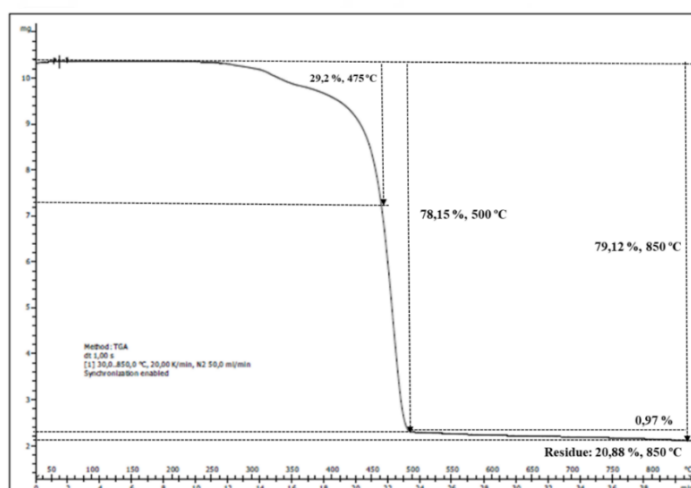


Figure 4.10 : TGA graph of PP/IFR15/M15 sample.

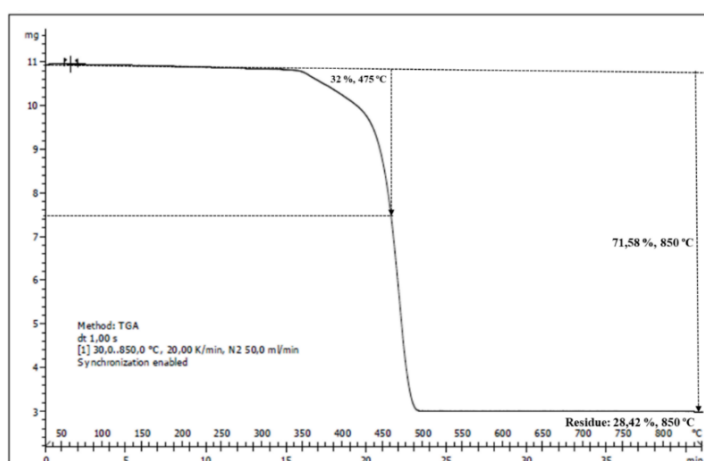


Figure 4.11 : TGA graph of PP/IFR0/M30 sample

4.2.7 Limiting oxygen index

The minimum concentration of oxygen in a flowing mixture of oxygen and nitrogen that helps ignition of neat PP, IFR filled PP and IFR and Mica filled PP compounds was measured by LOI technique. LOI of neat PP is approx. 18.2 %. The LOI of the testing parts including both IFR and mica were lower than that of sample containing only IFR, and the LOI of the sample containing 2 wt% mica reached a maximal value of 37.5 %. The results indicated that the replacement of IFR with mica at a reasonable amount level can improve the flame retardancy properties of PP matrix. However, PP compounds with increasing mica content levels decrease the LOI values. This phenomenon can be resulted by combustion process, superior concentration of filler like char is too rigid and brittle due to mica so LOI values starts to decrease when mica content increased in PP compound. Huang and Chen observed the same effect in their work with sepiolite and IFR [20]. The LOI test results of neat PPs, IFR, Mica and IFR/Mica filled PP compounds are indicated in Table 4.14.

Table 4.14 : LOI test results of neat PP, mica and IFR filled PP compounds.

Samples Name	LOI (%)
Neat PP	18.0 ± 0.25
PP70/IFR30/M0	37.8 ± 0.17
PP70/IFR28/M2	37.5 ± 0.14
PP70/IFR26/M4	36.6 ± 0.21
PP70/IFR24/M6	34.9 ± 0.07
PP70/IFR22/M8	33.9 ± 0.15
PP70/IFR15/M15	24.2 ± 0.03
PP70/IFR0/M30	20.4 ± 0.18

4.2.8 UL 94 flammability test (vertical)

UL 94 flammability testing is utilized to observe ignition performance and fire spread of polymeric parts. Flammability ratings are categorized as V0, V1, or V2 with UL 94 flammability testing. The best flammability property is obtained by V0 rating.

V-0: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 10 seconds. Flaming drips can't be allowed.

V-1: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips can't be allowed.

V-2: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips are allowed.

UL-94 flammability testing outcomes of the PP/IFR compounds towards mica amount level are listed in Table 4.15. When amount of mica was adjusted in between 2 wt% and 8 wt% in IFR, and testing parts of the PP/IFR compounds can achieve the V-0. Nevertheless, rising amount to 15 %, it is classified as horizontal burning (HB). According to these results, suitable amount of mica can create the synergistic effect IFR and mica filled compounds.

Table 4.15 : UL 94 vertical test results of IFR, Mica and IFR/Mica filled PP compounds.

Samples	UL 94 Test-Vertical				
	T1	T2	T3	Dripping	Flame Rating
PP70/IFR30/M0	0	2	0	No	V0
PP70/IFR28/M2	0	5	0	No	V0
PP70/IFR26/M4	0	7	0	No	V0
PP70/IFR24/M6	1	7	0	No	V0
PP70/IFR22/M8	2	6	0	No	V0
PP70/IFR15/M15	Horizontal Burning (HB)				
PP70/IFR0/M30	Horizontal Burning (HB)				

T1: The burning time with flame of samples after the first ignition.

T2: The burning time with flame of samples after the second ignition.

T3: The burning time without flame of samples after the second ignition.

4.2.9 Glow wire flammability test

Glow wire flammability results ensure to evaluate the capability of testing parts to remove fires and their capability not to obtain volatiles capable of spreading flame. The effects of IFR on flammability features of PP compounds were searched. Glow wire test results are given in Table 4.16.

Table 4.16 : Glow wire test results of of neat PPs, IFR/Mica filled PP compounds.

Samples	Glow Wire Temperature (°C)	
	750	850
PP70/IFR30/M0	There is no flaming and flashing.	There is no flaming and flashing.
PP70/IFR28/M2	There is no flaming and flashing.	There is no flaming and flashing.
PP70/IFR26/M4	There is no flaming and flashing.	Ignition time: 1 second; Burning time : 20 seconds. Ignition didn't observe on cotton.
PP70/IFR24/M6	There is no flaming and flashing.	Ignition time: 4 seconds. Burning time: 20 seconds. Ignition didn't observe on cotton.
PP70/IFR22/M8	There is no flaming and flashing.	Ignition time: 2 seconds. Burning time: 30 seconds. Ignition didn't observe on cotton.
PP70/IFR15/M15	Ignition time: 15 seconds. Failed	Failed.
PP70/IFR0/M30	Failed.	Failed.

The effects of IFR and mica mineral on flammability features of compounds were searched. Test was performed at temperatures of 750 °C and 850 °C. IFR decreased burning time of polypropylene compounds significantly. The glow wire test results indicated that the replacement of IFR with mica at a reasonable amount level (2 wt% ,4 wt%, 6 wt% and 8 wt%) can improve the flame retardancy properties of PP matrix due to dehydration and better char forming. When mica loading level increased to 15 wt% in PP compounds, flame retardancy properties of PP matrix decreased due to effecting the continuity of IFR system as explained by Huang [20]. According to test results, PP70/IFR0/M30 sample didn't passed both 750 °C and 850 °C. PP70/IFR0/M30 sample showed that only mica is not effective on flame retardancy on PP matrix.

4.2.10 Morphology analysis of IFR and mica filled PP compounds

The char residue was obtained after ash content test. The morphology analysis of ash residue was done by SEM. Figure 4.12 indicates the state before ash testing. Figure 4.13 indicates the SEM picture of ash residue of 6 wt% mica and 24 wt% IFR filled PP compound. It is observed that the structure of ash residue of PP70/IFR24/M6 compound has rigid structure. Having a rigid structure will prevent the flames from entering to the polymer structure therefore flame retardancy of polymeric compounds can be enhanced.



Figure 4.12 : The ash testing for PP70/IFR24/M6 sample.

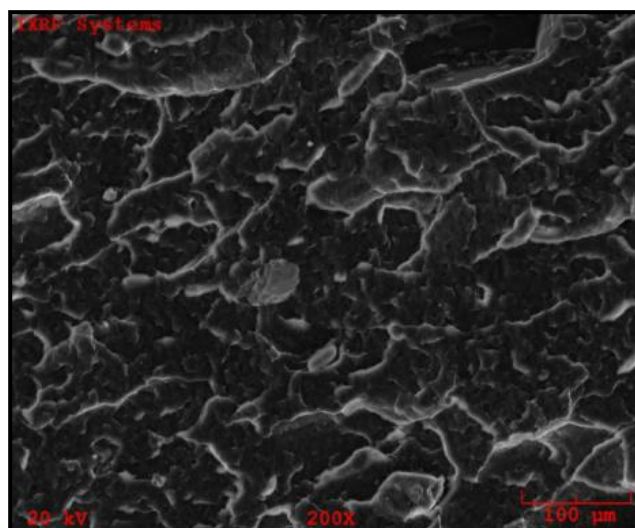


Figure 4.13: SEM micrograph of the char residue of PP70/IFR24/M6 sample.

4.3 Compounding of Intumescent Flame Retardants with Polypropylene and Expandable Graphite

4.3.1 Measurement of density

Density test results of compounds indicated stable rise with rising EG amount. EG and IFR have higher density of 2.25 g/cm^3 and 1.8 g/cm^3 respectively. They have higher density than polypropylene density is 0.906 g/cm^3 . Thereof, the addition of EG and IFR into polypropylene concluded in compounds with superior density results as obeying the rule mixture. Moreover, even though total FR ratios were fixed due to higher density of EG, increased EG content increased the density of compounds slightly. Density testing outcomes are represented in Table 4.17.

Table 4.17 : Density results of neat PPs, IFR, EG and IFR/EG filled PP compounds.

Samples Name	Density (gr/cm^3)
Neat PP	0.9069 ± 0.002
PP80/EG20	1.0823 ± 0.002
PP75/EG25	1.0947 ± 0.002
PP70/EG30	1.1326 ± 0.002
PP70/IFR28/EG2	1.0581 ± 0.003
PP70/IFR26/EG4	1.0590 ± 0.002
PP70/IFR24/EG6	1.0603 ± 0.003
PP70/IFR20/EG10	1.0611 ± 0.003
PP70/IFR15/EG15	1.0629 ± 0.002
PP70/IFR10/EG20	1.0702 ± 0.002

4.3.2 Melt flow index (MFI) test results

When IFR added to polypropylene, MFI value started to decrease from 22.35 to 14.88 g/10 min at 230 °C and 2.16 kg loading. When EG added to PP at 20-25-20 wt% loading levels. EG is rigid particle therefore more free volumes were occupied between molecular chains. Flexibility of the molecular chains were decreased. MFI values decreased dramatically from 22.35 to 7.05 g/10 min at 30 wt% loading level. MFI values decreased when the amount of EG in IFR filled PP compound increased. MFI values have also effect on dripping behaviour of the pyrolysing polymer. Well specified melf flow and dripping are usually helpful to pass UL 94 vertical test and also glow wire test. The flame retardant materials can change the melt behaviour of polymeric materials critically. The MFI testing outcomes were represented in Table 4.18.

Table 4.18 : MFI graph of IFR, Mica and IFR/EG filled PP compounds

Samples Name	MFI (g/10 min)
Neat PP	22.35 ± 0.2
PP80/EG20	9.00 ± 0.2
PP75/EG25	8.03 ± 0.2
PP70/EG30	7.05 ± 0.2
PP70/IFR28/EG2	16.40 ± 0.2
PP70/IFR26/EG4	15.82 ± 0.2
PP70/IFR24/EG6	14.75 ± 0.2
PP70/IFR20/EG10	12.34 ± 0.2
PP70/IFR15/EG15	10.33 ± 0.2
PP70/IFR10/EG20	9.35 ± 0.2

4.3.3 Mechanical properties tensile test results

Tensile features of polypropylene and fire retardant compounds with various amount of expandable graphite are indicated in Table 4.19. Putting of IFR by high quantity to PP material decreases strength and strain values due to effect of mineral like reinforcing effect. Increasing the amount of expandable graphite content in polypropylene compounds increases elastic modulus. Tensile strength value of polypropylene homopolymer decreased when IFR and expandable graphite added to system. The addition of expandable graphite with IFR to the polypropylene results in significant changes in mechanical properties. An addition of 6 wt% of expandable graphite and 24 wt% IFR leads to 61% lower tensile strength values at yield point compared to neat PP. Compounds with higher expandable graphite contents up to 20

wt% indicated a slight decrease of tensile strength. Elastic modulus values increased linearly with increasing expandable graphite content in the formulation. It means that expandable graphite reinforced compound have higher stiffness. Tensile strain at yield point values indicated an important decrease after the addition of expandable graphite with IFR to polypropylene matrix. PP70/IFR30/EG0 showed better tensile strain properties than PP70/EG30 compounds. Additives have different mechanical properties compared to neat PP. Especially, expandable graphite is brittle material, IFR shows filler type properties and PP is plastic material with high elasticity. It comes in view that compounded materials were more probably to adopt the mechanical properties of graphite and IFR than polypropylene. This was the proof in the tensile strength and tensile strain at yield point where the values changed significantly with addition of expandable graphite and IFR. Addition of the IFR increased elastic modulus values until certain amount and even at 30 wt% loading level of IFR was higher than that of PP. Consequently, synergistic effect between IFR and expandable graphite couldn't be observed prominently for tensile test. However, when expandable graphite and IFR used together in the compound, elastic modulus values also increased. But expandable graphite was dominant compared to IFR.

Table 4.19 : Mechanical properties of EG and IFR filled PP compounds

Samples Name	Elastic Mod. (MPa)	Tensile Strength at Yield Point (MPa)	Tensile Strain at Yield Point (MPa)
Neat PP	1578 ± 10.69	35.7 ± 0.23	9.43 ± 0.06
PP80/EG20	2650 ± 40.80	20.2 ± 0.2	4.2 ± 0.2
PP75/EG25	2725 ± 15.60	18.8 ± 0.2	3.7 ± 0.2
PP70/EG30	2860 ± 25.38	15.3 ± 0.2	2.8 ± 0.04
PP70/IFR30/EG0	2760 ± 42.71	26.4 ± 0.5	4.05 ± 0.12
PP70/IFR28/EG2	2790 ± 15.63	25.4 ± 0.5	3.8 ± 0.06
PP70/IFR26/EG4	2832 ± 12.04	23.7 ± 0.2	3.7 ± 0.06
PP70/IFR24/EG6	2850 ± 10.69	22.2 ± 0.2	3.2 ± 0.06
PP70/IFR20/EG10	2903 ± 10.69	20.3 ± 0.2	2.9 ± 0.05
PP70/IFR15/EG15	2982 ± 10.69	18.2 ± 0.3	2.5 ± 0.06
PP70/IFR10/EG20	3160 ± 10.69	16.8 ± 0.3	2.4 ± 0.06

4.3.4 Izod impact test results-notched

Testing outcomes of neat PPs, expandable graphite and IFR filled PP compounds were indicated in Table 4.20. It has been tested that izod impact value of PP homopolymer is around 3.21 kJ/m². Izod impact values of PP reduced with putting of expandable graphite but when IFR was added to the system, the impact resistance decreased more.

When expandable graphite and IFR used together in polymer matrix, better impact resistance was obtained than using IFR alone. In case of using IFR alone, the decrease in impact strength can be compensated somewhat by adding expandable graphite and increasing the amount of expandable graphite.

Table 4.20 : Izod impact test results of IFR and mica filled PP compounds.

Samples Name	Izod Impact Strength kJ/m ²
Neat PP	3.21 ± 0.14
PP80/EG20	2.38 ± 0.05
PP75/EG25	2.25 ± 0.08
PP70/EG30	2.09 ± 0.14
PP70/IFR30/EG0	1.76 ± 0.14
PP70/IFR28/EG2	1.85 ± 0.01
PP70/IFR26/EG4	1.90 ± 0.05
PP70/IFR24/EG6	2.08 ± 0.05
PP70/IFR20/EG10	2.13 ± 0.04
PP70/IFR15/EG15	2.18 ± 0.04
PP70/IFR10/EG20	2.25 ± 0.04

4.3.5 Heat deflection temperature testing results

Heat deflection temperature (HDT) was conducted according to technique explained in characterization techniques part. According to testing results, HDT values were increased essentially by the addition of intumescent flame retardant additive and expandable graphite. It was observed that different loadings of intumescent flame retardant and expandable graphite had great synergistic effect on heat deflection temperature of PP compounds. This property will provide extra safety to PP compounds during the fire HDT values of sampling materials are indicated in Table 4.21.

Table 4.21 : Heat deflection test results of IFR and expandable graphite filled PP compounds.

Sample name	Heat Deflection Temperature °C at 0.45 MPa
Neat PP	87
PP80/EG20	97.1
PP75/EG25	100.2
PP70/EG30	101.8
PP70/IFR30/EG0	90.2
PP70/IFR28/EG2	93.4
PP70/IFR26/EG4	95.3
PP70/IFR24/EG6	96.1
PP70/IFR20/EG10	97.3
PP70/IFR15/EG15	98.5
PP70/IFR10/EG20	99.5

4.3.6 Thermal gravimetric analysis

This is significant technique to see decomposition behaviours and to calculate char residue. The TGA graphs of neat PP and IFR/EG filled PP compounds were shown in Figure 4.14. Polypropylene started to decomposition at 250 °C and used up fully at 500 °C. EG also started to decompose at 250°C when exposed to heat. According to TGA curve, decomposition temperature shifted when EG added to PP/IFR compound at 6 wt% loading level. As evidenced in the literature, IFR and EG form a strong structure and also improve the onset temperature. But it is very difficult to carry out TGA test with expandable graphite because when we increased temperature EG started to expand and come out of pan of TGA equipment. Therefore the test was repeated many times. This is also known as popcorn effect in the literature.

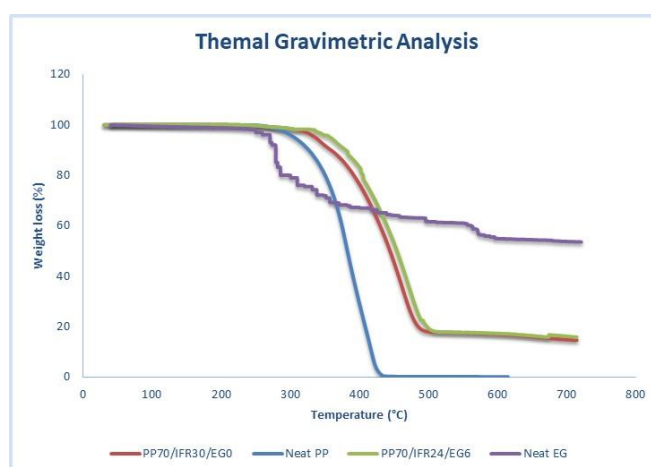


Figure 4.14 : TGA curve of neat EG and PP, PP70/IFR30/EG0 and PP70/IFR24/EG6.

4.3.7 Limiting oxygen index

LOI of pure PP is approx. 18.2 %. Furthermore, the influence of expandable graphite on flammability features of IFR system was searched well organised. The LOI values of the samples containing both IFR and expandable graphite were lower than that of sample containing only IFR, and the LOI of the sample containing 6 wt% expandable graphite reached a maximal value of 36.5 %. The results indicated that the replacement of IFR with expandable at a reasonable amount level can show improvement on the flame retardancy properties of PP matrix. However, PP compounds with increasing expandable graphite content levels decrease the LOI values after 10 wt% expandable graphite loading level. Expandable graphite makes char residue more rigid and brittle during ignition process so LOI values starts to decrease when expandable graphite content increased in PP compound. Zheng and Liu detected the same effect in their search with expandable graphite and IFR system[41]. When Expandable graphite content increased in the system LOI values increased in the first stage then it started to decrease. The LOI test results of pure PPs, IFR, Expandable graphite and IFR/expandable filled PP compounds are indicated in Table 4.22.

Table 4.22 : LOI test results of neat PP, expandable graphite and IFR filled PP compounds.

Samples Name	LOI (%)
Neat PP	18.0 ± 0.2
PP80/EG20	26.15 ± 0.08
PP75/EG25	28.6 ± 0.15
PP70/EG30	30.25 ± 0.11
PP70/IFR30/M0	37.8 ± 0.05
PP70/IFR28/EG2	37.4 ± 0.07
PP70/IFR26/EG4	37.2 ± 0.15
PP70/IFR24/EG6	36.5 ± 0.09
PP70/IFR20/EG10	27.2 ± 0.23
PP70/IFR15/EG15	26.5 ± 0.19
PP70/IFR10/EG20	25.4 ± 0.04

4.3.8 UL 94 flammability test (vertical)

UL 94 flammability testing is utilized to observe ignition performance and fire spread of polymeric parts. Flammability ratings are categorized as V0, V1, or V2 with UL 94 flammability testing. The best flammability property is obtained by V0 rating.

V-0: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 10 seconds. Flaming drips can't be allowed.

V-1: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips can't be allowed.

V-2: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips are allowed.

UL-94 flammability testing outcomes of the PP/IFR compounds toward expandable graphite amount are listed in Table 4.23. When amount of expandable graphite was adjusted in between 2 wt% and 6 wt% in IFR, and testing parts of the PP/IFR compounds can achieve the V-0 classification. Nevertheless, rising loading level to 20 %, it is classified as horizontal burning (HB). According to these results, suitable amount of expandable graphite can create the synergistic influence in the PP/IFR/EG compounds with sufficient way.

Table 4.23 : UL 94 vertical test results of IFR, EG and IFR/EG filled PP compounds.

Samples	UL 94 Test-Vertical				
	T1	T2	T3	Dripping	Flame Rating
PP80/EG20	20	25	0	YES	V2
PP75/EG25	18	20	0	YES	V2
PP70/EG30	15	20	0	YES	V2
PP70/IFR30/EG0	2	3	0	NO	V0
PP70/IFR28/EG2	2	2	0	NO	V0
PP70/IFR26/EG4	3	4	0	NO	V0
PP70/IFR24/EG6	2	5	0	NO	V0
PP70/IFR20/EG10	10	15	0	NO	V1
PP70/IFR15/EG15	20	30	0	YES	V2
PP70/IFR10/EG20	Horizontal Burning (HB)				

T1: The burning time with flame of samples after the first ignition.

T2: The burning time with flame of samples after the second ignition.

T3: The burning time without flame of samples after the second ignition.

4.3.9 Glow wire flammability tests

Glow wire test was carried out at 750 and 850 °C to observe flashing and glowing properties of end product. Testing plates can be used to observe mentioned features. GWT test results ensure a way of controlling and checking the capability of materials to remove fires and their capability not to manufacture flame particles capable of spreading flame. Burning and ignition time can be calculated to determine performance. At the end of test, ignition of cotton are not allowed in terms of fire retardancy performance Glow wire test results are given in Table 4.24.

Table 4.24 : Glow wire test results of neat PPs, IFR/EG filled PP compounds.

Samples	Glow Wire Temperature (°C)	
	750	850
PP80/EG20	There is no glowing and flashing	Burning time is 45 seconds
PP75/EG25	There is no glowing and flashing	Burning time is 38 seconds
PP70/EG30	There is no glowing and flashing	Burning time is 30 seconds
PP70/IFR30/M0	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR28/EG2	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR26/EG4	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR24/EG6	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR20/EG10	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR15/EG15	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR10/EG20	There is no glowing and flashing	There is no glowing and flashing

The synergistic effects of IFR and expandable graphite on flammability features of compounds were searched. IFR decreased burning time of polypropylene compounds significantly. The glow wire test results indicated that the replacement of IFR with expandable at a reasonable amount level (2 wt% ,4 wt%, 6 wt% and 10 wt%) can improve the flame retardancy properties of PP matrix due to creating extra char foming on the burning surface. Furthermore, when expandable graphite was used in the system without IFR, they can pass the test for 850 °C but the same flame retardancy performance can't be observed as when used with IFR.

4.3.10 Morphology analysis of IFR and EG filled PP compounds

The char residue was obtained after glow wire test. The morphology analysis of ash residue was done SEM equipment. Figure 4.15 indicates the state before glow wire testing. Figure 5.3 indicates the SEM picture of ash residue of 6 wt% EG and 24 wt% IFR filled PP compound. It is observed that the structure of char residue of PP70/IFR24/EG compound has rigid structure. Having a rigid structure will prevent the flames from entering to the polymer structure therefore flame retardancy of polymeric compounds can be enhanced. In addition to them, after burning, expanded graphite particles are scattered around.

**Figure 4.15 :** Char forming on polypropylene surface during glow wire test.

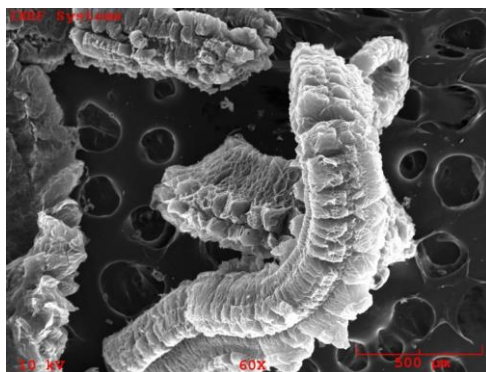


Figure 4.16 : SEM micrograph of PP70/IFR24/EG6 sample.

4.4 Compounding of Intumescent Flame Retardants with Polypropylene and Colemanite

4.4.1 Measurement of density

Density test results of compounds indicated stable rise with rising colemanite amount. Colemanite and IFR have higher density of 2.42 g/cm^3 and 1.8 g/cm^3 respectively. They have superior density than polypropylene because its density 0.906 g/cm^3 . Thereof, the addition of colemanite and IFR to polypropylene concluded in compounds with superior density results as obeying rule mixture. Moreover, even though total FR ratios were fixed due to higher density of colemanite, increased colemanite content increased the density of compounds slightly. Density testing outcomes are indicated in Table 4.25.

Table 4.25 : Density results of neat PPs, IFR, colemanite and IFR/colemanite filled PP compounds.

Samples Name	Density (gr/cm^3)
Neat PP	0.9069
PP70/IFR30/C0	1.053
PP70/IFR28/C2	1.062
PP70/IFR26/C4	1.064
PP70/IFR24/C6	1.067
PP70/IFR22/C8	1.073
PP70/IFR15/C15	1.082
PP70/IFR0/C30	1.120

4.4.2 Melt flow index (MFI) test results

When IFR added to polypropylene, MFI value started to decrease from 22.35 to 14.88 g/10 min at 230 °C and 2.16 kg loading. When colemanite added to polypropylene with IFR, MFI values began to increase from 14.88 to 21.8 g/10 min. After 15% loading level of colemanite, MFI values decreased from 21.40 g/10 min to 20.30 g/10 min. It can be said that processability of colemanite is easy in PP compound due to their structure compared to other additives. According to literature, it was demonstrated that MFR values of final product were increased with increasing colemanite loading. Therefore, process temperature can be reduced to eliminate risk of release of IFR additives during compounding. In addition to them, it was observed that minerals which have flat or lamellar structure can slide against each other during the application of shear forces. It causes to increase of flowability in the final compounds. The MFI testing outcomes were represented in Table 4.26.

Table 4.26 : MFI graph of IFR, Colemanite and IFR/Colemanite filled PP compounds.

Samples Name	MFI (gr/10 min.)
Neat PP	22.35
PP70/IFR30/C0	14.88
PP70/IFR28/C2	21.80
PP70/IFR26/C4	22.00
PP70/IFR24/C6	21.00
PP70/IFR22/C8	21.40
PP70/IFR15/C15	20.30
PP70/IFR0/C30	22.00

4.4.3 Mechanical properties tensile test results

Testing outcomes are indicated in Table 4.27. Putting of IFR by high quantity to PP material decreases strength and strain values due to effect of mineral like reinforcing effect. The important mechanical properties of neat PP, PP/IFR/colemanite filled compounds were also searched by discussing the effectiveness of colemanite content in polymer matrix. Increasing the amount of colemanite content in polypropylene compounds increases elastic modulus of neat polypropylene. Tensile strength value of polypropylene homopolymer decreased when IFR and colemanite added to polymeric system. No selective difference is observed on tensile strength values of only IFR and IFR/colemanite filled PP compounds. 30% colemanite filled PP compound showed better tensile strength properties compared to IFR/colemanite filled PP compounds at

different loading levels. Strain value of neat polypropylene homopolymer decreased with increasing amounts of colemanite content in PP/IFR/colemanite compounds. No selective difference is observed on tensile strain values of 30% IFR and 30% colemanite in PP compounds. When colemanite amount increased in the system, it resulted with increase of the modulus of elasticity and decrease in tensile strength and strain at yield point. According to literature, Sahin observed that elastic modulus values increased with increasing of colemanite amount. It is generally believed that the polymer matrix around the inclusions can produce plastic deformation thanks to stress concentration. Liang, Li and Feng observed that elastic modulus nonlinearly increased when the amount of IFR content in polypropylene compound increases. IFR material has stiffening effect on the final compound. This effect is related to the movement of the big chains of the matrix material is blocked by IFR particles. Stiffness of filled PP compounds can be improved by adding IFR content to the PP compound. However, increasing IFR content leads to a decrease tensile strength of PP compound. It is related to interfacial adhesion between inorganic materials and polymer matrix. If interfacial adhesion improves, tensile yield strength values can start to increase [55].

Table 4.27 : Mechanical properties of colemanite and IFR filled PP compounds.

Samples	Elastic Mod. (MPa)	Tensile Strength at Yield Point (MPa)	Tensile Strain at Yield Point (%)
Neat PP	1578 ± 10.69	35.7 ± 0.23	9.43 ± 0.06
PP70/IFR30/C0	2760 ± 102.7	26.4 ± 1.00	4.05 ± 0.12
PP70/IFR28/C2	2410 ± 50.4	24.2 ± 0.184	4 ± 0.068
PP70/IFR26/C4	2270 ± 115	24.0 ± 0.209	4 ± 0.082
PP70/IFR24/C6	2090 ± 138	23.7 ± 0.423	4.1 ± 0.063
PP70/IFR22/C8	2220 ± 72	23.9 ± 0.165	4.2 ± 0.060
PP70/IFR15/C15	2440 ± 101	23.4 ± 0.058	4.1 ± 0.068
PP70/IFR0/C30	2210 ± 62.2	24.1 ± 0.197	5.1 ± 0.14

4.4.4 Izod impact test results-notched

Izod impact testing outcomes of neat PPs, colemanite and IFR filled PP compounds were indicated in Table 4.28. According to many investigation, impact properties of mineral filled plastic compounds bound up with particle size and amount of mineral in the system. Another item can be related to improvement of the interface between plastic material and mineral. Oral specified that the addition of calcium carbonate decreased izod impact properties of polypropylene but when maleic anhydride polypropylene added to system, interface between calcium carbonate and polypropylene has been improved so it resulted with higher izod impact values

compared to neat polypropylene. It has been tested that izod impact value of PP homopolymer is around 3.22 kJ/m². Colemanite and IFR filled PP compounds showed negative effect on izod impact strength values at different loading levels. No selective difference is observed on izod impact values at 2%, 4%, 6%, 8 and 15% colemanite loading level in PP compounds. The reduction of Izod impact strength with IFR and colemanite putting to PP can be examined by hindering of chain versatility and decrease in fracturing energy according to neat polypropylene material. Izod impact properties of flame retardant additives can be improved with addition of the impact modifiers but impact modifiers have negative effect on flame retardancy properties so these type of additives weren't added to compound.

Table 4.28 : Izod impact test results of IFR and colemanite filled PP compounds.

Samples	Izod Impact Strength (kJ/m ²)
Neat PP	3.21 ± 0.14
PP70/IFR30/C0	1.76 ± 0.14
PP70/IFR28/C2	1.83 ± 0.09
PP70/IFR26/C4	1.88 ± 0.12
PP70/IFR24/C6	1.76 ± 0.10
PP70/IFR22/C8	1.97 ± 0.10
PP70/IFR15/C15	1.77 ± 0.10
PP70/IFR0/C30	1.80 ± 0.10

4.4.5 Heat deflection temperature testing results

This test is utilized to define short period heat resistance of polymeric materials and to distinguish between materials that are able to sustain light loads at high temperatures and those that lose stiffness over a tight temperature range. The HDT values of neat PP and its flame retardant compounds with various amount of colemanite are given in Table 4.29. Putting of IFR by high amount into the plastic compound increased HDT from 87°C to 90.2°C. HDT values were increased essentially by the addition of intumescent flame retardant additive. It was observed that different loadings of intumescent flame retardant and colemanite had effect on heat deflection temperature of PP compounds. This property will provide extra safety to PP compounds during the fire. PP70/IFR0/C30 sample has higher heat deflection temperature than PP70/IFR30/C0. Because the stiffness of PP70/IFR0/C30 sample was higher than PP70/IFR30/C0 sample when temperature increased. The higher heat deflection temperature is related to faster molding process in injection molding machine so energy efficiency can be achieved with colemanite filled IFR/PP compounds.

Table 4.29 : Heat deflection test results of colemanite and IFR filled PP compounds.

Samples Name	Heat Deflection Temperature °C
Neat PP	87.0
PP70/IFR30/C0	90.2
PP70/IFR28/C2	91.8
PP70/IFR26/C4	92.4
PP70/IFR24/C6	93.6
PP70/IFR22/C8	94.1
PP70/IFR15/C15	96.7
PP70/IFR0/C30	98.7

4.4.6 Thermal gravimetric analysis

The TGA graphs in below represent all colemanite filled flame retardant polypropylene compounds with Figure 4.17, 4.18, 4.19, 4.20, 4.21, 4.22. According to TGA graph of colemanite, it started to decompose at above 225 °C. The amount of residue of colemanite was approx. 75 wt%. When graphs of the colemanite and IFR filled compounds were investigated, it was observed that these compounds shifted through higher temperature compared to neat polypropylene and also char residue amount was higher than neat polypropylene.

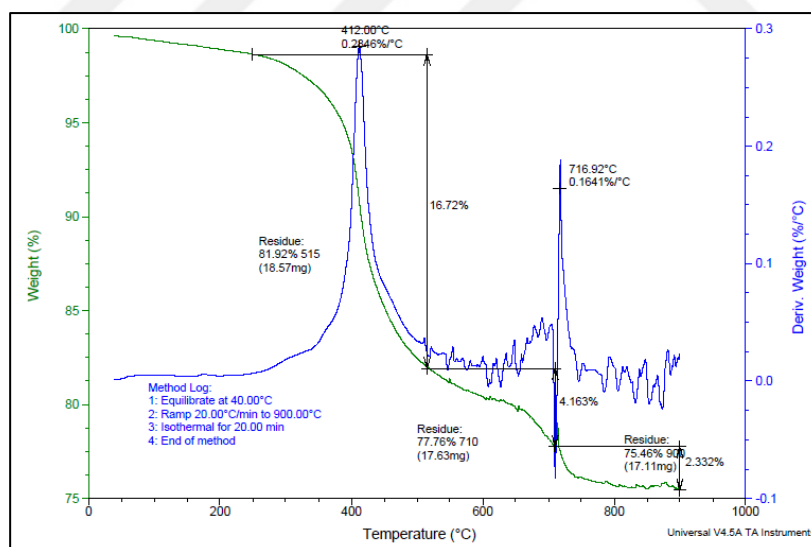


Figure 4.17 : TGA analysis of colemanite sample.

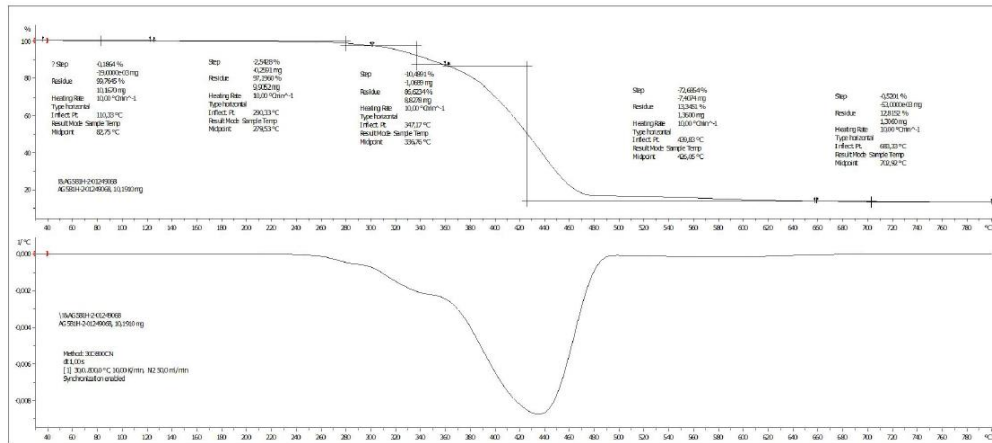


Figure 4.18 : TGA analysis of PPH/IFR26/C4 sample.

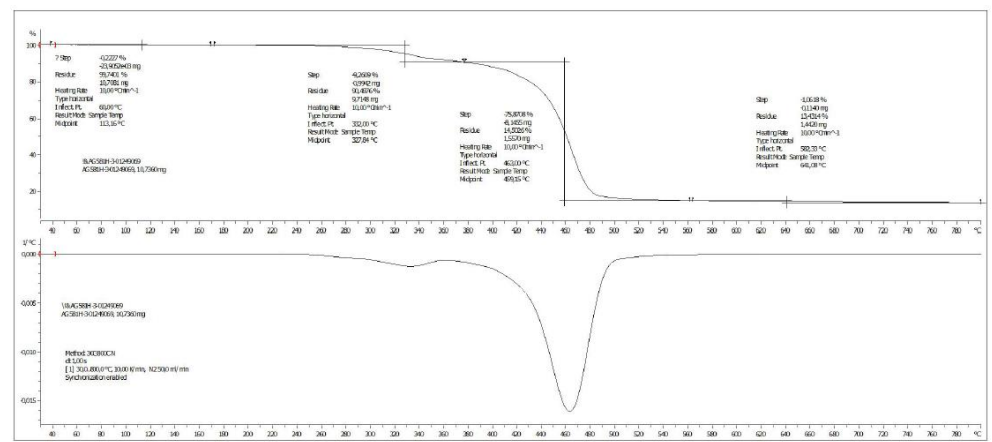


Figure 4.19 : TGA analysis of PPH/IFR24/C6 sample

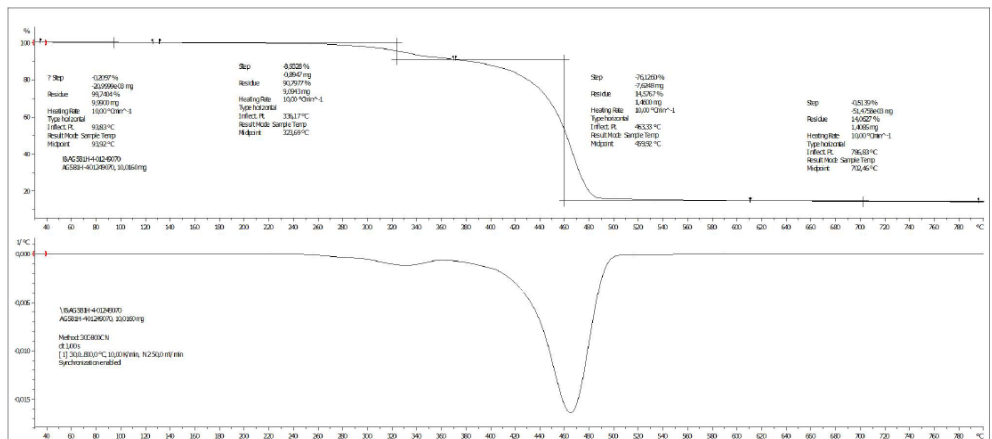


Figure 4.20 : TGA analysis of PPH/IFR22/C8 sample.

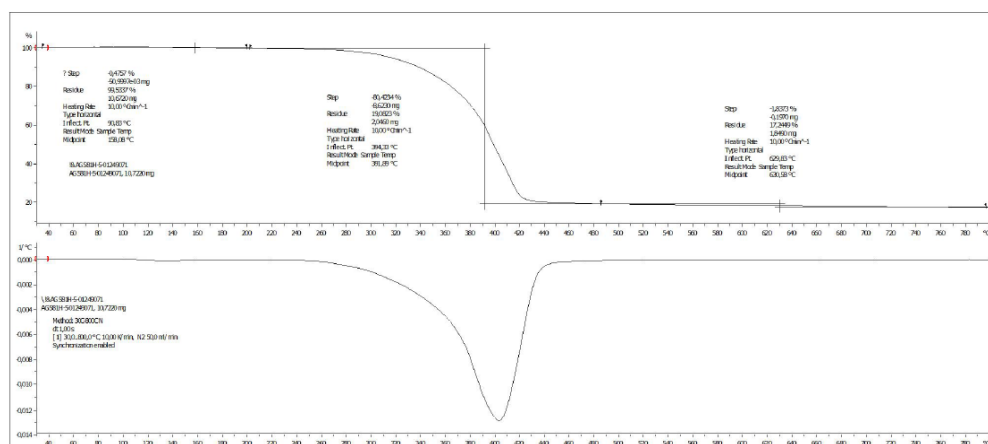


Figure 4.21 : TGA analysis of PPH/IFR15/C15 sample.

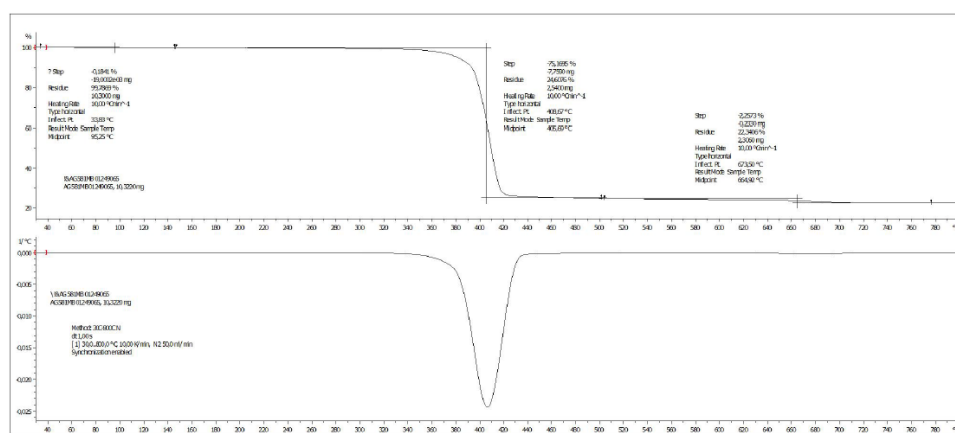


Figure 4.22 : TGA analysis of PPH/IFR0/C30 sample.

4.4.7 Limiting oxygen index

Neat PP can burn easily with very fast combustion rate and it generates a large amount of black smoke during fire due to this reason flammability properties needs to be improved. The flammability behavior of PP and IFR/colemanite filled PP compounds are indicated in Table 4.30 which shows the differences of LOI values towards colemanite content for the PP/IFR/colemanite compounds at overall quantity of 30 wt% flame retardant ingredients fixed constant. It has been observed that LOI grade of the IFR filled PP compound including 30 wt% IFR increased to 37.8 from 18% of neat PP. It showed that IFR can increase flame retardancy properties of PP when it used alone in the PP compound. Addition of colemanite with IFR to PP compound showed better flame retardancy properties. The LOI values increased to 37.6 % with 2 wt% loading level of colemanite in the compound. LOI values decreased rapidly after addition of 8 wt% loading of colemanite. When amount of colemanite caught up to 8 wt% the LOI value of sample decreased to 33%. The results indicated that the

replacement of IFR with colemanite at a reasonable amount level can improve the flame retardancy properties of PP matrix. Major cause for this event can be that, during the combustion, superior amount of filler like colemanite makes the char too rigid and brittle so LOI values starts to decrease when mica content increased in PP compound. Huang and Chen observed the same effect in their work with sepiolite and IFR [58]. Synergistic effect was observed between IFR and colemanite when colemanite was used at reasonable amount in the PP compound. Isitman and Kaynak also observed synergistic effect between aluminium trihydrate (ATH) and colemanite in polyethylene compound. Partial replacement of ATH by colemanite bring higher LOI values at 10 wt% colemanite loading level in the resin [35]. Atikler and coworkers observed that LOI value reached up to 39.3% with 2.1 wt% colemanite loading level [59].

Table 4.30 : LOI test results of neat PP, mica anf IFR filled PP compounds.

Samples Name	LOI (%)
Neat PP	18.0 ± 0.2
PP70/IFR30/C0	37.8 ± 0.14
PP70/IFR28/C2	37.6 ± 0.06
PP70/IFR26/C4	36.9 ± 0.21
PP70/IFR24/C6	34.9 ± 0.05
PP70/IFR22/C8	33.7 ± 0.18
PP70/IFR15/C15	24.9 ± 0.09
PP70/IFR0/C30	19.0 ± 0.22

4.4.8 UL 94 flammability test (vertical)

UL 94 flammability testing is utilized to observe ignition performance and fire spread of polymeric parts. Flammability ratings are categorized as V0, V1, or V2 with UL 94 flammability testing. The best flammability property is obtained by V0 rating.

V-0: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 10 seconds. Flaming drips can't be allowed.

V-1: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips can't be allowed.

V-2: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips are allowed.

UL-94 flammability testing outcomes of the PP/IFR compounds toward colemanite amount are summarized in Table 4.31. When amount of colemanite was adjusted in

between 2 wt% and 8 wt% in IFR, and samples of the PP/IFR compounds can achieve the V-0 classification. Nevertheless, rising loading level to 15 %, it is classified as horizontal burning (HB). According to these results, suitable amount of colemanite can create the synergistic effect in the PP/IFR/Colemanite compounds more sufficient.

Table 4.31 : UL 94 vertical test results of IFR, colemanite and IFR/colemanite filled PP compounds.

Samples	UL 94 Test-Vertical				
	T1	T2	T3	Dripping	Flame Rating
PPH/IFR30/C0	0	2	0	No	V0
PPH/IFR28/C2	0	6	0	No	V0
PPH/IFR26/C4	0	7	0	No	V0
PPH/IFR24/C6	2	8	0	No	V0
PPH/IFR22/C8	2	6	0	No	V0
PPH/IFR15/C15	15	15	0	Yes	V2
PPH/IFR0/C30	Horizontal Burning (HB)				

T1: The burning time with flame of samples after the first ignition.

T2: The burning time with flame of samples after the second ignition.

T3: The burning time without flame of samples after the second ignition.

4.4.9 Glow wire flammability tests

Glow wire test carried out at 750 and 850 °C to observe flaming and glowing properties of end product. Testing plates can be used to observe mentioned features. GWT test results ensure a way of controlling and checking the capability of materials to remove fires and their capability not to manufacture flame particles capable of spreading flame. Glow wire test results are given in Table 4.32.

Table 4.32 : Glow wire test results of of neat PPs, IFR/Colemanite filled PP compounds.

Samples	Glow Wire Temperature (°C)	
	750	850
PPH/IFR30/C0	There is no glowing and no flashing.	There is no glowing and no flashing.
PPH/IFR28/C2	There is no glowing and no flashing.	There is no glowing and no flashing.
PPH/IFR26/C4	There is no glowing and no flashing.	Ignition time: 1 second. Burning time: 20 seconds. Cotton ignition didn't observe.
PPH/IFR24/C6	There is no glowing and no flashing.	Failed.
PPH/IFR22/C8	There is no glowing and no flashing.	Failed.
PPH/IFR15/C15	Failed.	Failed.
PPH/IFR0/C30	Failed.	Failed.

IFR at 30 wt% loading level decreased burning time of polypropylene compounds significantly. The glow wire test results indicated that the replacement of IFR with colemanite at a reasonable amount level (2 wt% ,4 wt%, 6 wt% and 8 wt%) can

improve the flame retardancy properties of PP matrix due to dehydration and better char forming. When colemanite loading level increased to 15 wt% in PP compounds, flame retardancy properties of PP matrix decreased due to effecting the continuity of IFR system as explained by Huang [20]. According to test results, PP70/IFR0/C30 sample didn't passed both 750 °C and 850 °C. PP70/IFR0/C30 sample showed that colemanite can't show good flame retardancy properties when it used alone in PP.

4.4.10 Morphology analysis of IFR and colemanite filled PP compounds

The char residue was obtained after ash content test. The morphology analysis of ash residue was done by SEM. Figure 4.23 indicates the state after ash content determination testing. Figure 4.24 shows the SEM picture of the char residue of 6 wt% Colemanite and 24 wt% IFR filled PP compound. It is observed that the structure of char residue of PP70/IFR24/C6 compound has rigid structure. Having a rigid structure will prevent the flames from entering to the polymer structure therefore flame retardancy of polymeric compounds can be enhanced.



Figure 4.23 : Carbon char creation of IFR and colemanite.

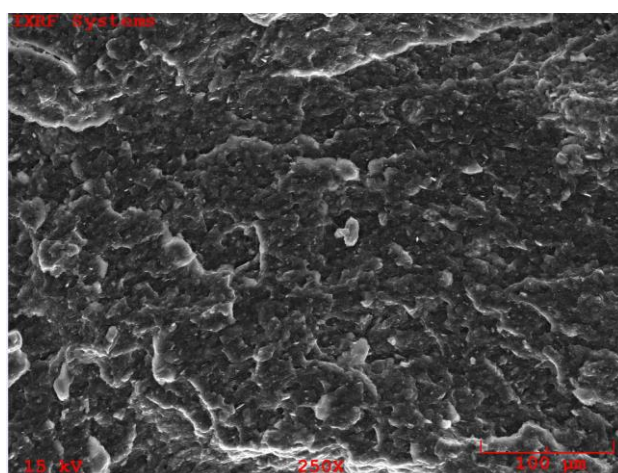


Figure 4.24 : SEM micrograph of PP70/IFR24/C6 sample.

4.5 Compounding of Intumescent Flame Retardants with Polypropylene and Minerals Together

4.5.1 Measurement of density

Density test results of compounds indicated a stable rise with rising flame retardant additives loading level. Colemanite, mica, expandable graphite and IFR have higher density of 2.42, 2.83, 2.25 g/cm³ and 1.8 g/cm³ respectively than that of polypropylene, which is 0.906 g/cm³. Thereof, the corporation of flame retardant additives (FR) and IFR to polypropylene finalized in compounds with higher density results as obeying rule mixture. Moreover, even though total FR ratios were fixed due to higher density of additives, increased FR content increased the density of compounds slightly. Testing results are represented in Table 4.33.

Table 4.33 : Density results of flame retardant additives filled PP compounds.

Samples Name	Density (gr/cm ³)
Neat PP	0.906 ± 0.002
PP70/IFR20/M8/C2	1.070 ± 0.002
PP70/IFR22/M6/C2	1.070 ± 0.002
PP70/IFR22/M4/C4	1.072 ± 0.002
PP70/IFR22/EG6/C2	1.050 ± 0.002
PP70/IFR22/EG4/C4	1.060 ± 0.002
PP70/IFR22/EG6/M2	1.070 ± 0.002
PP70/IFR22/EG4/M4	1.070 ± 0.002
PP70/IFR22/EG2/M6	1.060 ± 0.002
PP70/IFR20/EG2/M8	1.075 ± 0.002

4.5.2 Melt flow index (MFI) test results

When IFR added to polypropylene, MFI value started to decrease from 22.35 to 14.88 g/10 min at 230 °C and 2.16 kg loading. When colemanite and mica mineral were used together with IFR and polypropylene, MFI value decreased from 19.6 to 18.1 g/10 min at 8 wt% mica loading level. By the way mica was used with IFR in PP compound at the same amount, MFI value of final compound was around 17.16 gr/10 min. It means that colemanite and mica create synergistic effect on MFI values. When mica was compounded with expandable graphite instead of colemanite, the same effect in the system has been observed due to flexibility of compound due to plastic deformation owing to stress concentration. Results were represented in Table 4.34.

Table 4.34 : MFI graph of flame retardant additives filled PP compounds.

Samples Name	MFI (gr/10 min)
Neat PP	
PP70/IFR20/M8/C2	18.1 ± 0.1
PP70/IFR22/M6/C2	18.2 ± 0.1
PP70/IFR22/M4/C4	19.6 ± 0.1
PP70/IFR22/EG6/C2	20.1 ± 0.1
PP70/IFR22/EG4/C4	19.5 ± 0.1
PP70/IFR22/EG6/M2	18.4 ± 0.1
PP70/IFR22/EG4/M4	19.4 ± 0.1
PP70/IFR22/EG2/M6	18.8 ± 0.1
PP70/IFR20/EG2/M8	18.5 ± 0.1

4.5.3 Mechanical properties tensile test results

Tensile properties of all compounds with different amount of colemanite, mica and expandable graphite and IFR are indicated in Table 4.35. The corporation of IFR by high quantity into PP material decreases strength and strain values due to effect of mineral like reinforcing effect. In addition to them, tensile strength and strain at yield point values started to decrease due to platy structure of mica.

When tertiary mixtures were prepared with IFR, mica and colemanite into the system mica content increased up to 8 wt% loading level in the compound, elastic module increased from 2560 MPa to 2740 MPa. Tensile strength value of PP70/M8/C2 compound is higher than 1.2 %. There is no selective difference when mica content increased in compound but PP70/IFR22/M4/C4 is higher tensile strain at yield point values compared to PP70/IFR22/M8/C2 compound.

PP70/IFR30 and PP70/IFR20/M8/C2 samples indicated the same tensile properties in terms of elastic module value. Tensile strength and tensile strain at yield point values of PP70/IFR20/M8/C2 are lower than PP70/IFR30 sample. Increasing of mica content increased elastic module but decreased tensile strength and strain values. PP70/IFR20/EG2/M8 and PP70/IFR20/M8/C2 showed the same tensile strength and strain values but the formula containing expandable graphite indicated lower elastic modulus. Reduction in the tensile modulus when small amount of expandable graphite was added . No further reduction is observed when the amount of expandable graphite increased. Tensile strength and tensile strain values started to decrease due to platy structure of mica mineral. Expandable graphite and mica mineral show the same mechanical properties due to their flake and platy structure when they used together in system. Addition of expandable graphite at high amount results in increase in modulus

therefore expandable graphite needs to be used at reasonable amount in the final compound.

Consequently, it is observed that the usage of colemanite, mica and expandable graphite in certain proportions instead of IFR into the PP compound doesn't adversely affect the mechanical properties of final compound.

Results of prepared compounds are listed in Table 4.35.

Table 4.35 : Mechanical properties of colemanite, mica, expandable graphite and IFR filled PP compounds.

Samples	Elastic Mod. (MPa)	Tensile Strength at Yield Point (MPa)	Tensile Strain at Yield Point (%)
Neat PP	1578 ± 10.69	35.7 ± 0.23	9.43 ± 0.06
PP70/IFR30	2760 ± 102.7	26.4 ± 1.00	4.05 ± 0.12
PP70/IFR20/M8/C2	2740 ± 45.3	25.0 ± 0.33	2.8 ± 0.06
PP70/IFR22/M6/C2	2600 ± 50.2	23.7 ± 0.44	2.9 ± 0.05
PP70/IFR22/M4/C4	2560 ± 25.3	24.7 ± 0.23	3.0 ± 0.06
PP70/IFR22/EG6/C2	2550 ± 30.1	24.9 ± 0.65	2.9 ± 0.06
PP70/IFR22/EG4/C4	2640 ± 40.3	24.1 ± 0.24	2.9 ± 0.04
PP70/IFR22/EG6/M2	2560 ± 42.5	24.9 ± 0.75	3.0 ± 0.10
PP70/IFR22/EG4/M4	2550 ± 22.3	24.5 ± 0.23	3.0 ± 0.03
PP70/IFR22/EG2/M6	2590 ± 20.2	24.4 ± 0.41	2.9 ± 0.04
PP70/IFR20/EG2/M8	2650 ± 20.3	25.0 ± 0.04	3.0 ± 0.04

4.5.4 Izod impact test results-notched

Izod Impact Strength values of flame retardant filled PP compounds were listed in Table 4.36. Impact value of PP homopolymer is approx. 3.22 kJ/m². At different loading level of flame retardant materials in PP compounds represented unfavorable influence on izod impact test values. Izod impact strength was 1.74 kJ/m² when mica was used at the 8% loading level in PP compound with IFR. After reducing the amount of IFR in the system and adding colemanite or expandable graphite, the impact resistance of the PP compound decreased at 8% loading level of mica. It means that flame retardant additives don't improve impact resistance and also don't create a synergistic effect in terms of izod impact properties. No selective difference is observed on izod impact values at different flame retardant materials loading level in PP compounds. Reduction in izod impact strength values is examined by the hindering effect of chain mobility.

Table 4.36 : Izod impact test results of colemanite, mica, expandable graphite and IFR filled PP compounds.

Samples	Izod Impact Strength (kJ/m ²)
Neat PP	3.21 ± 0.14
PP70/IFR30	1.76 ± 0.14
PP70/IFR20/M8/C2	1.61 ± 0.14
PP70/IFR22/M6/C2	1.73 ± 0.14
PP70/IFR22/M4/C4	1.68 ± 0.14
PP70/IFR22/EG6/C2	1.76 ± 0.14
PP70/IFR22/EG4/C4	1.75 ± 0.14
PP70/IFR22/EG6/M2	1.81 ± 0.14
PP70/IFR22/EG4/M4	1.75 ± 0.14
PP70/IFR22/EG2/M6	1.64 ± 0.14
PP70/IFR20/EG2/M8	1.70 ± 0.14

4.5.5 Heat deflection temperature testing results

This test is done to define short period heat durability of polymeric materials and to distinguish between materials that are capable to maintain light loads at high temperatures and those that lose stiffness over a tight temperature range. The HDT values of neat PP and prepared compounds with different amount of flame retardant fillers are given in Table 4.37. Putting of IFR by higher quantity into the plastic compound increased HDT from 87°C to 90.2°C. HDT values were increased essentially by the addition of intumescent flame retardant additive. It was observed that different loadings of flame retardant additive like colemanite, mica and expandable graphite had effect on heat deflection temperature of PP compounds.

In the mica, colemanite and IFR mixtures, when mica used at 8% loading level, HDT value reached to 94.5°C. When colemanite started to increase in the compound with mica and IFR, HDT values decreased. In the expandable graphite mixtures, expandable graphite filled flame retardant compound reached to 96.2 °C. The higher heat deflection temperature is related to faster molding process in injection molding machine so energy efficiency can be achieved with colemanite filled IFR/PP compounds.

Table 4.37 : Heat deflection test results of colemanite and IFR filled PP compounds.

Samples Name	Heat Deflection Temperature °C
Neat PP	87.0
PP70/IFR30/C0	90.2
PP70/IFR20/M8/C2	94.5
PP70/IFR22/M6/C2	94.2
PP70/IFR22/M4/C4	93.7
PP70/IFR22/EG6/C2	96.4
PP70/IFR22/EG4/C4	95.8
PP70/IFR22/EG6/M2	96.2
PP70/IFR22/EG4/M4	95.3
PP70/IFR22/EG2/M6	94.0
PP70/IFR20/EG2/M8	93.6

4.5.6 Thermal gravimetric analysis

The TGA graph in Figure 4.25 represent IFR and mineral filled flame retardant polypropylene compounds. When graphs of the mineral and IFR filled compounds were investigated, it was observed that these compounds shifted through higher temperature compared to neat polypropylene and also char residue amount was higher than neat polypropylene.

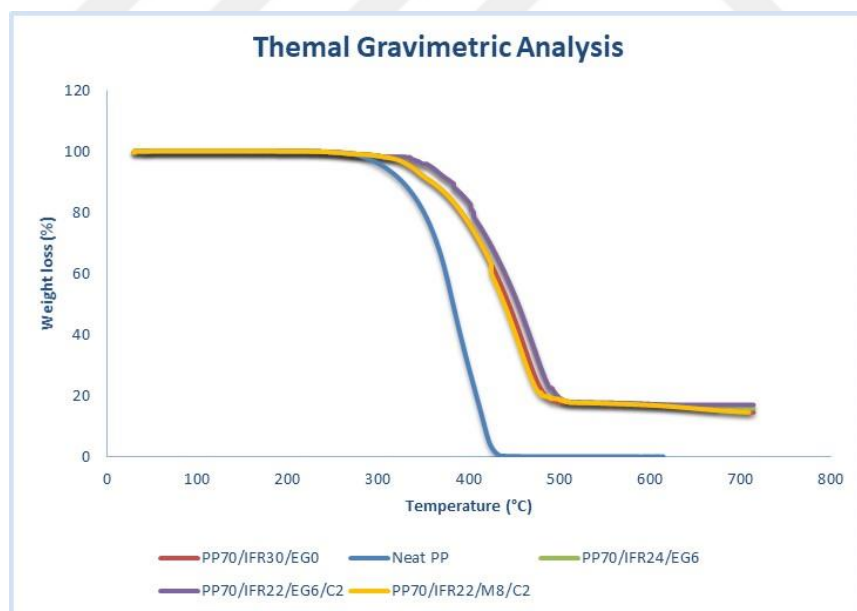


Figure 4.25 : TGA graph of compounds.

4.5.7 Limiting oxygen index

Neat PP can burn easily with very fast combustion rate and it generates a large amount of black smoke during fire due to this reason flammability properties needs to be

improved. PP LOI value is approx. 18.2% and can't obtain any levels in UL 94 tests as well. This situation severely limits the other applications in more fields. As for PPH/IFR22/M4/C4, PPH/IFR22/M6/C2, and PPH/IFR20/M8/C2, the LOI values of these samples are 32.5, 33, 27.5 %, respectively. When mica content is increased in system, LOI values starts to decrease. The results indicated that 6wt.% mica and 2 wt.% colemanite with 22 wt.% IFR showed synergistic effect in the flame retardant system. When mica and colemanite used together in the compound, 2 wt.% mica and 6wt.% expandable graphite with 22 wt.% IFR showed good synergistic effect with 29 % LOI value. When colemanite and expandable graphite used in system together, according to LOI values, they have not showed synergistic effect with lower LOI values. They also have a negative effect on IFR. This negative effect may be possibly due to deterioration in intumescence originated from interaction between IFR and EG. Especially, Simone reported that ammonium polyphosphate and pentaerythritol system and mica formed synergistic effect on final compound because mica is not expandable. Increasing of interlayer structure hindered synergic action in final compound. So this is the explanation why we have observed synergistic effect between mica and colemanite minerals with IFR system. LOI values are indicated in Table 4.38.

Table 4.38 : LOI test results of neat PP, mica and IFR filled PP compounds.

Samples Name	LOI (%)
Neat PP	18.0 ± 0.2
PP70/IFR30	37.8 ± 0.25
PP70/IFR20/M8/C2	27.5 ± 0.12
PP70/IFR22/M6/C2	33.0 ± 0.03
PP70/IFR22/M4/C4	32.5 ± 0.13
PP70/IFR22/EG6/C2	23.5 ± 0.21
PP70/IFR22/EG4/C4	24.0 ± 0.08
PP70/IFR22/EG6/M2	29.0 ± 0.06
PP70/IFR22/EG4/M4	28.8 ± 0.16
PP70/IFR22/EG2/M6	28.5 ± 0.13
PP70/IFR20/EG2/M8	28.5 ± 0.22

4.5.8 UL 94 flammability test (vertical)

UL 94 flammability testing is utilized to observe ignition performance and fire spread of polymeric parts. Flammability ratings are categorized as V0, V1, or V2 with UL 94 flammability testing. The best flammability property is obtained by V0 rating.

V-0: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 10 seconds. Flaming drips can't be allowed.

V-1: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips can't be allowed.

V-2: Fire applied to testing bar two times with overall 10 seconds. Burning of testing parts has to stop within 60 seconds. Flaming drips are allowed.

UL-94 flammability testing outcomes of fire retardant additives filled PP compounds are summarized in Table 4.39. When the amount of mica was fixed in between 2 wt% and 6 wt% in IFR with colemanite and testing parts of the PP/IFR compounds can achieve the V-0 classification. It was observed that mica and colemanite created synergistic effect with IFR in the PP compound at reasonable amount of loading level. Consequently, the decrease of IFR in the compounds was the major cause of the decrease of UL 94 classification. Additionally, it is obvious that minerals may reverse operations in the degradation of PP compounds; a barrier effect has to develop thermal uniformity and catalytic influence on the degradation of the compound which should reduce the thermal stability.

Table 4.39 : UL 94 vertical test results of flame retardant additives filled PP compounds.

Samples	UL 94 Test-Vertical				
	T1	T2	T3	Dripping	Flame Rating
PPH/IFR30	0	2	0	No	V0
PP70/IFR20/M8/C2	0	7	0	No	V0
PP70/IFR22/M6/C2	0	6	0	No	V0
PP70/IFR22/M4/C4	0	2	0	No	V0
PP70/IFR22/EG6/C2	0	9	0	No	V0
PP70/IFR22/EG4/C4	2	6	0	No	V0
PP70/IFR22/EG6/M2	2	8	0	No	V0
PP70/IFR22/EG4/M4	2	6	0	No	V0
PP70/IFR22/EG2/M6	2	8	0	No	V0
PP70/IFR20/EG2/M8	0	7	0	No	V0

T1: The burning time with flame of samples after the first ignition.

T2: The burning time with flame of samples after the second ignition.

T3: The burning time without flame of samples after the second ignition.

4.5.9 Glow wire flammability tests

Glow wire flammability testing results are indicated in Table 4.40.

Table 4.40 : Glow wire test results of of neat PPs, IFR/Colemanite filled PP compounds.

Samples	Glow Wire Temperature (°C)	
	750	850
PPH/IFR30	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR20/M8/C2	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR22/M6/C2	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR22/M4/C4	There is no glowing and flashing	There is no glowing and flashing
PP70/IFR22/EG6/C2	There is no glowing and flashing	Failed.
PP70/IFR22/EG4/C4	There is no glowing and flashing	Failed.
PP70/IFR22/EG6/M2	There is no glowing and flashing	There is no flame and no glowing.
PP70/IFR22/EG4/M4	There is no glowing and flashing	Failed.
PP70/IFR22/EG2/M6	There is no glowing and flashing	Failed.
PP70/IFR20/EG2/M8	There is no glowing and flashing	Failed.

The effects of colemanite, mica, expandable graphite and IFR on flammability features of compounds were searched with glow wire test. The tests were carried out at temperatures of 750 °C and 850 °C. IFR at 30 wt% loading level decreased burning time of polypropylene compounds significantly. The glow wire test results indicated that the replacement of IFR with mica and colemanite at a reasonable amount level can improve the flame retardancy properties of PP matrix due to dehydration and better char forming. Mica and colemanite worked together with creating synergistic effect in the system. Colemanite and expandable graphite samples passed the 750 test but they couldn't pass the 850 glow wire tests. They didn't create synergistic effect between each other. When mica and expandable graphite added to system at 2 wt% and 6 wt % loading level respectively, they can pass both 750 and 850 glow wire tests. When the addition of mica content increased in PP compound with IFR and expandable graphite, it affected flame retardancy properties of PP compounds adversely.

According to glow wire test results, mica and colemanite showed synergistic effect and the burning time remained within acceptance limits for glow wire ignition tests. Glow wire test is indicated in Figure 4.26.

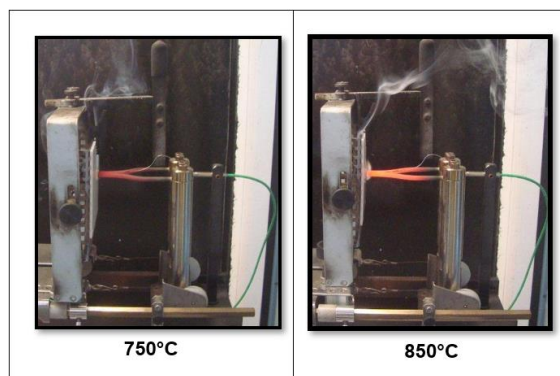


Figure 4.26 : Glow wire test of PP70/IFR22/M6/C2 sample for 750 °C and 850 °C.

4.5.10 Morphology analysis of IFR and additive filled PP compounds

The char residue was obtained after ash content test. The morphology analysis of ash residue was done by SEM. Figure 4.27 and Figure 4.28 indicate the state of char residues of compounds after ash content determination testing. Figure 4.29 shows the SEM picture of the char residue of 6 wt% mica, 2 wt% colemanite and 22 wt% IFR filled PP compound. Figure 4.30 shows SEM picture of the char residue of 6 wt% EG, 2 wt% colemanite and 22 wt% IFR filled PP compound. A rigid and porous structure was observed in Figure 4.29. Intumescent height was moderate and there are dark and light grey areas on the sample. Figure 4.30, It has a foamy structure. Although it has a grey appearance, there are also white areas. There is no flat area on the surface of sample. There are places where the foamy structure is more or less.



Figure 4.27 : Carbon char creation of PP70/IFR22/M6/C2 sample.



Figure 4.28 : Carbon char creation of PP70/IFR22/EG6/C2 sample.

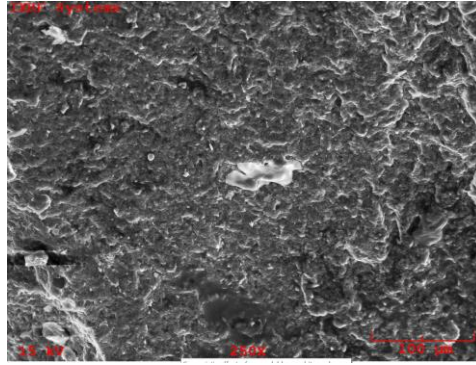


Figure 4.29 : SEM micrograph of PP70/IFR22/M6/C2 sample.

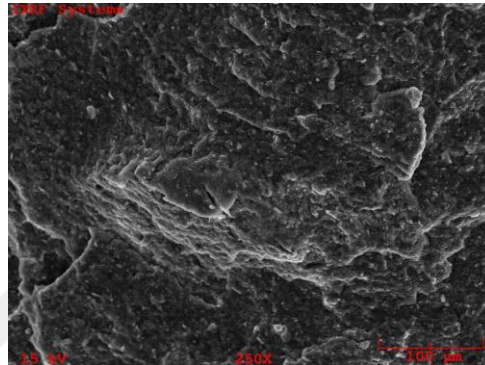


Figure 4.30 : SEM micrograph of PP70/IFR22/EG6/C2 sample.



5. CONCLUSIONS

The main of the this work is to enhance flammability properties of polypropylene with using potential fire retardant materials. It is planned to obtain a synergistic influence with the usage of fire retardant additives together because intumescent flame retardant systems are very expensive and it creates a soap effect during compounding process so flame retardant properties should be maintained by using alternative additives instead of intumescent flame retardant system. Mica, colemanite and expandable graphite additives have been choosen as potential flame retardant additive to use as a replacement of IFR.

In the first chapter, IFR compounded with PP material at loading level of 20-25-30 wt% in twin screw extrusion to observe flame retardancy effect on PP. Flame retardancy properties were determined using with LOI, UL 94 vertical and glow wire flammability tests. The LOI, UL 94 flammability and glow wire tes results represented that IFR had a important effect on flame retardancy and LOI value reached to 37.9 % with loading level of 30 wt% IFR. PP75/IFR25 and PP70/IFR30 compounds passed UL 94 V0 rating, but PP80/IFR20 compound didn't pass to UL 94 test due to dripping behaviour. All compounds passed the glow wire tests both 750 and 850 °C. Through thermal gravimetric analysis (TGA), the results indicated that IFR increased the thermal stability of PP/IFR compounds and also enhanced the formation of char layer. MFI test is a key factor to determine dripping behaviour of polymer compounds. MFI values decreased with increasing IFR additive in PP compound so this improved dripping behaviour and to pass UL 94 flammability test and also glow wire test. In terms of mechanical properties of final compound, increasing the amount of IFR in compound increased elastic modulus values. Tensile strength and tensile strain at yield point values decreased with the addition of IFR to the system. Izod Impact Notched testing values also decreased dramatically when IFR added to system. IFR additive acted as a filler and reduced mechanical properties of final PP compound. In addition to this, heat deflection temperature values increased with addition of IFR. This helped system to create extra safety during fire. According to morphology analysis of char

residue by SEM, it is observed that the structure of char residue of PP/IFR compound is loose and it has porous structure which is needed to be improved to form good flame shield for plastic material.

Effect of mica

IFR and mica were mixed with PP material in co-rotating twin screw extrusion to increase flammability features of PP. The LOI, UL 94 and glow wire test represented that mica had a important influence on fire retardancy and LOI which can catch up to 37.5 % with loading level of 2 wt% mica at the overall quantity of flame retardant additives fixed stable at 30 wt.%. Additionally, the PP/IFR compounds passed UL 94 V0 rating and both 750 °C and 850 °C glow wire tests and with 2-8 wt% mica loading. According to TGA analyses, the results indicated that mica improved the thermal stability of PP/IFR compounds and also promoted the formation of ash layer. When mica mineral added to polypropylene without IFR system, it has no influence on fire retardancy features of polypropylene. In terms of mechanical properties, increasing the amount of mica mineral content in polypropylene compounds increases the elastic modulus. Tensile strength value of polypropylene homopolymer decreased when IFR and mica mineral added to the system. No selective difference is observed on tensile strength values of only IFR and IFR/mica filled PP compounds. As a result, 30 wt. % IFR polypropylene compound and PP70/IFR28/M2, PP70/IFR26/M4, PP70/IFR24/M6 and PP70/IFR22/M8 samples have similar features in terms of mechanical and flame retardancy properties. It was observed that the structure of char residue of PP70/IFR24/M6 compound has rigid structure. Having a rigid structure will prevent the flames from entering to the polymer structure therefore flame retardancy of polymeric compounds can be enhanced. Therefore, mica content can be used up to 8 wt.% in polypropylene compound with IFR material.

Effect of Expandable Graphite

The search was carried out to observe the synergistic influence between IFR and EG in PP compounds. IFR and EG were compounded with PP material in co-rotating twin screw extrusion to increase flame retardancy of PP. The LOI, UL 94 and glow wire test results represented that EG had a important influence on fire retardancy and LOI which can catch up to 37.2 % with loading level of 4 wt.% EG at the overall quantity of flame retardant additives fixed stable at 30 wt.%. Additionally, the PP/IFR

compounds passed UL 94 V0 classification and both 750 °C and 850 °C glow wire tests and with 2-6 wt.% EG loading. These tests demonstrated that the addition of EG to PP/IFR compound improved fire retardancy features of PP compounds. It means that synergistic is available between IFR and EG additives. EG can be used with IFR in PP compounds at reasonable levels. When IFR added system, better LOI values were obtained and polymeric material didn't burn but it become softer. It reduces load carrying capability of material so heat deflection temperature of polymeric material has to be increased. HDT values can be increased with addition of EG as a result, the load carrying ability will be increased during fire. It will bring extra safety to polymeric material. According to TGA analyses, the results indicated that EG improved the thermal stability of PP/IFR compounds and also promoted the generation of extra char layer on the polymer surface. When EG added to polypropylene without IFR system, it has no effect on flame retardancy properties of polypropylene. Furthermore, it is difficult to process EG with PP material at 30 wt% loading level of EG. It is not suitable in terms of processability. In terms of mechanical properties, elastic modulus values increased with addition of EG to PP/IFR compound. Addition of IFR increased elastic modulus until a certain amount. However even at 30 wt% loading level, elastic modulus is higher than that of PP. It was not observed synergistic effect in terms of tensile testing but it was detected that EG and IFR used together, elastic modulus values were increased. But EG had dominant effect on elastic modules compared to IFR. Izod impact values decreased when EG added to system but izod impact values reduced more when IFR added to system. When EG and IFR used together in PP, better impact resistance was obtained than using only IFR. In case of using IFR alone, the reduction in impact strength can be compensated somewhat by adding EG and increasing the amount of EG in the system.

Effect of Colemanite

IFR and colemanite were mixed with PP material in co-rotating twin screw extrusion to create fire retardant composition and increase fire retardancy of PP. The LOI, UL 94 and glow wire test results indicated that colemanite had important influence on fire retardancy and LOI which can reach to 37.6 % with loading level of 2 wt.% colemanite at the total amount of flame retardant additives fixed stable at 30 wt.%. Additionally, the PP/IFR compounds passed UL 94 V0 rating and both 750 °C and 850 °C glow wire tests and with 2-8 wt.% colemanite loading. According to TGA analyses, the results

indicated that colemanite improved the thermal stability of PP/IFR compounds and also promoted the formation of char layer. When colemanite mineral added to polypropylene without IFR system, it has no effect on flame retardancy properties of polypropylene. When colemanite was added to system at 30 wt% loading level, LOI value reached to 19.0 % but it wasn't enough to increase flame retardancy properties of polypropylene because of this reason colemanite needs to be used with strong flame retardant additives to create synergistic effect. In terms of mechanical properties, increasing the amount of colemanite content in polypropylene compounds increases elastic modulus of neat polypropylene. Tensile strength value of polypropylene homopolymer decreased when IFR and colemanite added to polymeric system. No selective difference is observed on tensile strength values of only IFR and IFR/colemanite filled PP compounds. 30% colemanite filled PP compound showed better tensile strength properties compared to IFR/colemanite filled PP compounds at different loading levels. Strain value of neat polypropylene homopolymer decreased with increasing amounts of colemanite content in PP/IFR/colemanite compounds. Izod impact values of flame retardant filled PP compound increased with addition of the colemanite. It has been observed that colemanite and IFR created synergistic effect to increase izod impact strength of compound. HDT values were increased essentially by the addition of intumescent flame retardant additive. It was observed that different loadings of intumescent flame retardant and colemanite had effect on heat deflection temperature of PP compounds. This property will provide extra safety to PP compounds during the fire. PP70/IFR0/C30 sample has higher heat deflection temperature than PP70/IFR30/C0. Because the stiffness of PP70/IFR0/C30 sample was higher than PP70/IFR30/C0 sample when temperature increased. Consequently, IFR is expensive flame retardant additive so it needs to be used with cheaper and abundant mineral in the polymeric compounds. Since colemanite is a very common mineral in Turkey, cost advantage can be achieved when they used together with IFR. When all properties have been taken into consideration, colemanite can be used up to 6 wt% in IFR filled PP compound.

Effect of Flame Retardant Additives Mixtures

IFR, colemanite, mica and expandable graphite were compounded with PP material in the different combinations and loading levels to create synergistic flame retardant system and increase flame retardancy properties of final compound. Combinations and

loading levels were determined according to test results of binary mixtures of IFR and other potential flame retardant materials. The LOI, UL 94 and glow wire test results indicated that mica and colemanite created synergistic influence with IFR in PP compound when they used at reasonable amount. The LOI can catch up to 33%, and UL 94 test can reach V0 grade for PP/IFR/mica/colemanite samples at the total amount of flame retardant additives kept constant at 30 wt.%. Additionally the PP/IFR/mica/colemanite compounds passed UL 94 V0 rating and both 750 °C and 850 °C glow wire tests. According to TGA analyses, it can be observed that the initial degradation temperature increased from 250 °C in PP to between 260 °C – 270 °C in PP compounds. Mica indicated also a mass loss around to 700 °C related to dehydroxylations process. Addition of mica gave minimal effect on TGA curves. However, char residue was increased from 8.46 % to 10.25 %, 11.55 %, 15.74 %, 20.88 % and 28.42 % at 2, 4, 6, 8 wt.% mica content respectively. It is obvious that the char residue increased by the increasing loading of mica. Colemanite gives their structure water to the system and they create cooling effect on the surface. They formed such a strong and porous structure that flames can't penetrate and grow inside. They also improved thermal stability of PP compounds and promoted the formation of char layer. PP70/IFR30 and PP70/IFR20/M8/C2 samples indicated the same mechanical properties in terms of elastic module value. Tensile strength and tensile strain at yield point values of PP70/IFR20/M8/C2 are lower than PP70/IFR30 sample. Increasing of mica content increased elastic module but decreased tensile strength and strain values. PP70/IFR20/EG2/M8 and PP70/IFR20/M8/C2 showed the same tensile strength and strain values but the formula containing expandable graphite indicated lower elastic modulus. Reduction in the tensile modulus when small amount of expandable graphite was added. No further reduction is observed when the amount of expandable graphite increased. Tensile strength and tensile strain values started to decrease due to platy structure of mica mineral. Expandable graphite and mica mineral show the same mechanical properties due to their flake and platy structure when they used together in system. Addition of expandable graphite at high amount results in increase in modulus therefore expandable graphite needs to be used at reasonable amount in the final compound. Consequently, it is observed that the usage of colemanite, mica and expandable graphite in certain proportions instead of IFR into the PP compound doesn't adversely affect the mechanical properties of final compound. Flame retardant additives don't improve impact resistance and also don't create a synergistic effect in

terms of izod impact properties. No selective difference is observed on izod impact values at different flame retardant materials loading level in PP compounds. In the mica, colemanite and IFR mixtures, when mica used at 8% loading level, HDT value reached to 94.5°C. When colemanite amount started to increase in the compound with mica and IFR, HDT values decreased. In the expandable graphite mixtures, expandable graphite filled flame retardant compound reached to 96.2 °C.

According to all test results, mica and colemanite materials can show synergistic effect when they used with IFR in PP compound at reasonable amount. Especially, colemanite is abundant and commercial available material in Turkey. Usage of this material with reduction of IFR amount in the final compound will bring cost reduction and also national resource will be used



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