

DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

**FABRICATION, DEVELOPMENT AND
INDUSTRIAL APPLICATIONS OF FLAME
RETARDANT POLYMERIC NANOCOMPOSITE
MATERIALS FOR BATTERY SYSTEMS**

by
Metin YURDDAŞKAL

December, 2017
İZMİR

**FABRICATION, DEVELOPMENT AND
INDUSTRIAL APPLICATIONS OF FLAME
RETARDANT POLYMERIC NANOCOMPOSITE
MATERIALS FOR BATTERY SYSTEMS**

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**by
Metin YURDDAŞKAL**

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İZMİR**

Ph.D. THESIS EXAMINATION RESULT FORM

We have read the thesis entitled “**FABRICATION, DEVELOPMENT AND INDUSTRIAL APPLICATIONS OF FLAME RETARDANT POLYMERIC NANOCOMPOSITE MATERIALS FOR BATTERY SYSTEMS**” completed by **METİN YURDDAŞKAL** under supervision of **PROF. DR. ERDAL ÇELİK** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

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Metin YURDDAŞKAL

FABRICATION, DEVELOPMENT AND INDUSTRIAL APPLICATIONS OF FLAME RETARDANT POLYMERIC NANOCOMPOSITE MATERIALS FOR BATTERY SYSTEMS

ABSTRACT

Nowadays, polymers are used industrially in many fields such as automotive, electronics and decoration. However, it is known that these materials, which have such a wide range of use, have advantages as well as their low resistance to fire. In addition to this, the use of eco-friendly halogen free flame retardant additives, which are not harmful to health, is also increasing. In this study, it is aimed to produce, develop and apply to industry flame retardant additives by adding flame retardant additive into polypropylene matrix. For this purpose, additives such as halogen free antimony oxide, bentonite, zinc borate and huntite hydromagnesite are used in single, double, triple and quadruple compositions to determine the best flame retardant mixture composition. The size of the additive materials has been reduced to nano size as it is thought to provide better flame retardant properties. While the flame retardant property is being developed, care has been taken not to lose its mechanical performance. The composites used in this study were produced using extruder and injection molding methods. Structural, morphological, elemental, spectroscopic, thermal, mechanical and flame retardant properties were determined by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), FT-IR, differential thermal analysis-thermogravimetry (DTA-TG), tensile test, needle flame test (UL 94) and limiting oxygen index (LOI) tests. As a result of the thesis, flame retardant property has been successfully achieved for polypropylene. Polymer nanocomposites produced using halogen free flame retardant nanoparticles have been successfully applied in battery components used in the automotive industry as industrial applications.

Keywords: Polymer nanocomposite, flame retardant, halogen free, nanoparticle, battery

AKÜMÜLATÖR SİSTEMİNDE KULLANILAN ALEV GECİKTİRİCİ POLİMERİK NANOKOMPOZİT MALZEMELERİN ÜRETİLMESİ, GELİŞTİRİLMESİ VE ENDÜSTRİYEL UYGULAMASI

ÖZ

Günümüzde polimerler endüstriyel olarak otomotiv, elektronik ve dekorasyon başta olmak üzere birçok alanda sıklıkla kullanılırlar. Ancak bu denli geniş kullanım alanına sahip olan bu malzemelerin avantajlarının yanı sıra yanmaya karşı dirençlerinin oldukça düşük olduğu bilinmektedir. Bununla birlikte alev geciktirici olarak sağlığa zararı olmayan çevre dostu halojen içermeyen katkı maddelerinin kullanımı da gittikçe artmaktadır. Bu çalışmada polipropilen matriks içerisine alev geciktirici katkı maddelerinin ilavesiyle yanmaya karşı dirençli kompozitlerin üretilmesi, geliştirilmesi ve endüstriye uygulanması amaçlanmıştır. Bu amaç için halojen içermeyen antimuan oksit, bentonit, çinko borat ve huntit hidromanyezit gibi katkı malzemeleri tekli, ikili, üçlü ve dördümlü kompozisyonlarda kullanılarak en iyi alev geciktirici karışım kompozisyonunun belirlenmesi hedeflenmiştir. Daha iyi alev geciktirici özellik sağlayacağı düşünüldüğü için katkı malzemelerinin boyutu nano boyuta indirilmiştir. Alev geciktirme özelliği geliştirilirken mekanik performansının da istenen seviyede kalmasına dikkat edilmiştir. Bu çalışmadaki kompozitler ekstrüder ve enjeksiyon kalıplama metotları kullanılarak üretilmiştir. Yapısal, morfolojik, elementel, spektroskopik, termal, mekanik ve alev geciktirme özellikleri X-ışını difraksiyonu (XRD), taramalı electron mikroskobu (SEM), X-ışını fotoelektron spektroskopisi (XPS), FT-IR, diferansiyel termal analiz-termogravimetri (DTA-TG), çekme testi, iğne alev testi (UL 94) ve sınırlayıcı oksijen indeksi (LOI) deneyleri ile saptanmıştır. Çalışmanın neticesinde polipropilende alev geciktirme özelliği başarıyla elde edilmiştir. Halojen içermeyen alev geciktirici nanopartiküller kullanılarak üretilen polimer nanokompozitler endüstriyel uygulama olarak otomotiv sektöründe kullanılan akümülatör bileşenlerinde başarıyla uygulanmıştır.

Anahtar kelimeler: Polimer nanokompozit, alev geciktirici, halojensiz, nanopartikül, akümülatör

CONTENTS

	Page
Ph.D. THESIS EXAMINATION RESULT FORM	ii
ACKNOWLEDGMENT	iii
ABSTRACT	iv
ÖZ	v
LIST OF FIGURES	ix
LIST OF TABLES	xi
CHAPTER ONE - INTRODUCTION	1
1.1 General	1
1.2 Organization of the Thesis	5
CHAPTER TWO - THEORETICAL BACKGROUND	7
2.1 Polymers and Polymer Nanocomposites	7
2.1.1 Polypropylene	7
2.1.2 Polymer Nanocomposites	9
2.1.3 Processing of Thermoplastics and Thermosets	12
2.1.4 Nanoadditives	13
2.2 Thermal Decomposition and Combustion of Polymers	15
2.3 Flame Retardancy of Polypropylene	16
2.4 Flame Retardancy Mechanisms	17
2.5 Flame Retardant Additives	18
2.5.1 Halogenated Flame Retardants	19
2.5.2 Phosphorus Flame Retardants	20
2.5.3 Nitrogen Flame Retardants	22
2.5.4 Silicon Flame Retardants	22
2.5.5 Boron Flame Retardants	23
2.5.6 Antimony Compounds	24
2.5.7 Inorganic Hydroxide Flame Retardants	24

2.5.8 Synergism	25
CHAPTER THREE - EXPERIMENTAL PROCEDURE.....	26
3.1 Purpose	26
3.2 Materials	26
3.3 Nano Grinding Process and Particle Size Distribution	27
3.4 Production of Composites	27
3.5 Characterization of PP, Nanoadditives and PP Composites.....	29
3.5.1 X-Ray Diffractometer (XRD).....	29
3.5.2 X-Ray Photoelectron Spectroscopy (XPS).....	31
3.5.3 Fourier Transform Infrared Spectroscopy (FT-IR)	32
3.5.4 Scanning Electron Microscopy (SEM).....	34
3.5.5 Mechanical Tests	35
3.5.6 Differential Thermal Analysis – Thermogravimetry (DTA-TG)	35
3.5.7 Flame Retardant Test.....	36
3.5.8 Limiting Oxygen Index Test (LOI)	37
3.5.9 Industrial Applications Tests	37
CHAPTER FOUR - RESULTS AND DISCUSSION	40
4.1 Measurement of Particle Size Distribution	40
4.2 Phase Analysis.....	41
4.3 Elemental Analysis of PP Composites	44
4.4 FTIR Analysis	46
4.5 Microstructure and Morphology Analysis	47
4.6 Mechanical Properties	51
4.7 Thermal Properties	53
4.8 Flame Retardancy Properties.....	59
4.9 Industrial Applications	62
4.9.1 Mechanical Properties of Final Products.....	63
4.9.2 Performance and Corrosion Properties of Final Products	64

4.9.3 Recycling Properties of Final Products	67
CHAPTER FIVE - CONCLUSIONS AND FUTURE PLANS.....	68
5.1 Conclusions	68
5.2 Future Plans.....	70
REFERENCES.....	72



LIST OF FIGURES

	Page
Figure 2.1 PP polymer molecule in isotactic, syndiotactic and atactic forms.....	7
Figure 2.2 Schematic representation of smectite clay minerals formation and structure	13
Figure 2.3 Schematic illustration of combustion cycle of polymer	16
Figure 2.4 Fire triangle and combustion cycle of polymers.....	16
Figure 2.5 Stages of the burning process	18
Figure 2.6 Different phosphorous based flame retardants a) tetrakis hydroxy methyl phosphonium chloride (THPC), b) tris-aziridiny l phosphine oxide (APC) and c) phosphor nitrile chloride polymers (PNC)	21
Figure 3.1 A co-rotating twin screw extruder	29
Figure 3.2 An injection molding machine.....	29
Figure 3.3 Diffraction of X-rays by planes of atoms (A–A` and B–B`).....	30
Figure 3.4 Schematic illustration of XPS physics.....	32
Figure 3.5 Schematic diagram of a FTIR spectrometer	33
Figure 3.6 Schematic illustration of SEM.....	34
Figure 3.7 Schematic illustration of UL 94 vertical test	36
Figure 4.1 Particle size distribution of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite	40
Figure 4.2 XRD patterns of the additives a) antimony trioxide, b) bentonite, c) zinc borate and d) huntite/hydromagnesite	42
Figure 4.3 XRD patterns of a) pure PP and PP composites reinforced with b) antimony trioxide, c) bentonite, d) zinc borate and e) huntite/hydromagnesite	42
Figure 4.4 XRD patterns of the multi-additive reinforced composites.....	43
Figure 4.5 XPS survey spectra of a) pure PP and b) antimony trioxide, c) bentonite, d) zinc borate and e) huntite/hydromagnesite reinforced PP composites	45
Figure 4.6 FTIR analysis of the pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites.....	46

Figure 4.7 SEM micrographs of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite additives.....	47
Figure 4.8 SEM micrographs of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite 30 wt% reinforced composites	48
Figure 4.9 SEM micrographs of polished (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite 30 wt% reinforced composites ...	49
Figure 4.10 SEM micrographs of PP composite specimens reinforced with different additives and different ratio	49
Figure 4.11 Tensile strength and elastic modulus of pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites	51
Figure 4.12 DTA-TG curves of pure PP specimen	54
Figure 4.13 DTA-TG curves of a) 5 %, b) 10%, c) 20% and d) 30% antimony trioxide reinforced PP composite specimens	54
Figure 4.14 DTA-TG curves of a) 5% and b) 10% bentonite reinforced PP composite specimens.....	55
Figure 4.15 DTA-TG curves of a) 5%, b) 10%, c) 20% and d) 30% zinc borate reinforced PP composite specimens	55
Figure 4.16 DTA-TG curves of huntite/hydromagnesite a) 5%, b) 10%, c) 20%, d) 30%, e) 40% and f) 50% reinforced PP composite specimens.....	56
Figure 4.17 TGA curves of PP and PP/30A, PP/30B, PP/30Z, PP/30H, PP/40H and PP/50H composites	57
Figure 4.18 DTG curves of PP/30A, PP/30B, PP/30Z, PP/30H, PP/40H and PP/50H composites	57
Figure 4.19 DTA-TG curves of PP composite specimens reinforced with different additives and different ratio	58
Figure 4.20 Industrial application of flame retardant huntite/hydromagnesite reinforced PP composites	62
Figure 4.21 Experimental setup of the impact tests for battery boxes	63

LIST OF TABLES

	Page
Table 1.1 Minerals with potential fire retardant benefits, and their decomposition temperatures	3
Table 2.1 Characteristics of types of polypropylene.....	8
Table 2.2 Improvements and disadvantages of nanoparticles to polymers.....	11
Table 2.3 Chemical families of nanoadditives	14
Table 2.4 Morphological properties of nanoadditives	14
Table 2.5 Advantages and drawbacks of flame retardants used in PP.....	19
Table 3.1 The physical properties of PP	27
Table 3.2 Designation and composition of PP and PP composites.....	28
Table 3.3 Classification of UL 94 test	37
Table 4.1 Mechanical properties of pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites.....	52
Table 4.2 Mechanical properties of the multi-additive reinforced composites.....	53
Table 4.3 Thermal properties of PP and PP composites	57
Table 4.4 The initial values of the combustion temperatures of all PP composites...	60
Table 4.5 UL 94-V and LOI testing results of PP and PP composites.....	61
Table 4.6 UL 94-V and LOI testing results of the multi-additive reinforced PP composites.....	61
Table 4.7 General test results of the boxes for PP/50H, PP/25H and commercial product.....	64
Table 4.8 Performance (cycle) test results of the commercial product and PP/25H..	65
Table 4.9 Corrosion test results of the commercial product	65
Table 4.10 Corrosion test results of the box produced with PP/25H.....	66
Table 4.11 Control of recycling process using crushing products in different ratio..	66

CHAPTER ONE

INTRODUCTION

1.1 General

Polypropylene (PP) is one of the most important thermoplastic widely used in many fields, such as automobiles, electronics, wires and cables, interior decorations and other areas due to its superior mechanical properties, low cost, easy processing and chemical stability (Bakar, Ishak, Taib, Rozman, & Jani, 2010; Dai & Li, 2010; Leong, Ishak, & Ariffin, 2004; X. Wang, Li, Liao, Gu, & Li, 2008). However, its severe flammability, frequently accompanied by the production of corrosive or toxic gases and smoke through combustion, due to its aliphatic hydrocarbon structure is a main limitation, which restricts the use in some fields requiring good flame retardant performance. Thus, it is very important to strengthen the flame retardant properties of PP. Recent developments in flame retardant polymeric materials have focused on the flame retardancy of polymer matrix nanocomposites. (Feng, Li, Liang, Huang, & Liu, 2015; Lai, Tang, Li, & Zeng, 2015). In order to improve its fire resistance, flame retardants (FRs) are added to PP, which is one of the most efficient methods. The most commonly used flame retardant additive types are halogenated, inorganic and phosphorous compounds.(Kashiwagi et al., 2004; HL Qin et al., 2004). Furthermore, ammonium phosphates and borates, zinc chloride and borate, boric acid, antimony oxide, ammonium sulphate and chlorides, dicyanodiamide and sodium borate have also been used as flame retardant additives (Lai et al., 2015; S. Wang et al., 2004).

It is said that halogenated compounds increase the conversion of polymeric materials into a char residue during pyrolysis, thereby reducing the formation of flammable carbon containing gases in the phosphorus compounds by means of a radical reaction with a vapor phase flame retarding mechanism. The superior performance of halogen-containing flame retardants during combustion is quite remarkable using inorganic materials like metallic hydroxide additives. Metallic hydroxides supply important flame retarding effects by (P. R. Hornsby & Watson, 1989; Turi, 1981):

- Producing a metal oxide coating that can function as an insulating protective layer during combustion,
- Releasing the water that they involve at high temperatures and thereby diluting the amount of fuel in the environment to sustain combustion during fire,
- Producing a char which results in the prevention of burning and the production of less smoke during combustion,
- Absorbing heat from the combustion area, which reduces the possibility of continuous burning.

Halogen-containing flame retardants release metal halides, halogen acids and some high toxic outputs such as dibenzofurans and brominated dibenzo-dioxines that cause serious problems to environment and body health during combustion, while they are highly effective and widely used in engineering plastics (Chigwada, Jash, Jiang, & Wilkie, 2005). Therefore, the potential applications of halogen based flame retardants are limited because of their hazardous effect on health and environments (Lu & Hamerton, 2002; Rahman, Langford, Scrimshaw, & Lester, 2001). For example, the waste electrical and electronic equipment (WEEE) and restriction of hazardous substances (RoHS) directives limit the use of halogen-containing flame retardants. Although halogen-containing flame retardants are highly efficient, they are gradually being phased out when WEEE and RoHS regulations are taken into consideration. It is expected to develop non-toxic, eco-friendly flame retardant polymer nanocomposites taking advantage of the superior properties of nano-sized additives. Therefore, several studies have been performed on non-halogen additives such as metal hydroxides, phosphorus, boron containing compounds and inorganic clay fillers. There are also numerous research articles illustrating effectiveness of non-halogenated additives to improve mechanical strength and thermal stability as well as flame retardancy (Bakar et al., 2010; Samyn, Bourbigot, Duquesne, & Delobel, 2007).

The requirements of environmentally friendly flame retardants in order to overcome negative effect of halogen-containing flame retardants have been provided by halogen-free flame retardants. In recent years, halogen-free FRs have attracted considerable attention and been considered as candidates to substitute halogen-containing flame

retardants (Feng, Zhang, et al., 2015a). Despite magnesium hydroxide and aluminum trihydroxide (ATH) are the most notable mineral fire retardants, Rothon (Rothon, 2003) has revealed that there are some minerals (Table 1.1) that could be of beneficial in polymers. Each one of all dissociates endothermically with the evolution of either water, carbon dioxide or both. Hydromagnesite is the most commercially interesting one among these minerals. When the decomposition temperature of hydromagnesite is considered, the use of hydromagnesite instead of ATH, which is more widely used, is increasing. This is because the ATH has a higher process temperature.

Table 1.1 Minerals with potential fire retardant benefits, and their decomposition temperatures (Rothon, 2003)

Mineral	Chemical Formula	Approximate onset of decomposition (°C)
Nesquehonite	$MgCO_3 \cdot 3H_2O$	70-100
Gypsum	$CaSO_4 \cdot 2H_2O$	60-130
Magnesium phosphate octahydrate	$Mg_3(PO_4)_2 \cdot 8H_2O$	140-150
Aluminium hydroxide	$Al(OH)_3$	180-200
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	220-240
Dawsonite	$NaAl(OH)_2CO_3$	240-260
Magnesium hydroxide	$Mg(OH)_2$	300-320
Magnesium carbonate subhydrate	$MgO \cdot CO_{2(0.96)}H_2O_{(0.3)}$	340-350
Boehmite	$AlO(OH)$	340-350
Calcium hydroxide	$Ca(OH)_2$	430-450

The use of hydromagnesite in polymers is quite common when the literature about flame retardant publications is investigated. Many published articles claim that hydromagnesite is more effective when used in combination with huntite as flame retardant materials, therefore less effort has been spent analysing possible fire retardant mechanisms of huntite. Kirschbaum (G. Kirschbaum, 2001; G. S. Kirschbaum, 1998) states that huntite is not a very effective fire retardant when used alone because of its high decomposition temperature, over 400 °C. He also pointed out that the combined use of huntite and hydromagnesite is as effective as flame retarding performance of metal hydroxides such as ATH and magnesium hydroxide.

Many efforts have been devoted to improve the both flame retardant and mechanical properties of PP over the past decades. It is well known that the excessive use of the high loading of metal hydroxides impairs the mechanical properties of PP based materials (Li, Li, Dai, Jia, & Gao, 2008; Wu, Ding, & Yang, 2010). Therefore, halogen-free flame retardant additives such as organo-bentonite, antimony trioxide, zinc borate and ammonium polyphosphate are attracting more and more attention in order to improve such properties. These additives have been used as the sole reinforcing material or the combination of them in terms of the effects of inorganic additives on mechanical, thermal stability and flame retardancy mechanism by many researchers (Du et al., 2009; Kipcak, Baran Acarali, Moroydor Derun, Tugrul, & Piskin, 2014; Xu, Huang, Chen, Tan, & Wang, 2013; Zanetti, Camino, et al., 2002). These flame retardants have some advantages including non-toxic gases, low smoke density, anti-dripping melt during burning, strength and stability of char layer (Feng, Zhang, et al., 2015b).

There are many combinations of fire retardant additives and few of them are used to prevent flame. It is very important to understand the flame retarding mechanism of each material and to choose the effective combinations. The main objective of this study is to produce flame retardant nanocomposites by reinforcing different halogen-free nanoparticles with various compositions and to investigate the potential use of these nanocomposites in industry. Within this scope, halogen-free nano sized huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate particles were used to reinforce polypropylene matrix. The influence of different mineral type/content was investigated for polypropylene nanocomposites containing halogen-free flame retardants on the structural, thermal, mechanical and flame retardant properties. The objective of this study is to evaluate the effects of halogen free flame retardant additives on flame retardancy as well as structural, mechanical and thermal properties of PP based composites. The effects of filler content on the flame retardancy, thermal and mechanical properties of the PP composites have also been investigated.

1.2 Organization of the Thesis

The primary objective of this thesis is to produce flame retardant PP based nanocomposites thanks to halogen-free additives using extrusion and injection molding processes. Polypropylene (PP) pellets were used as a polymer matrix to produce huntite/hydromagnesite, bentonite, antimony trioxide and zinc borate reinforced nanocomposites. Firstly, four different sets of flame retardant composites were formulated. Then, various combinations were processed by using four different flame retardant additives in the same structure. This study revealed that nano sized halogen free flame retardants used in this study exhibited a synergistic effect and enhanced the flame retardant, thermal stability and mechanical properties of PP based nanocomposites. Another important aspect of this study is that good thermal stability behaviors were provided with low additive amount.

It was subjected to grinding process to use all halogen-free flame retardant additives at the nanoscale. For analyzing particle size distribution of the additives, dynamic light scattering (DLS) method was used. In order to produce flame retardant PP based nanocomposites, extrusion and injection molding processes were selected. Differential Thermal Analysis-Thermogravimetry (DTA-TG) and Fourier Transform Infrared (FTIR) equipments were performed to determine thermal properties and chemical bond structure of the PP based nanocomposites. Structural analysis of the produced nanocomposites was characterized through X-Ray Diffraction (XRD) and surface morphology was investigated using Scanning Electron Microscopy (SEM). Mechanical properties of the composites were investigated using tensile test. The flame retardant properties of PP based composites were investigated using vertical burning test (UL94) and limiting oxygen index (LOI) analysis.

This thesis contains five chapters. In Chapter Two, flammability of polymers and flame retardants, behavior of polymeric materials in fires, types of flame retardants, characterization and applications were explained as a theoretical background. In Chapter Three, experimental procedures of non-halogenated flame retardant PP based nanocomposites were explained. This chapter also described the characterization

techniques of polymer matrix and/or flame retardant PP based composites. In Chapter Four, the results regarding flame retardant composites were discussed and demonstrated effect of additive type and/or amount in details. The general conclusion of this study and future plans were summerized in Chapter Five.



CHAPTER TWO

THEORETICAL BACKGROUND

2.1 Polymers and Polymer Nanocomposites

2.1.1 Polypropylene

Polypropylene (PP) was first produced by G. Natta with the polymerization of propylene monomer in 1954, following the study of K. Ziegler. Polypropylene macromolecule contains more than 10,000 monomer units. Polypropylenes are named according to the place in which the methyl groups are attached to the chain, including isotactic, syndiotactic and atactic polypropylene. Their structures are seen in Figure 2.1.

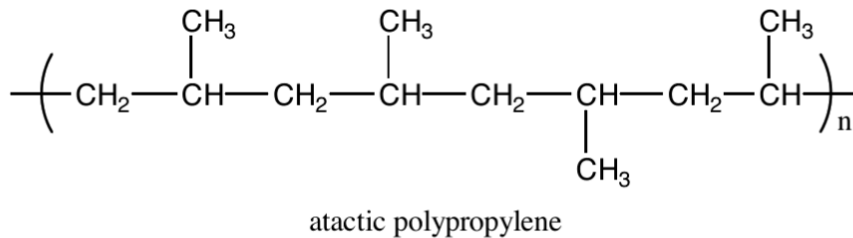
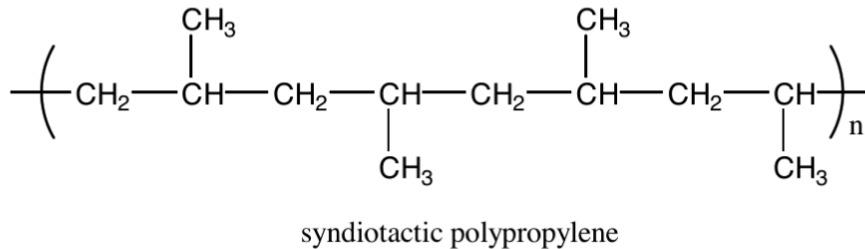
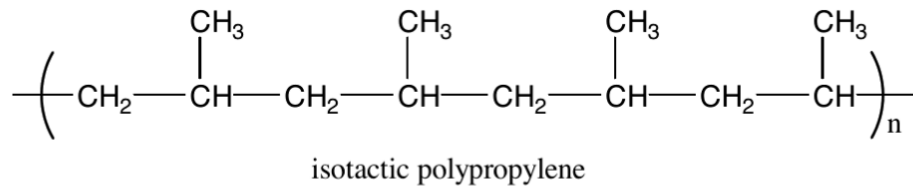


Figure 2.1 PP polymer molecule in isotactic, syndiotactic and atactic forms

Polypropylene is a semi-crystalline thermoplastic and made by polymerizing its homopolymer form called propylene monomer. The most widely used types of

polypropylene are homopolymer (HP), random copolymer (RACO) and heterophasic (impact) copolymer (HECO). Densities of HP, RACO and HECO are all in the range of 0.89-0.91 g/cm³. The key parameters of each major type of polypropylene are summarized in Table 2.1.

Table 2.1 Characteristics of types of polypropylene (Malpass & Band, 2012)

Type of PP	Typical olefin comonomer	Range of comonomer content (wt %)	Impact resistance	Film clarity	Tensile strength
Homopolymer	None	0	Poor	Poor	Good
Random copolymer	Ethylene	1-7	Medium	Good	Medium
Heterophasic (impact) copolymer	Ethylene	5-25	Good	-	Poor

The physical properties and processing parameters of polypropylene are generally determined by the following methods; the molecular weight distribution (variation in average length of chains), the type and amount of copolymerizing monomer and the molecular weight (average number of propylene units in a chain).

PP and polyethylene (PE) have many similar properties, particularly in their solution behavior, electrical properties and swelling behaviors. In spite of many similarities, areas of usage determine the polymer selection. The melting point of PP ranges from 160-170 °C that is approximately 50 °C higher than that of PE. PP has higher tensile, flexural and compressive strength and elastic modulus than PE.

The molecular weight of PP is normally estimated through the viscosity measurement. Melt flow rate (melt flow index, MFI, MFR) is widely used for the simple measurement of viscosity. MFI is inversely related to molecular weight. Although the molecular chains in PP are linear, the structure is not completely regular, for example, chains can be entangled or branching. Since the molecular chains are able to pack together in an ordered crystal structure, they are linear. Hence, PP is the best

described as a semi-crystalline polymer (Tripathi, 2002). The degree of crystallinity and crystal structure in a polymer vary dependent on thermal history.

2.1.2 Polymer Nanocomposites

The studies on polymer nanocomposites have increased considerably in recent years. They are composed of dispersed particles, fibers or sheets of which at least one dimension is below a hundred nanometers. When the size of additive materials decreases from micro to nano scale even with small loadings, improved electrical, mechanical, thermal and optical properties can be achieved. The obtained superior properties are resulted from high reinforcement aspect ratio and surface area.

Nanocomposites can be considered in three different classes depending on the number of dimensions of additives. The first type of nanocomposites containing nanofillers that have only one dimension in nanometer range such as nanocoatings, nanolayers and nanofilms. Nanofillers having two dimensions in nanometer range, namely, nanofibers, nanotubes, etc. Nanoparticles can be given as an example of the third type of the nanofiller that have all three dimensions in nanometer scale.

The use of semi-crystalline polymeric matrices in nanocomposites is a major concern to exhibit good mechanical properties for engineering applications. Although they perform ductile behaviour at high temperatures or low strain, low temperatures, high strain rates and the presence of stress often lead to brittle failure of materials.

Modification of organic polymers through the incorporation of additives yields, with few exceptions, multiphase systems containing the additive embedded in a continuous polymeric matrix. The resulting mixtures are characterized by unique microstructures or macrostructures that are responsible for their properties. The primary reasons for using additives are:

- Property modification or enhancement,
- Overall cost reduction,

- Improving and controlling of processing characteristics.

Polymer composites are formed by bringing the polymer and organic or inorganic additive with various geometries (fibers, flakes, spheres, and particulates). Thus, this results in a structure with two or more components and two or more phases. The additives may be continuous in the form of long fibers are embedded in the polymer in regular geometric arrangements extending along the dimensions of the product. Well known examples are the fiber-based thermoset laminates that are generally classified as high-performance polymer composites, or as nanocomposites based on the length of the fibers or ribbons (Ajayan, Schadler, & Braun, 2003).

Composite materials are also classified according to the type (natural or synthetic) of filler or matrix material. It is possible to see the most of the composite structures are hard materials in the nature. These complicated structures consist of continuous or discontinuous fiber bundle embedded in a matrix that holds the particles together and holds them together. For example, wood is a composite of cellulose fibrous and lignin. Bone is a composite formed by collagen, other proteins and calcium phosphate salts. Spider silk comprise of organic nanocrystals in an organic amorphous matrix (Vogel & Berg, 1998).

These additives of polymer composites have been classified as reinforcements, reinforcing fillers or fillers. Reinforcement materials are much stiffer and stronger than the polymer, usually increasing their strength. In this way, mechanical property modification may be considered as the major function, although their presence can significantly affect thermal stability, thermal expansion, transparency, etc (Mallick & Newman, 1990).

In general, regardless of whether continuous or discontinuous, the parameters affecting the properties of the polymer composites include:

- the composition;
- the properties of the fillers (size, shape and inherent properties);

- the interaction of components at the phase boundaries, which is also associated with the existence of a thick interface, also known as the interphase; this is often considered as a separate phase, controlling adhesion between the components;
- the procedure of the production.

With regard to methods of fabrication, all processes that are applicable to unfilled, unmodified thermoplastics can also be used for discontinuous systems (with the exception of expandable bead molding). Fillers can also be used in the thermoset processes often in combination with the primary continuous fiber reinforcement. According to the type of additive, some properties of the polymer could be affected; for instance, melt viscosity could be significantly increased through the incorporation of fibrous materials. Besides, mold shrinkage and thermal expansion would be reduced, a routine effect of most inorganic additives (Blum, 2008).

Table 2.2 Improvements and disadvantages of nanoparticles to polymers (Koo, Lao, & Lee, 2012)

Improvements	Disadvantages
Mechanical properties (tensile strength, stiffness, toughness)	Viscosity increase (limits processability)
Gas barrier	Dispersion difficulties
Synergistic flame retardant additive	Optical issues
Dimensional stability	Sedimentation
Thermal expansion	Black color when different carbon containing nanoparticles are used
Thermal conductivity	
Ablation resistance	
Chemical resistance	

The particular structures of polymeric nanocomposites have resulted in major improvements in mechanical properties, gas barrier properties, thermal stability, fire retardancy, electrical properties, etc. However, besides these exciting improvements, there still some disadvantages come along with nanocomposites (Table 2.2) (Koo et al., 2012). Consequently, the majority of the research in polymeric nanocomposites is focused on how to disperse nanofillers uniformly into matrix and how to modify the surface of nanofillers so that not only the particles can be well distributed but also the

desired properties can be achieved and/or enhanced. (Hough, Islam, Janmey, & Yodh, 2004; Tibbetts, Lake, Strong, & Rice, 2007; Vaia, Vasudevan, Krawiec, Scanlon, & Giannelis, 1995).

2.1.3 Processing of Thermoplastics and Thermosets

Most composites consist of two constituents. The matrix or binder surrounds and binds together fibres or fragments of a much stronger second material (the reinforcement). Polymer processing is used for converting solid and/or liquid polymers to finished products. It consists of three steps; (i) pre-shaping (melt mixing, softening, pumping etc.), (ii) shaping (molding, casting, etc.), (iii) post-shaping (decorating, fastening, etc.) (Marino Xanthos, 2005). The conversion of solid or liquid polymers into finished products is generally known as polymer processing. Polymer processing has several steps (Tadmor & Gogos, 2013):

1) The preforming operations include some or all of the following steps:

- handling of particulate solids (particle packing, agglomeration, gravitational flow, compaction, and others);
- melting or heat softening;
- pressurization and pumping of the polymer melt;
- mixing for melt homogenization or dispersion of additives;
- devolatilization and stripping of residual monomers, solvents, contaminants, and moisture.

The major purpose of the above steps is to make the liquid cross-linkable thermosets or thermoplastics, which can be deformable, liquids so that they can be molded in a mold; afterwards, they can be solidified by cooling under T_g or T_m (thermoplastics) or by a chemical reaction (thermosets).

2) Shaping steps during which “structuring” happens (morphology development and molecular orientation that change and enhance mechanical and physical

properties). Principal shaping methods involve molding, die forming, casting, coating and calendering.

3) Postshaping steps, such as fastening, decorating, sealing, bonding, dyeing, welding, metallizing and printing.

2.1.4 Nanoadditives

Nanoadditives usually exhibit improved performance of nanocomposites compared to conventional composites owing to their unique phase, morphology and improved interfacial properties. For these reasons, nanostructured organic-inorganic composites have attracted considerable attention from both fundamental research and an applications point of view. For example, smectites are a group of hydroxyl alumino-silicates containing alkalis and alkaline earths such as monmorillonite, aliettite, ferrosaponite. Structure of a typically smectite clay nanolayer is presented in Figure 2.2.

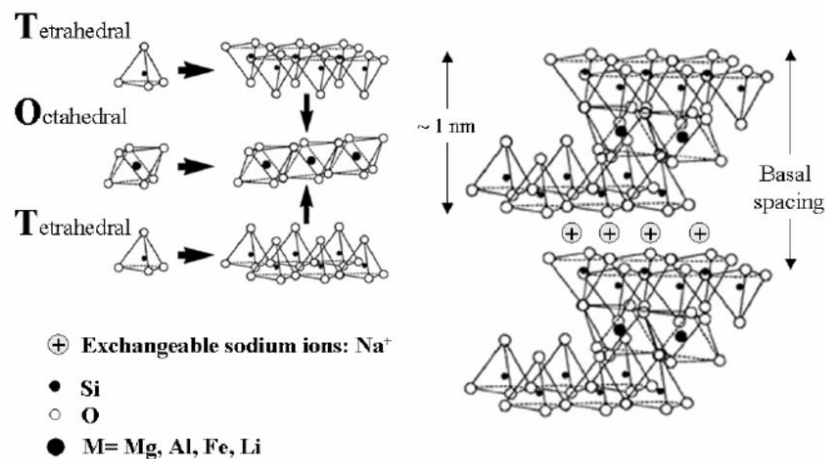


Figure 2.2 Schematic representation of smectite clay minerals formation and structure (Bourgeat-Lami, Sheibat-Othman, & Santos, 2010)

Montmorillonite is a type of clay and is classified as magnesium aluminum silicate which has a sheet morphology, and can be used to make a new class of polymer/clay nanocomposites. The total surface area of montmorillonite can be as large as $750 \text{ m}^2/\text{g}$

and the high aspect ratio (70-150) contributes to its rheological benefits. In order to make the clay into organoclay it is reacted them with organ-cationic surfactants.

Table 2.3 Chemical families of nanoadditives (M. Xanthos., 2005)

Chemical family	Examples
Oxides	Glass, MgO, SiO ₂ , Sb ₂ O ₃ , Al ₂ O ₃ , and ZnO
Hydroxides	Al(OH) ₃ and Mg(OH) ₂
Salts	CaCO ₃ , BaSO ₄ , CaSO ₄ , phosphates, and hydrotalcite
Silicates	Talc, mica, kaolin, wollastonite, montmorillonite and feldspar
Metals	Boron and steel
Carbon based additives	Carbon fibers, graphite fibers and flakes, carbon nanotubes and carbon black
Natural polymers	Cellulose fibers, wood flour and fibers, flax, cotton, sisal, and starch
Synthetic polymers	Polyamide, polyester, aramid, and polyvinyl alcohol fibers

Table 2.4 Morphological properties of nanoadditives (M. Xanthos., 2005)

Shape	Aspect ratio	Example
Cube	1	Feldspar and calcite
Sphere	1	Glass spheres
Block	1-4	Quartz, calcite, silica, and barite
Plate	4-30	Kaolin, talc, and hydrous alumina
Flake	50-200+	Mica, graphite, and montmorillonite nanoclays
Fiber	20-200+	Wollastonite, glass fibers, carbon nanotubes, wood fibers, asbestos fibers, and carbon fibers

Various inorganic and organic compounds used as nanoadditives have an important diversity in their natural properties, chemical structures, shapes, forms and sizes. Their common characteristic is that they are used at relatively high concentrations (>5% by volume), although some surface modifiers and processing aids are used at lower concentrations. Fillers may be classified as inorganic or organic substances and further subdivided according to chemical family (Table 2.3) or according to their shape and size or aspect ratio (Table 2.4).

2.2 Thermal Decomposition and Combustion of Polymers

All organic polymeric materials are flammable. When they are exposed to the sufficient heat, they decompose or pyrolyze generating flammable volatiles. Thermal decomposition of a polymer is an endothermic process which necessitates that binding energy of around 200–400 kJ/mol (typical for most C-C backbone polymers) is supplied to break covalent bonds. It is important to distinguish thermal decomposition in the absence of oxygen (pyrolysis) and in the presence of oxygen (thermo-oxidative decomposition).

The products from pyrolytic decomposition include combustible gases, non-combustible gases, and carbonaceous char. When the combustible gases (fuel) mix with oxygen, ignition occurs due to the presence of an external flame or spark. Flame and heat are generated after ignition, and some of the heat is transferred back to the polymer pyrolysis process. Figure 2.3 summarizes the polymer combustion process. The burning process is comprised of five fundamental steps, which are, heating, decomposition, ignition, combustion and propagation (Jang & Lee, 2001; Zaikov & Lomakin, 2002). Flame retardancy can be achieved by the disruption of the burning process at any of these stages that can lead to the termination of the process before actual ignition occurs.

Combustion, defined as the reaction of oxygen and fuel accompanied by heat release, can occur when three essential elements coexist; fuel (combustible), oxygen (combustive) and energy in the form of heat (Figure 2.4). Polymers are long chain macromolecules that generally consist of carbon and hydrogen. When heated to a sufficient temperature, energy barrier for thermal decomposition of a polymer can be overcome leading to extensive changes in the chemical structure.

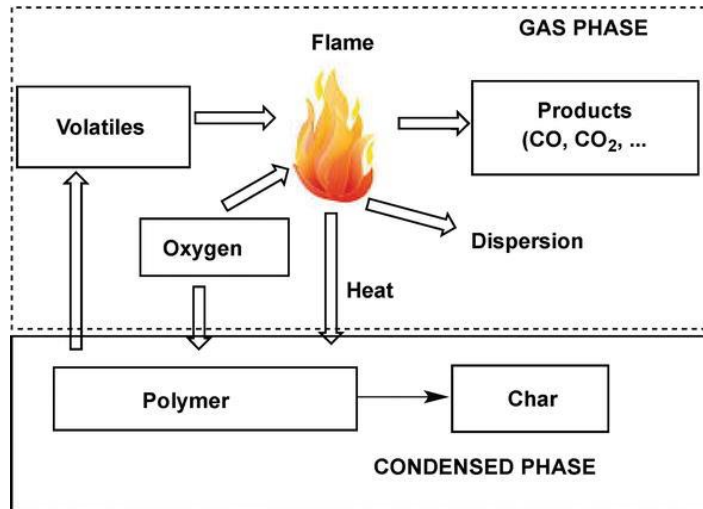


Figure 2.3 Schematic illustration of combustion cycle of polymer (Malucelli, 2016)

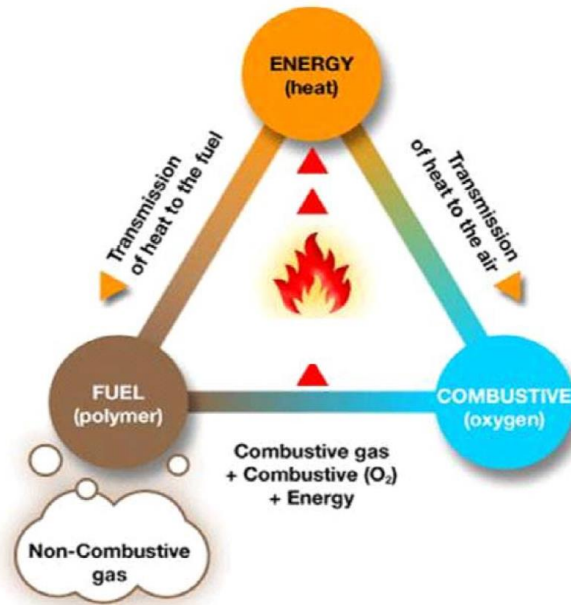


Figure 2.4 Fire triangle and combustion cycle of polymers (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009)

2.3 Flame Retardancy of Polypropylene

In order to improve the flame retardant property of polypropylene, various additives have been developed by the additive manufacturers. However, their activity is generally reduced since the high crystal structure of polypropylene complicates the homogeneous distribution in the polymer matrix. These additives may also have

adverse effects on other properties of the polymer. For example, while improving the flame retardancy of polypropylene with additives, the mechanical performance of the polymer can be reduced by the addition of a low strength additive. In addition, flame retardants may reduce processability due to chemical interactions or may cause a phase separation between the polymer and the applied additives (Pawelec, 2014).

2.4 Flame Retardancy Mechanisms

Throughout the history, fire has been a major reason for death and property losses. Depending upon the polymer, flame retardants act in one or more of the stages of the combustion process: heating, decomposition, ignition, flame spread, smoke process. Once the combustion process is understood, it is possible to plan the strategies to stop the propagation of the fire. When a polymer is under external heat flux, the polymer can decompose to form the high energy free radicals and evaporate. If the concentration of volatile products is sufficient, within the flammability limits and the temperature is above the ignition temperature, the combustion proceeds (Camino, Costa, & Luda di Cortemiglia, 1991).

The objective of flame retardants is to prevent the ignition of materials and reduce the flame propagation. The flame retarded materials minimize fire risk but not completely become non-flammable. They function at different stages of the burning process, and allow people more time to escape (Figure 2.5). Flame retardants increase ignition time and decrease development of smoke flame propagation, toxic gases release and heat release rate (Rault et al., 2009; Tang & Lewin, 2008). Ignition can be triggered at a lower temperature (termed as the flash point) by an intense external source such as a flame or spark. Once the volatiles are ignited, combustion is self-sustained either by the act of an external source of irradiation or by substantial heat release due to exothermic chain reactions occurring in the gas phase which facilitate the decomposition of polymer thereby maintaining the critical concentration of evolved flammable volatiles in the gas phase.

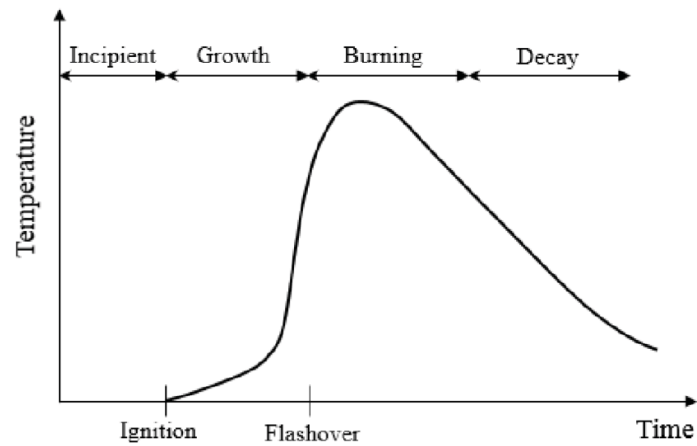


Figure 2.5 Stages of the burning process (Gooranorimi, 2016)

The general view of the flame retardant mechanism is that a carbonaceous silicate char builds up on the surface during burning which creates a protective barrier to heat and mass transfer (Huaili Qin, Su, Zhang, Zhao, & Yang, 2003; Zanetti, Kashiwagi, Falqui, & Camino, 2002).

2.5 Flame Retardant Additives

A wide range of flame retardant materials has been developed for polymers, around 150 to 200 different compounds being commercially available. Several types of flame retardants (FR) have been used for suppression of the combustion process. Flame retardants can be classified as additive or reactive compounds. Additive flame retardants are usually added during the transformation process and only react with the polymer at high temperature. On the other hand, reactive flame retardants are usually incorporated into the polymer chain during synthesis or by chemical grafting (Laoutid et al., 2009). Table 2.5 shows the advantages and disadvantages of commonly used flame retardant systems in polypropylene. For this reason, there is a need for new formulations that do not have these shortcomings for products that are applied successfully and easily in flame retardant sectors where regulations that are more stringent exist. Although halogen-free flame retardants have still some technical limitations, they have emerged as the obvious choice for the industry.

Table 2.5 Advantages and drawbacks of flame retardants used in PP (Dufton, 1995)

Type of additive	Advantages	Drawbacks
Halogen compounds	Inexpensive Commonly used Efficient at low loadings with synergists Easy to process	Emissions of smoke and toxic gases Low heat and light stability Corrosive emissions
Metal hydroxides	No acidic gas emissions Effective smoke reduction Non-toxic Low price	Very high loading necessary Decrease mechanical properties
NOR compounds	Halogen-free Good FR at low loading in thin PP films Light stability function	Effectiveness limited to thin section Not able to reach UL94 V2 or V0 alone
Red phosphorus	Effective at low levels Excellent mechanical properties	Safety concern Discoloration of polymer
Intumescent (P,N)	Halogen-free Low smoke occurring Low toxicity	Poor processability High price Volatility problem
Silicon compounds	Environmentally friendly Anti-dripping properties Good processability	Few structures effective in PP
Nanocomposites	Synergistic effect with other FRs Reduce dripping Improved quality of char Reduced peak heat release rate	Poor thermal stability Difficult to incorporate High cost

2.5.1 Halogenated Flame Retardants

When polymers are exposed to sufficient heat, highly reactive H• and OH• radicals are generated that propagate chain branching reactions, leading to decomposition and burning (Lewin & Weil, 2001). Halogenated compounds, most commonly brominated (Arthur F. Grand & Charles A. Willkie, 2000; De Wit, 2002; Georlette, Simons, & Costa, 2000), are often mixed into polymers as additives or introduced by copolymerization (Babrauskas, 2004). The primary halogenated flame retardant

mechanism is chemical reaction in the gas phase. Three types of halogen-containing compounds are known for their flame retardant character; derivatives of compounds with aliphatic, cycloaliphatic and aromatic structures. In each class the type of halogen atom is varied. Especially for textiles most antimonyhalogen systems include antimony III oxide and bromine-containing organic molecules like decabromodiphenyloxide (DBDPO) or hexabromocyclododecane (HBCD). By exposing halogenated flame retardants to high temperatures they decompose and release halogens as free radicals. Especially in the last years halogenated compounds represent one of the most widely employed groups of flame retardants, but they have big disadvantages. One of the major problems is their potential of bioaccumulation and high persistency upon release into the environment (Prinz, 2011).

2.5.2 Phosphorus Flame Retardants

Phosphorous containing compounds are commonly used as flame retardants for thermoplastics, paper, coatings, mastics and textiles which make them particularly interesting for this work. They influence the burning process mainly in the solid phase of materials. Phosphorus-containing flame retardants include elemental red phosphorus, inorganic phosphates, and organophosphates. It is believed these flame retardants are significantly more effective in oxygen-containing polymers (Green, 1992). Additive compounds are mixed into polymer during processing, but do not chemically react with polymer. Reactive compounds are polymerized with a resin during processing to become integrated into the molecular network structure.

A very effective flame retardant for polypropylene (in the absence of halogen or nitrogen FRs) is red phosphorus. It can be used alone at a loading of 2.5 wt.% to give UL94 V2 rate (N Gatti & Costanzi, 2004). In combination with nitrogen (spumific agent) or oxygen (carboniphic agent) containing synergistic additives, the higher UL94 V0 rating is achieved when red phosphorus is used at high loads (20-25 wt.%) (Norberto Gatti, 2002).

Different phosphorous containing flame retardants can be either mixed into plastics and physically bound in the material during curing processes or built in as co-monomers into the polymers during polymerisation. A wide range of different phosphorous based flame retardants are on the market. The most important product lines are given in Figure 2.6.

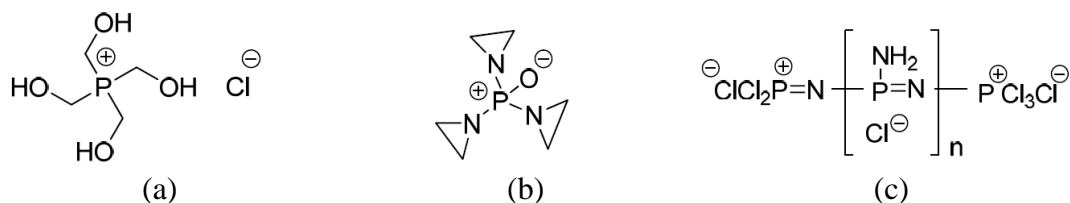


Figure 2.6 Different phosphorous based flame retardants a) tetrakis hydroxy methyl phosphonium chloride (THPC), b) tris-aziridinyl phosphine oxide (APC) and c) phosphor nitrile chloride polymers (PNC) (Rouette, Lindner, & Schwager, 1995)

Phosphorous acts in the vapor phase by a radical mechanism to interrupt the exothermic process and suppress combustion (Lu & Hamerton, 2002). Phosphorous also act as a catalyst in the condensed phase in three steps (Weil & Levchik, 2015):

1. By thermal decomposition phosphorous may form anhydrides of phosphoric or related acids, which in turn act as dehydrating agents, extracting water from pyrolysing PU, promoting char formation.
2. Phosphoric and related acids retard the formation of CO₂ via oxidation (which is exothermic), decreasing the heating process.
3. The acids form a glassy protective layer on the surface, decreasing the diffusion of fuel to the flame front of the burning polymer, which reduces heat and mass transfer between the polymer and atmosphere. Thus the barrier disturbs the oxidation process of carbon at the CO stage, decreasing the exothermic heat of combustion.

2.5.3 Nitrogen Flame Retardants

Nitrogen containing flame retardants are considered as environmentally friendly because they are less toxic, do not add additional elements to those already present in the polymer and are suitable for recycling (Lomakin & Zaikov, 2003; Lu & Hamerton, 2002). The most important type of nitrogen containing flame retardants are melamine and its derivatives. Melamine and its derivatives show their flame retardant effect by acting both in condensed and gas phase (Levchik & Weil, 2000; Lomakin & Zaikov, 2003). In the condensed phase they form a cross-linked structure by transformation of melamine which inhibits combustible gases formation. In the gas phase, they release nitrogen or ammonia gas, which dilute flammable gases and reduce flame. Nitrogen based compounds act in synergy with phosphorous based FRs and most of them are based on melamine compounds (Mercimek, 2010).

2.5.4 Silicon Flame Retardants

Many types of silicon containing compounds have been used as potential flame retardants with polymers. Silicones, silanes, silsesquioxane, silica, and silicates are widely used silicon based materials for their flame retarding and synergistic effect (Arthur F. Grand & Charles A. Willkie, 2000; Cinausero et al., 2008; Zhang & Horrocks, 2003). The silicone compounds in polypropylene can play a role both in the gas (capture of radicals) and in the condensed phase (char formation) (Walid, 2009). They are considered to have better dielectric and gloss properties, to be more environmentally friendly, anti-dripping properties, improved moldability, impact resistance and processability, non-corrosive smoke evolution and thermal stability in comparison with halogen FRs. In addition, they were recently considered as alternatives to phosphorus-containing flame retardants (Walid, 2009).

Due to this high effectiveness and the usually low amount of loading, nanoclays are effective flame retardant additives where reduction of HRR is desired depending to the type of the application where the polymeric composite will be used. Polymer-layered silicate (PLS) nanocomposites, as a new class of filled polymers with

ultrafine phase dimensions, offer the potential to combine the advantages of both organic and inorganic materials, such as light-weight, flexibility, high strength and heat stability, which are difficult to be obtained separately from the individual components. Organic silicon based flame retardants have the advantage of the possibility to attach different functional groups (phosphorous, nitrogen or boron based) to the structure in order to improve the flame retardant efficiency and also compatibility with the polymer matrix. Furthermore, because of the nano-phase distribution, interaction as well as the synergism between polymer and the layered silicate, PLS nanocomposites exhibit enhanced flame retardation, barrier properties and ablation resistance, which are not observed in either of their components as conventional composites (Morgan & Wilkie, 2014).

2.5.5 Boron Flame Retardants

Boron based flame retardants have very broad applications. They are multifunctional fire retardants and can function as flame retardants, smoke suppressants, afterglow suppressants, anti-tracking/anti-arcing agents, etc. They function as flame retardants in condensed phase. Boron based flame retardant is mainly refers to zinc borate, which has the characteristics of low toxicity, smoke abatement, high thermal stability and good synergistic effect with other flame retardants (Cong, Yu, Wu, & Luo, 2008; Tan, Lan, Ji, & Shang, 2009).

Boron based flame retardants act mainly in the condensed phase by redirecting the decomposition process in favor of carbon formation rather than CO or CO₂ formation. Boron compounds promote char formation which forms a protective barrier to prevent oxidation of carbon in the burning process. The char formation relates to the thermal action of boric acid with alcohol moieties. They reported a significant improvement of flame retardancy through a mechanism involving the formation of a protective barrier of boron oxide, which prevents the degradation of the polymer (Çelebi, Aras, Gündüz, & Akhmedov, 2003; Sacristán et al., 2010).

2.5.6 Antimony Compounds

Antimony trioxide is not a flame retardant alone, but it is used as a synergist. It is utilized in plastics, rubbers, textiles, paper and paints, typically 2-10% by weight. Antimony oxides and antimonates must be converted to volatile species. This is usually accomplished by release of halogen acids at fire temperatures. The halogen acids react with the antimony containing materials to form antimony trihalide and/or antimony halide oxide. These materials act both in the substrate (condensed phase) and in the flame to suppress flame propagation. In the condensed phase, they promote char formation, which acts as a physical barrier to flame and inhibits the volatilization of flammable materials.

A significant increase in fire retardancy effectiveness is observed when halogenated flame retardants are used in combination with antimony trioxide (Sb_2O_3). It is observed that it both assist and eases delivery of halogen atom in the gas phase and extends the time which halogens exist in the flame zone, in turn more radicals can be scavenged (Aseeva & Zaikov, 1986).

2.5.7 Inorganic Hydroxide Flame Retardants

Inorganic hydroxides are a very important class of flame retardants due to their relatively low cost, easy of handling and low toxicity (Bolger, 1996). Aluminium oxide trihydrate is used in the largest quantities by far as an inorganic flame retardant for polymers. It is normally introduced into polymers in large quantities (>50% by weight) in order to attain a significant flame-retardant effect. This addition reduces the amount of combustible materials available for decomposition. During decomposition, this compound acts as a heat sink and thus delays the polymer from reaching its decomposition temperature (Peter R Hornsby, 1994).

2.5.8 Synergism

Flame retardant additives are generally used to delimitate the risk of fire and its spread. In order to achieve high fire performance levels, it is required to develop a flame retardant system depending a combination of different flame retardant agents. Synergism is used to improve the performance of two or more additive mixtures and to optimize flame retardant formulations. Synergism is achieved with the expected performance of the mixture (Yen, Wang, & Guo, 2012).

The synergistic effect can be obtained by a combination of flame retarding mechanisms like char formation by a phosphorated flame retardant combined with a gas phase action by a halogenated flame retardant or a combination of flame retardant agents reinforcing the same mechanism. The action in the polymer of nanoparticles alone proves to be insufficient for ensuring adequate fire resistance to meet the required standards. However, their association with other flame retardant systems such as phosphorated compounds could potentially be a very interesting approach (Laachachi, Leroy, Cochez, Ferriol, & Cuesta, 2005).

CHAPTER THREE

EXPERIMENTAL PROCEDURE

3.1 Purpose

The objective of the thesis is to produce PP nanocomposites reinforced with halogen-free flame retardants, antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite, using a twin-screw extruder followed by injection molding technique. It was aimed to produce flame retardant nanocomposites by reinforcing different halogen-free nanoparticles with various compositions and to investigate the usability of the nanocomposites in industrial applications. The battery components using in automotive industry, which is a major requirement for industrial applications, has been selected to improve the flame retardancy properties of polymer based materials. Within this scope, halogen-free antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite nanoparticles were reinforced into PP matrix. The influence of different additive type/content was investigated for PP nanocomposites.

3.2 Materials

Polypropylene (PP) pellets were used as a polymer matrix to produce antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced nanocomposites. PP with a melt flow index (MFI, 230 °C, ASTM D 1238) of 7–8 g/10 min and melting point of 168 °C was supplied by Petkim Petrochemical Co. (Izmir, Turkey). The physical properties of PP are given in Table 3.1. Physical densities of huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$), hydromagnesite ($4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), antimony trioxide (Sb_2O_3), bentonite ($(\text{Na}, \text{Ca})(\text{Al}, \text{Mg})_6(\text{Si}_4\text{O}_{10})_3(\text{OH})_6 \cdot n\text{H}_2\text{O}$) and zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) minerals are 2.70, 2.24, 5.2, 1.65 and 3.64 g/cm³, respectively (Al-Maamori, Al-Mosawi, & Hashim, 2011; Azizi H., Barzin J., 2007; Baştürk, Madakbaş, Karadoğan, & Vezir Kahraman, 2016; Villar & Lloret, 2004). All additive materials supplied by İnci GS Yuasa Co. (Manisa, Turkey).

Table 3.1 The physical properties of PP

Property	Test Method	Unit	Value
Yield strength	ASTM D638	MPa	19.44
Tensile Strength	ASTM D638	MPa	25.25
Elastic modulus	ASTM D638	GPa	0.88
Melting point	ASTM D3417	°C	168
Hardness	ASTM D2240	Shore D	68.1
Melt Flow Index (MFI)	ASTM D1238	g/10 min	7.15

3.3 Nano Grinding Process and Particle Size Distribution

The antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite powders were separately milled to obtain nano-scale particles using a high energy ball milling machine (Fritsch, Pulverisette 7) at the rate of 700 rpm at room temperature for 20 min in air. In this process, a powder mixture placed in the ball mill was subjected to high-energy collision from the balls. This method could successfully produce fine and uniform dispersions of oxides. To understand the effect of grinding process, a particle size analysis was carried out using a particle size measurement machine (Malvern, Zetasizer Nano ZS).

3.4 Production of Composites

In the production of polymeric composite materials, extrusion and injection molding techniques were used for flame retardant applications. A co-rotating twin screw extruder (Thermo-Fisher, Eurolab 16) with screw diameter of 16 mm and L/D ratio of 40 was utilized for production of the composites by adjusting between 50-95 wt% of PP (pellets form) and 5-50 wt% of halogen-free inorganic nanoparticles. The screw speed was set at 300 rpm and the barrel temperatures of the zones were 160, 170, 180, 190, 200 and 180 °C, from the feeding zone to the die zone.

Table 3.2 Designation and composition of PP and PP composites

Sample code	PP (wt. %)	Antimony trioxide (wt. %)	Bentonite (wt. %)	Zinc borate (wt. %)	Huntite/ hydromagnesite (wt. %)
Pure PP	100	-	-	-	-
PP/5A	95	5	-	-	-
PP/10A	90	10	-	-	-
PP/15A	85	15	-	-	-
PP/20A	80	20	-	-	-
PP/25A	75	25	-	-	-
PP/30A	70	30	-	-	-
PP/5B	95	-	5	-	-
PP/10B	90	-	10	-	-
PP/15B	85	-	15	-	-
PP/20B	80	-	20	-	-
PP/25B	75	-	25	-	-
PP/30B	70	-	30	-	-
PP/5Z	95	-	-	5	-
PP/10Z	90	-	-	10	-
PP/15Z	85	-	-	15	-
PP/20Z	80	-	-	20	-
PP/25Z	75	-	-	25	-
PP/30Z	70	-	-	30	-
PP/5H	95	-	-	-	5
PP/10H	90	-	-	-	10
PP/15H	85	-	-	-	15
PP/20H	80	-	-	-	20
PP/25H	75	-	-	-	25
PP/30H	70	-	-	-	30
PP/40H	60	-	-	-	40
PP/50H	50	-	-	-	50
PP/40H-10A	50	10	-	-	40
PP/40H-10B	50	-	10	-	40
PP/40H-10Z	50	-	-	10	40
PP/45H-5A	50	5	-	-	45
PP/45H-5B	50	-	5	-	45
PP/45H-5Z	50	-	-	5	45
40H-7Z-3A	50	3	-	7	40
40H-7Z-3B	50	-	3	7	40
40H-5Z-3B-2A	50	2	3	5	40

An injection molding machine (Permak Co.) equipped with a self-designed mold was used to prepare specimens. Injection process was carried out at a melting temperature of 185 °C, a molding temperature of 25 °C and an injection pressure of 960 kg/cm². The twin-screw extruder and the injection molding machine are shown in

Figure 3.1 and 3.2, respectively. Sample code and composition of PP and PP composites were listed in Table 3.2.



Figure 3.1 A co-rotating twin screw extruder



Figure 3.2 An injection molding machine

3.5 Characterization of PP, Nanoadditives and PP Composites

3.5.1 X-Ray Diffractometer (XRD)

XRD is an effective technique used to identify the crystalline phases present in materials and to measure the structural properties of these phases such as grain size, strain state, epitaxial, phase composition, orientation and defect structure. The examination is non-destructive and non-contacted for XRD analysis. The ordered

atomic array in the crystalline material forms the 3D diffraction pattern for the waves where the distance between the atoms is the wavelength. As the waves enter a crystal, they are scattered by atoms in all directions. In some directions, these waves can interfere in a destructive way. In other directions, constructive interference will occur at the peak of X-ray intensity. The resulting diffraction pattern is a map of the reciprocal crystal lattice and can be used to determine the crystal structure. Bragg's law forms the basis of crystal diffraction:

$$n\lambda = 2d \sin\theta \quad (3.1)$$

where n is an integer known as the diffraction order, λ is the X-ray wavelength, the interval between two consecutive scattering planes and θ is the angle between the incident (and diffracted) X-ray beam and the atomic planes (Ahmed & Jackson, 2014). The diffraction of X-rays by planes of atoms is shown in Figure 3.7.

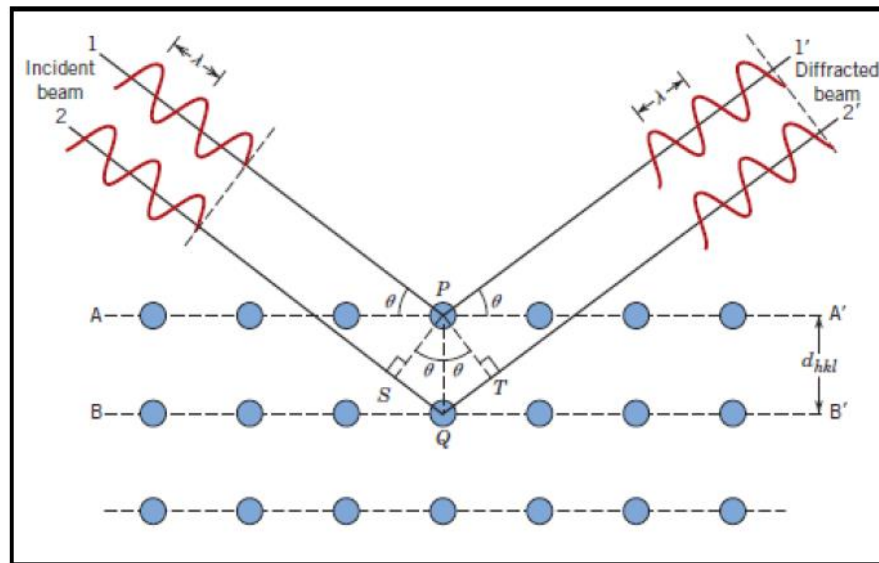


Figure 3.3 Diffraction of x-rays by planes of atoms (A–A` and B–B`) (Callister Jr & Rethwisch, 2012)

Bragg law is necessary, but not enough for diffraction by real crystals. It specifies when diffraction will occur for unit cells with only atoms positioned at cell corners. However, the interstitial atoms behave like additional scatter centers that can produce out-of-phase scatter at certain Bragg angles. The clear conclusion is the absence of some diffracted beams that, according to Bragg's law, should be present.

It is extensively used to investigate the structural properties of nanoadditives and flame retardant PP composites. Phase identification and crystal structures of all specimens were performed by means of a Thermo Scientific ARL K-alpha X-ray diffractometer. This instrument works with voltage and current settings of 45 kV and 44 mA, respectively, and uses Cu-K α X-radiation (1.5405 Å). For qualitative analysis, XRD diagrams were recorded in the interval $5^{\circ} \leq 2\theta \leq 80^{\circ}$ at a speed of 2 ($^{\circ}$)/min.

3.5.2 X-Ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the empirical formula, elemental composition, electronic state and chemical state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed (Figure 3.4). XPS detects all elements with an atomic number (Z) of three (lithium) and over. It cannot detect hydrogen and helium, because their atomic diameters are too small, reducing the catch possibility to almost zero. It is used routinely in the analysis of all solid materials (Crist & Crist, 2004).

Elemental composition and surface chemistry of all samples was analyzed by XPS (Thermo-Scientific) with monochromatic Al-K α (1486.7 eV) X-ray source and a beam size of 400 nm diameter. The device was calibrated according to gold; 4f $_{7/2}$. The pressure was kept below 5×10^{-10} mbar during spectral data acquisition. The XPS data of survey scan were scanned from -10 to 1350 eV applying a pass energy of 150 eV and a resolution of 1 eV. 20 scans from a single point were recorded.

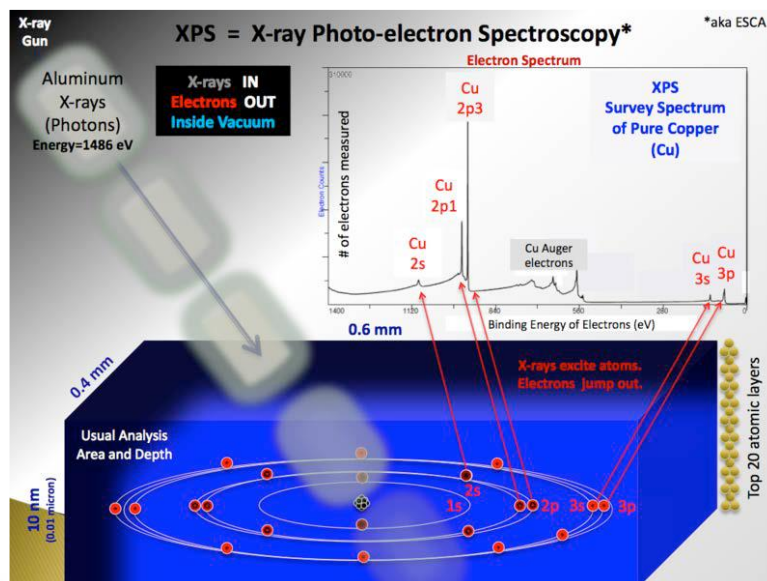


Figure 3.4 Schematic illustration of XPS physics (Crist & Crist, 2004)

3.5.3 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is a great tool to identify types of chemical bonds in a molecule by generating an infrared absorption spectrum that is like a molecular "fingerprint". Each material consists of a unique combination of atoms; hence, two different compounds definitely do not produce the exact same infrared spectrum. For this reason, infrared spectroscopy can lead to qualitative analysis of all kinds of different materials. The chemical bonds in a molecule can be determined by interpreting the infrared absorption spectrum. In principle, molecular bonds vibrate at various frequencies depending on the elements and the type of bonds. For any given bond, there are a few specific frequencies that can vibrate. As for that quantum mechanics, these frequencies correspond to the ground state (lowest frequency) and several excited states (higher frequencies). One way to increase the frequency of a molecular vibration is to excite the light energy of the bond. For any given transition between two states the light energy (determined by the wavelength) must exactly equal the difference in the energy between the two states. The energy corresponding to these transitions between molecular vibration states is usually below 10 kilocalories/mole which corresponds to the infrared range of the electromagnetic spectrum. The results are generally given as a function transmittance or absorbance versus the wavelength. The conversion

between transmittance to absorbance data is: $A = \log (1/T)$ where A is absorbance and T is transmittance.

The size of the peaks in the spectrum is a direct indicator of the amount of material available as well as the qualitative analysis. Infrared is also an excellent tool for quantitative analysis using suitable software algorithms. The attenuated total reflectance (ATR) technique has revolutionized for powder, bulk, thin film and liquid sample analyses in recent years since it combats the most challenging aspects of infrared analyses namely sample preparation and spectral reproducibility. An ATR accessory operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample as indicated in Figure 3.5. The infrared spectra of the samples were recorded with a Thermo Scientific Nicolet iS 10 instrument equipped with ATR apparatus in the spectra range between 4000 and 650 cm^{-1} with a resolution of 4 cm^{-1} .

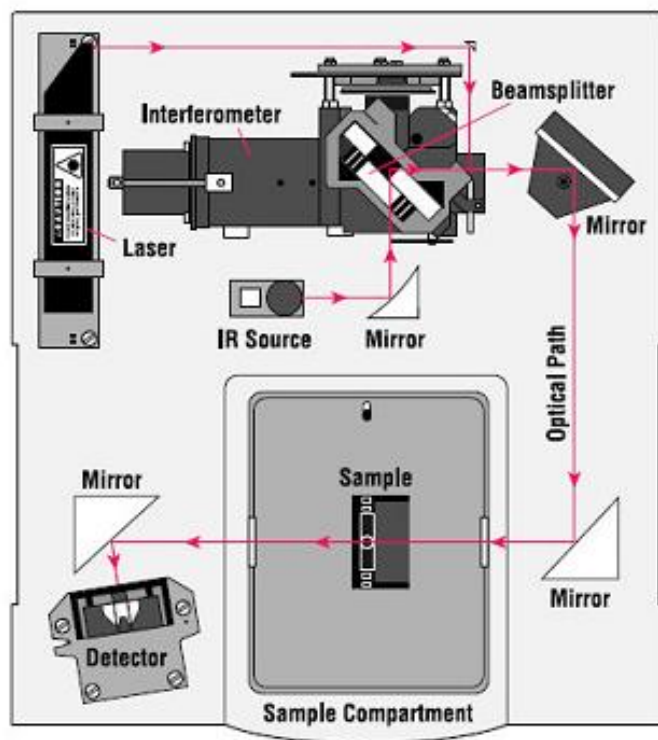


Figure 3.5 Schematic diagram of a FTIR spectrometer (Arellano et al., 2010)

3.5.4 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) examining the surface state of solid materials is the most commonly used imaging method. In the SEM device, a high-energy electron beam is scanned on the sample surface. Different radiation occurs because of the interaction between the sample and the electron beam. This device usually uses two types of radiation signals for imaging. These electrons are back-scattered (primary electrons) and removed from the material (secondary electrons). The back-scattered electrons give information about the composition and topography of the sample surface. Secondary electrons are used to show details about the surface morphology of the material. Figure 3.6 shows the schematic operating principle of the SEM.

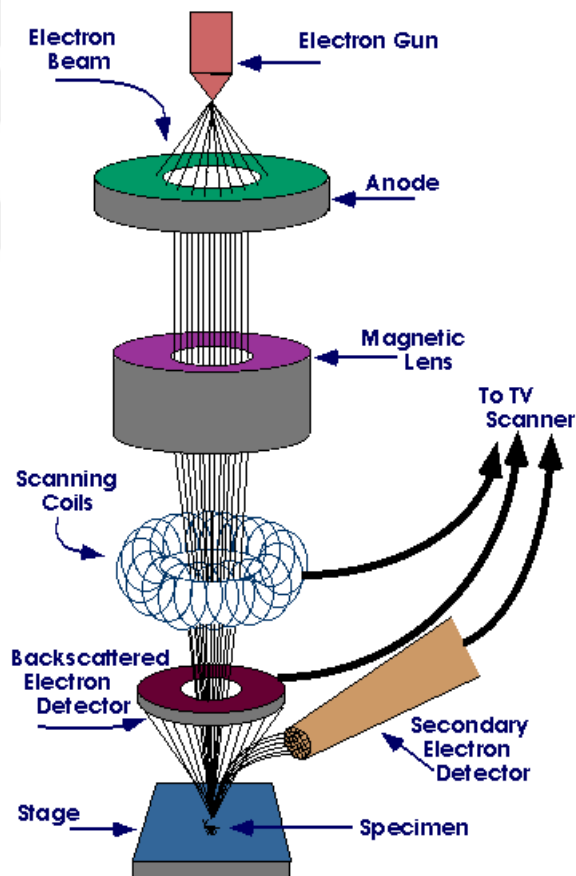


Figure 3.6 Schematic illustration of SEM (Vandaele, 2011)

The surface qualities, microstructural analysis and morphologies of nanoadditives and PP composites were examined by using SEM (COXEM E30 plus and JEOL, JSM 6060). Accelerating voltage of 10 kV was used for the SEM imaging.

3.5.5 Mechanical Tests

Tensile tests were conducted at room temperature on a Shimadzu model AG50kNG universal testing machine. The crosshead speed was 5 mm/min. During testing, stress-strain curves were recorded by a recorder. The yield stress, elastic modulus, ultimate tensile stress and elongation were determined from the tensile curves.

3.5.6 Differential Thermal Analysis – Thermogravimetry (DTA-TG)

Thermal methods often measure the dynamic relationship between certain properties of the material (mass and heat absorption or diffusion) that occur at varying temperatures. Therefore, differential thermal analysis (DTA) and thermogravimetry (TG) are an important method for determining the thermal properties of materials. In DTA the heat absorbed or emitted by a system is detected by measuring the temperature difference ΔT between the sample and an inert reference material (generally alumina powder), as the temperature of both is raised at a constant rate. The TG analysis gives the result of changing the weight of the material with the increase in temperature. Many series of thermal analysis techniques can be combined with other non-thermal technique for valuable multiple-parameter information as in our DTA/TG system.

The thermal behavior of PP and PP composites were performed to determine decomposition, phase formation, combustion temperatures, weight loss and derivative weight properties at a heating rate of 10 °C/min in the temperature range of 25-600 °C in air atmosphere by DTA/TG machine (Perkin Elmer, STA 6000).

3.5.7 Flame Retardant Test

The UL 94 test is commonly used to determine the ignition resistance of materials used in the electrical industry. The test results are given in flammability ratings V-0, V-1, or V-2. The V-0 rating is the best flammability rating, which a material can receive. The criteria for which the materials are rated are based on the time it takes for the burning material to extinguish after the flame source is removed from a vertical specimen, and also if drips fall from the burning specimen. The specifications for the size of the test specimen is either, 12.7 x 1.27 x 0.16 cm or 12.7 x 1.27 x 0.32 cm. Either one of these two samples is mounted into a clamp vertically so that the lower end is 30.5 cm above a 0.6 cm thick layer of a specified surgical cotton. The test specimen is exposed from a flame source from below for duration often seconds. The flame source is then removed. If the specimen extinguishes, the specimen is exposed to the flame for an additional ten seconds. Table 3.3 shown below outlines the criteria for each UL 94 rating. Schematic illustration of UL 94 vertical test is shown in Figure 3.7. These tests were conducted on a needle flame testing machine (Guangzhou Zhilitong Co., ZLT-ZY2).

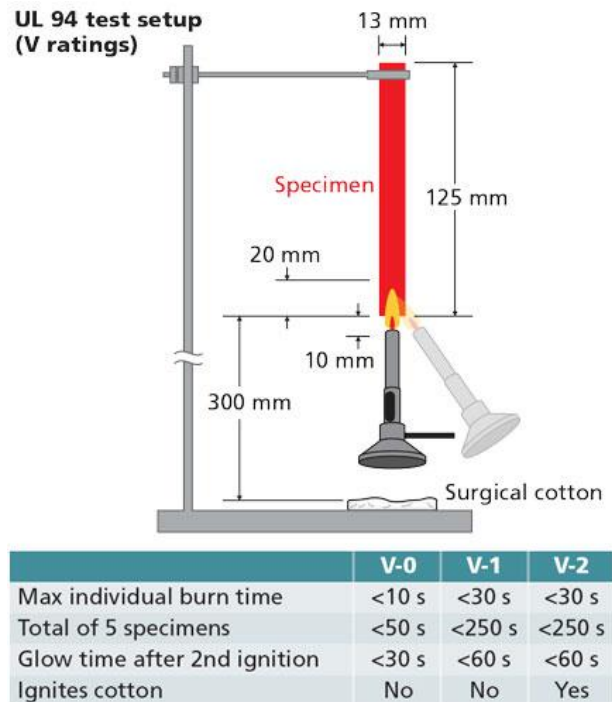


Figure 3.7 Schematic illustration of UL 94 vertical test (Marshall, 2015)

Table 3.3 Classification of UL 94 test

Rating	Criteria
Class 94 V-0	Having a series of five specimens with ten ignitions, the sum of the after flame times should not exceed 50 sec and no specimen should burn longer than 10 seconds. During ignition and combustion the cotton layer should not be set on fire by dripping material.
Class 94 V-1	Having a series of five specimens, which are ignited twice, the sum of after flame times should not exceed 250 seconds, no specimen should burn longer than 30 second, the dripping material should not ignite the cotton layer.
Class 94 V-2	Same as V-1, except that the cotton layer is ignited by burning drops.

3.5.8 Limiting Oxygen Index Test (LOI)

This test is probably the most accurate of the lab tests. In the LOI test a sample is suspended vertically so inside a closed chamber (usually a glass or clear plastic enclosure). The chamber is equipped with oxygen and nitrogen gas inlets so that the atmosphere in the chamber that it can be controlled. The sample is ignited from the bottom and the atmosphere is adjusted to determine the minimum amount of oxygen to just sustain burning. This minimum oxygen content, expressed as a percentage of the oxygen/nitrogen atmosphere, is called the oxygen index. Higher numbers are associated with decreased flammability. These tests carried out by LOI test equipment (Okur Machine Co.).

LOI value is calculated according to the equation given below:

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} \times 100 \quad (3.2)$$

3.5.9 Industrial Applications Tests

In order to test the mechanical strength, impact tests are performed on the manufactured boxes. The tests are conducted on the produced the boxes at room temperature and at -20 °C for 6 hours. The tests were carried out on a battery boxes by leaving a ball weight of 1 kg at 25 cm height for samples waiting at room temperature.

During the all performance tests, accumulator should be placed in a water bath at a temperature of $25\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$, except for the rapid discharge test at a temperature of $-18\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. The surface of the battery where the connectors are located must be at least 15 mm above the water level and at most 25 mm above the water level. If several batteries are in the same water bath, the distances between each other and the wall of the box must be at least 25 mm. The exception of batteries with low water loss, the distilled water should be added to the batteries in order to prevent the electrolyte level during the tests. The batteries are connected to a device comprising 180 cycles. They are discharged in 5 A current for 1 hour. After that, they are recharged with a constant voltage of $14.80\text{ V} \pm 0.05\text{ V}$ for 2 hours 55 min and with a current value between 2.5 A and 10 A for 5 min. If the battery voltage falls below 10.50 V during discharging before the completion of 180 cycles, the test shall be terminated. When the cycles are over, the accumulator should be placed in an air circulating cooling chamber for 20 hours or at a temperature of $-18\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ until the temperature of one of the cells in the middle reaches $-18\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$. The accumulator should be discharged with a current of 0.6 A after the cooling period. After 30 s discharging process, the voltage between the ends of the battery should be measured. The measured value should not be less than 7.20 V. Then, the discharging process is terminated.

Corrosion tests is carried out on fully charged batteries. The batteries are placed in a water bath at a temperature of $60\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. The surface of the battery where the connectors are located must be at least 15 mm above the water level and at most 25 mm above the water level. If several batteries are in the same water bath, the distances between each other and the wall of the box must be at least 25 mm. The battery kept at $60\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$ is charged for 13 days at $14\text{ V} \pm 0.10$ constant voltage. The battery is also left in an open circuit state for a period of 13 days at a temperature of $60\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$. No connection clamps or cables are connected to the connection terminals.

Recycling process of non-used polymeric materials is important nowadays. Reducing the need for raw materials will be very advantageous for some reasons such as reduction of environmental pollution and energy saving to recycle polymeric materials. The produced battery boxes reinforced with flame retardant additive

materials are recycled using the engineering losses and production waste that occur during production. The box materials brought to the small dimensions in the breakers for recycling process. However, the use of these materials, which are called as crushing in production, in large quantities affects the quality of the product. For this reason, in the box production for battery, the producers use the recycling materials in quantities determined according to the production conditions.



CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Measurement of Particle Size Distribution

The investigated additive materials, antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite, were obtained successfully following the nano grinding process in the range of nano scale. The results of particle size distribution are shown in Figure 4.1. As calculated from Figure 4.1, the mean particle size of antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite powders are 141, 380, 426 and 121 nm, respectively, which are reasonable results for flame retardant reinforcements in composite materials. These results proved that the nano grinding process was performed accurately.

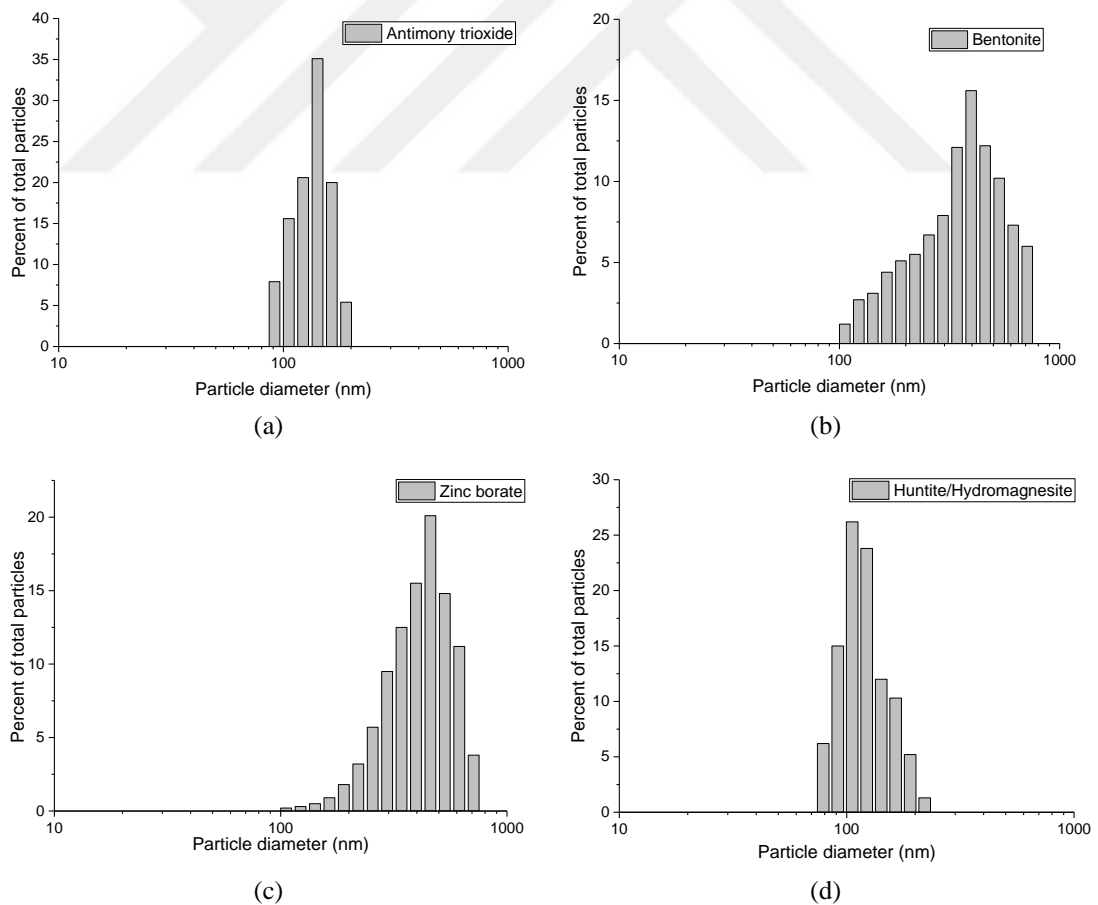


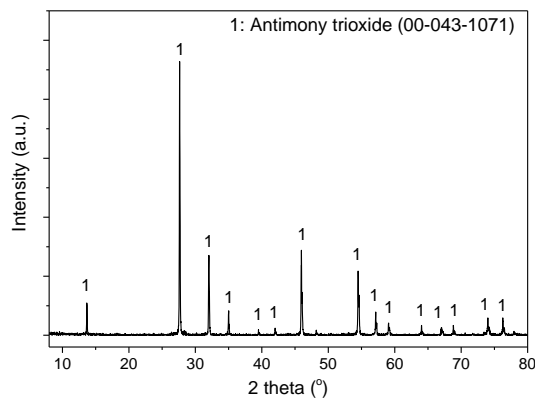
Figure 4.1 Particle size distribution of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite

4.2 Phase Analysis

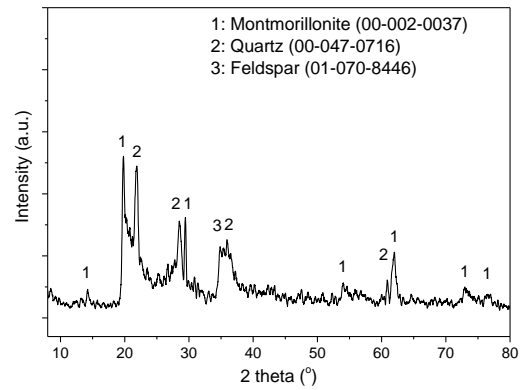
Figure 4.2 shows the XRD patterns of the flame retardant additives, antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite, respectively. The XRD pattern of antimony trioxide confirm the polycrystalline structure of the grinded nanoparticles. It is seen that the strong diffraction peaks at $2\theta = 27.7, 32.1, 35.1, 46.3, 54.9$ and 59.5 corresponds to (222), (400), (420), (440), (622) and (640) planes, respectively. The XRD pattern of bentonite is given in Figure 4.2b. This indicates that the bentonite primarily composed of montmorillonite known to be a kind of clay that contains water of hydration. The other peaks are impurities of sodium bentonite corresponding to quartz and feldspar. The XRD pattern of zinc borate is shown in Figure 4.2c. The characteristic peaks of hydrated zinc borate are between $15-70^\circ$ and its main strong peak is at $2\theta = 36.3^\circ$. The XRD result of the huntite/hydromagnesite additive shows that the basic minerals are hydromagnesite ($\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) and huntite ($\text{Mg}_3\text{Ca}(\text{CO}_3)_4$) in Figure 4.2d. The JCPDS numbers of all phases are shown inset of each XRD result.

XRD analysis was also performed to compare the crystallinity and to determine the phases of the pure polypropylene and produced composites. Figure 4.3 depicts the XRD patterns of the pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites. The XRD pattern of PP showed the typical α -form PP crystals, which exhibited four strong peaks at $14.12^\circ, 16.91^\circ, 18.61^\circ$ and 21.38° (Assouline et al., 2001). Looking at the PP composites, the main characteristic peaks of all additive materials are clearly seen in Figure 4.3. The details of the strong diffraction peaks of the flame retardant additives, antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite, were given above.

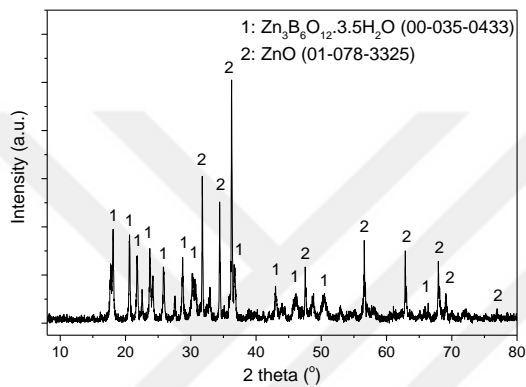
It can be seen from Figure 4.4, each of the multi-additive reinforced composites preserved its own phase structures. The obtained XRD patterns proved that the composites reinforced with antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite individually or mixed have been successfully produced.



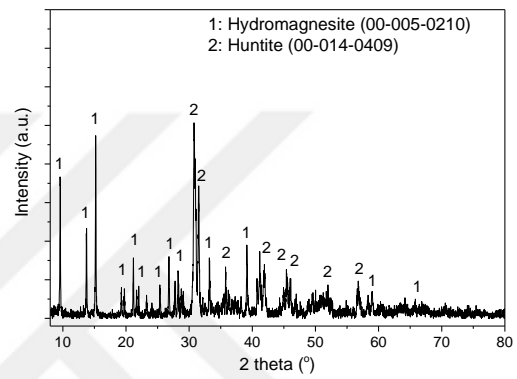
(a)



(b)

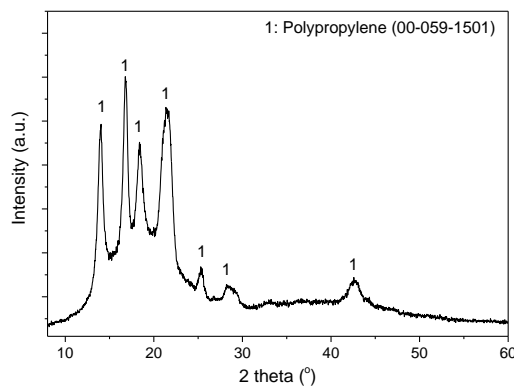


(c)

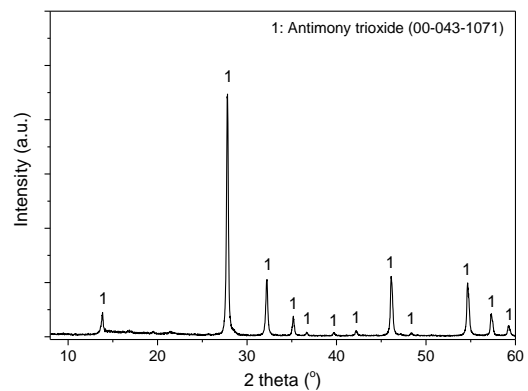


(d)

Figure 4.2 XRD patterns of the additives a) antimony trioxide, b) bentonite, c) zinc borate and d) huntite/hydromagnesite

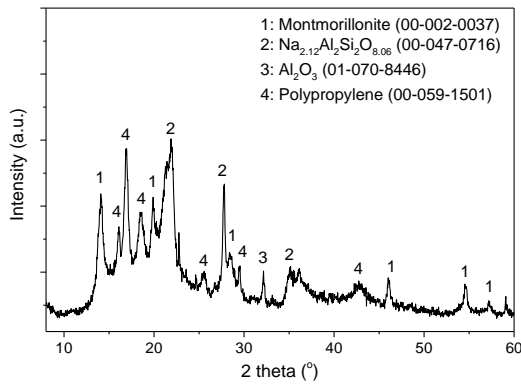


(a)

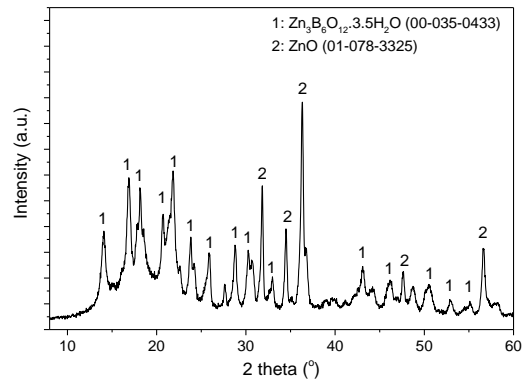


(b)

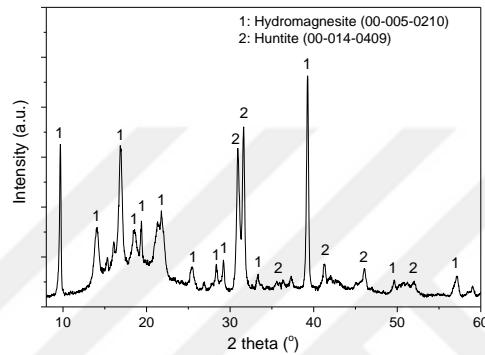
Figure 4.3 XRD patterns of a) pure PP and PP composites reinforced with b) antimony trioxide, c) bentonite, d) zinc borate and e) huntite/hydromagnesite



(c)

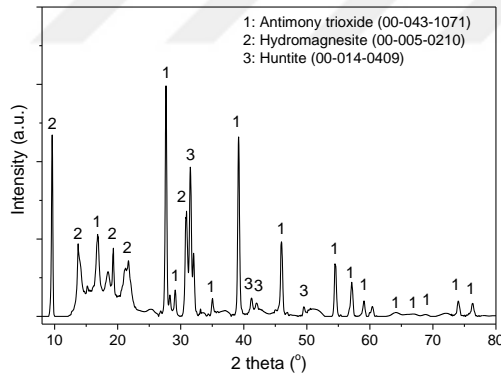


(d)

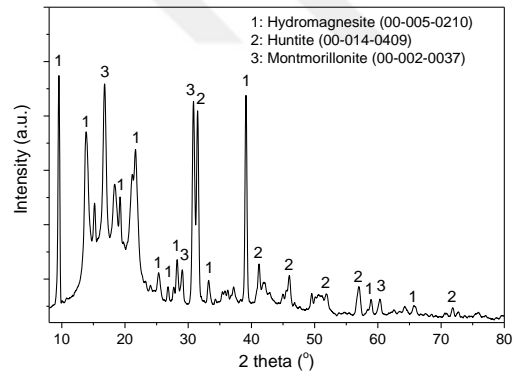


(e)

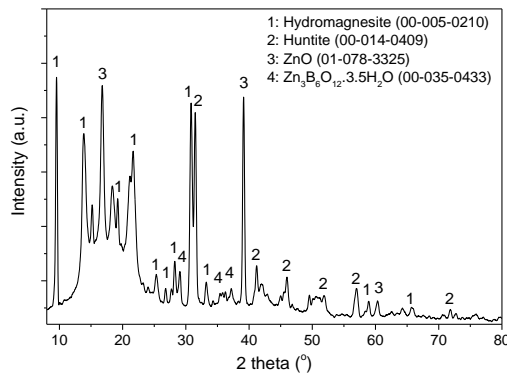
Figure 4.3 Continues



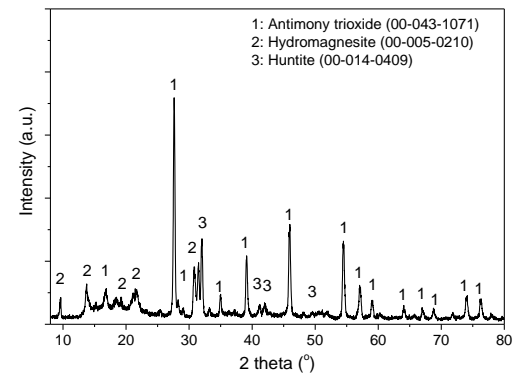
PP/40H-10A



PP/40H-10B



PP/40H-10Z



PP/45H-5A

Figure 4.4 XRD patterns of the multi-additive reinforced composites

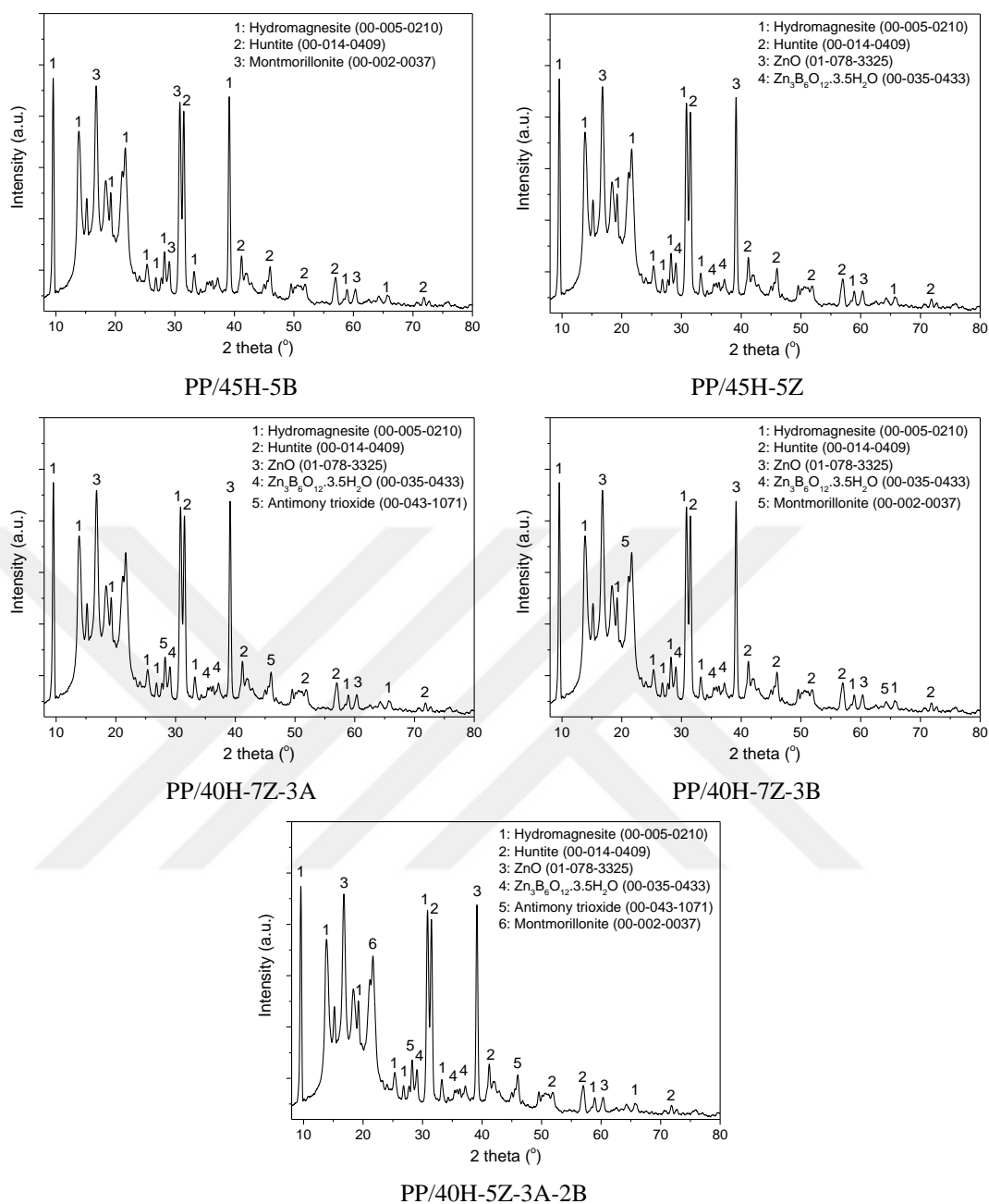


Figure 4.4 Continues

4.3 Elemental Analysis of PP Composites

XPS analysis were performed to determine the percentages of the elements of antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites at the surface. Figure 4.5 depicts the results of the survey analysis of the pure PP and PP composites. This shows the binding energies of C1s and O1s are around 285 and 533 eV, respectively. Figure 4.5a shows the only C and O elements belonging to the

PP. From the XPS analysis of antimony trioxide reinforce PP composite, only the presence of Sb and O elements were determined. All of the elements (Al, Mg, Si, Mg, Ca, O) in the bentonite structure are seen in Figure 4.5c. The elements of hydrated zinc borate mineral, ZnO and $Zn_3B_6O_{12} \cdot 3.5H_2O$, are seen in XPS result of zinc borate reinforced PP composite. According to the XPS analysis results for huntite/hydromagnesite reinforced PP composite, Mg, C, O and Ca elements were detected. Following the composites were formed, the percentages of the elements at the surface were determined and it was observed that there were no impurity in the composites.

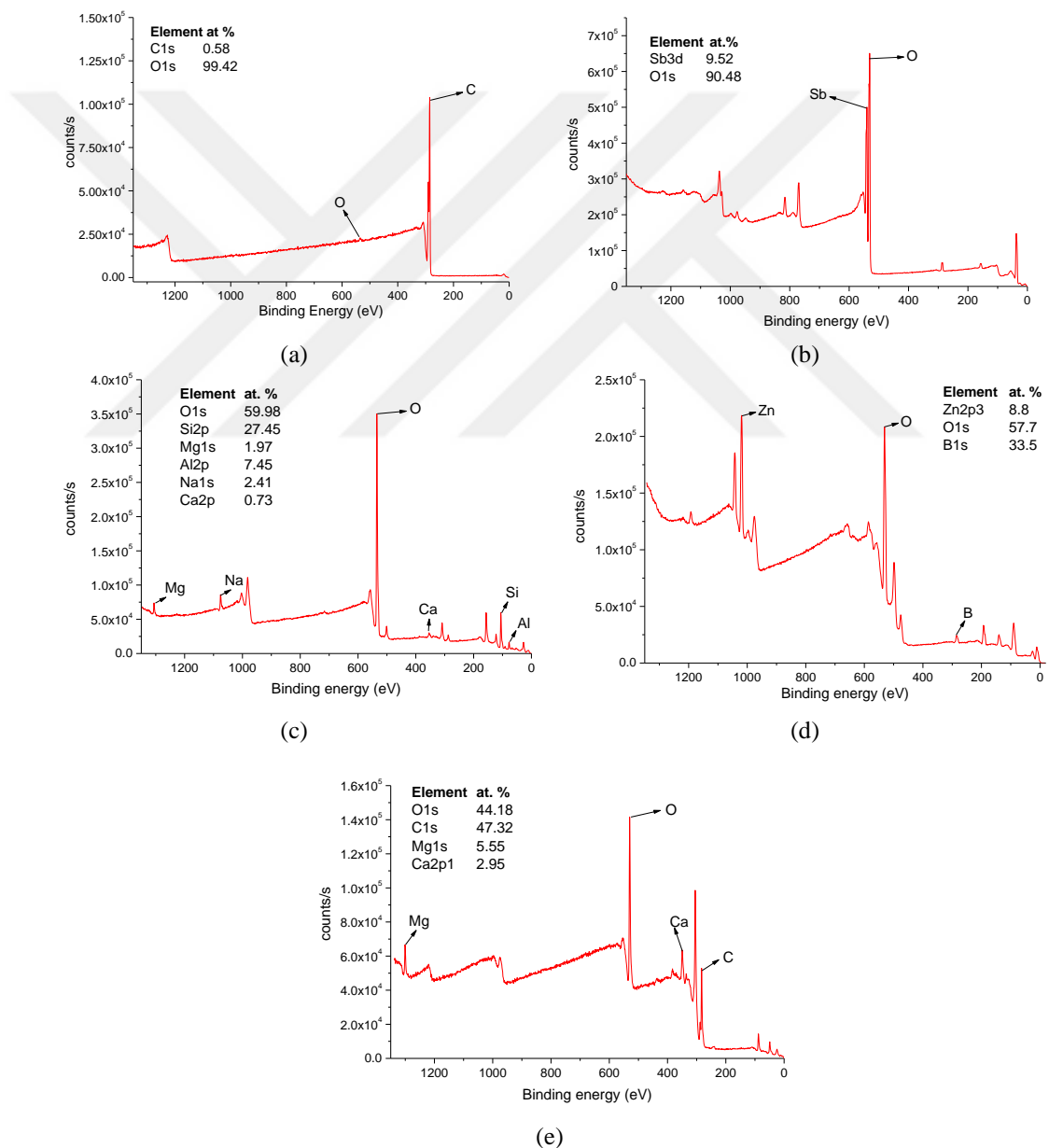


Figure 4.5 XPS survey spectra of a) pure PP and b) antimony trioxide, c) bentonite, d) zinc borate and e) huntite/hydromagnesite reinforced PP composites

4.4 FTIR Analysis

Figure 4.6 demonstrates the FTIR analysis of pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites. The main difference in the spectra was determined in the IR band at 1445 cm^{-1} attributed to the O–H stretching mode or $=\text{CH}_3-$ structure (X. Chen et al., 2009).

The bands at about 2965 , 2924 , 2865 , 2834 cm^{-1} were ascribed to the asymmetric and symmetric vibration of C–H in CH_2 and CH_3 (Zhou, Song, Wang, Hu, & Xing, 2008). Furthermore, the peaks at $650\text{--}750\text{ cm}^{-1}$ can be assigned to oxygen stretching vibration in oxides. FTIR analysis of the antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites show O–H stretching mode or $=\text{CH}_3-$ structure, the asymmetric and symmetric vibration of C–H in CH_2 and CH_3 and oxygen stretching vibration in oxides.

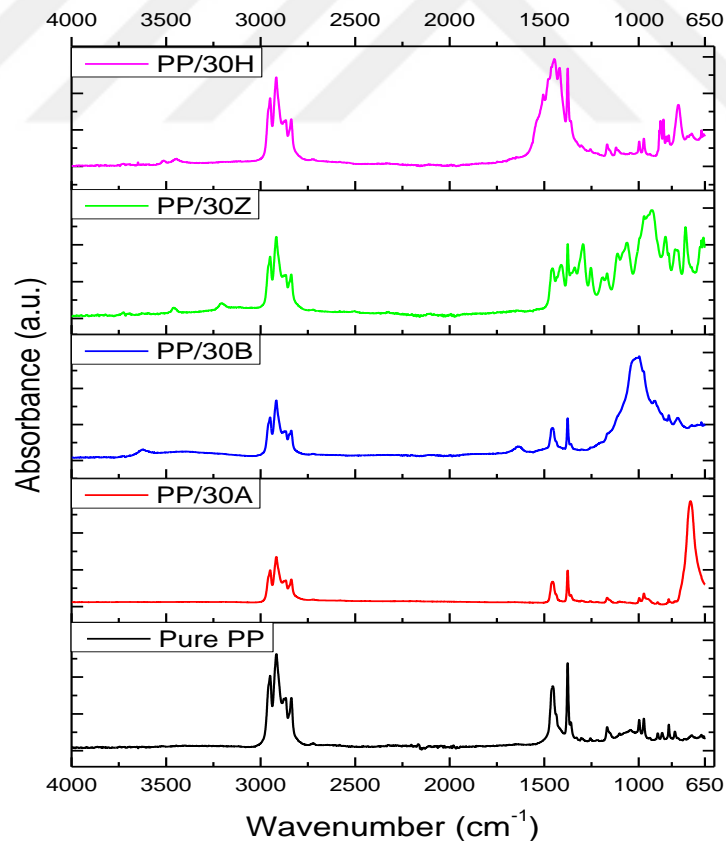


Figure 4.6 FTIR analysis of the pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites

4.5 Microstructure and Morphology Analysis

Figure 4.7 shows the SEM images of the reinforcing materials. The SEM images also demonstrated the degree of agglomeration of the all nanoparticles. As expected, the particle size of the additives is in accordance with the particle size distribution according to SEM images given inset of the Figure 4.7. The morphology of the PP composites was also investigated using SEM magnified by 20000 times. Figure 4.8 represents the SEM photographs of the PP based nanocomposites. It is generally believed that the properties of polymer nanocomposites depend upon the dispersion or distribution of the reinforcing materials in the polymer matrix (Ciecierska et al., 2016).

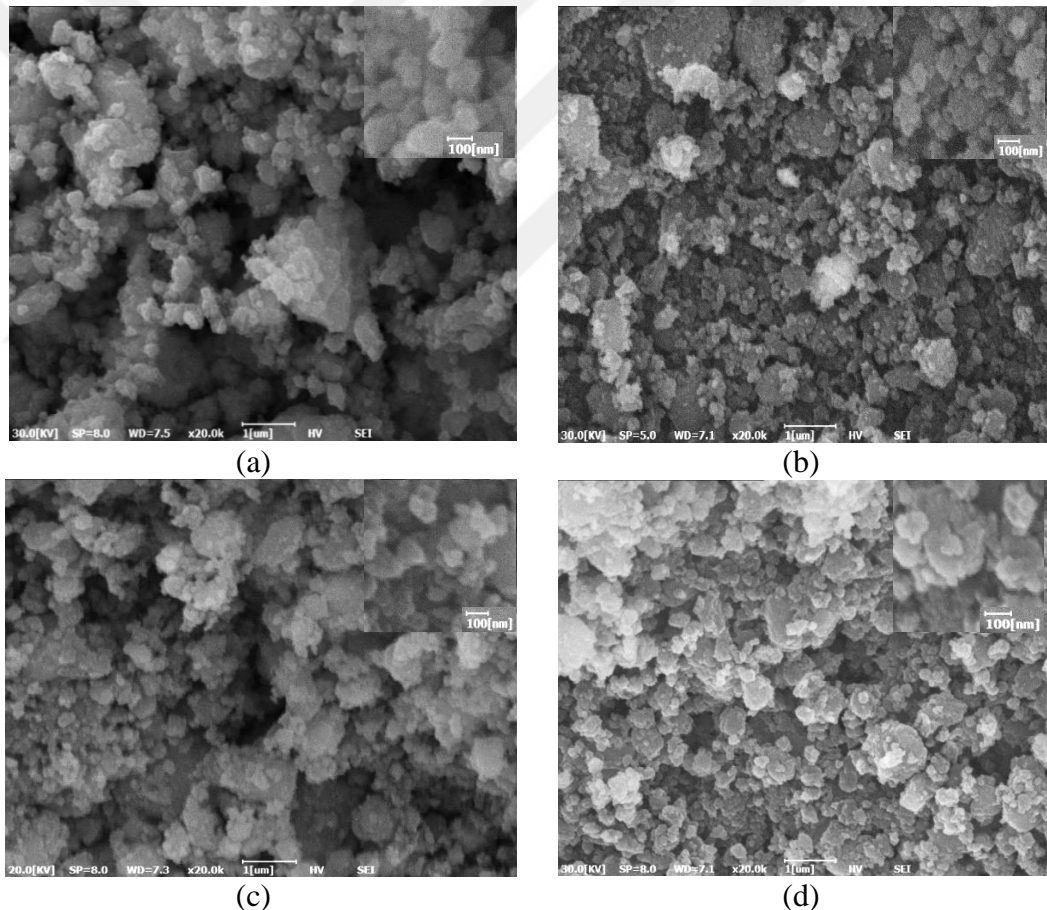


Figure 4.7 SEM micrographs of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite additives

Figure 4.8 shows that additives are agglomerated in some regions. When the additive ratio exceeds 5 wt% in composite materials, the trouble of preventing

agglomeration is a known fact from the literature. The samples of the composite materials were prepared by immersing liquid nitrogen and broken with a hammer in order to illustrate homogeneity when SEM images were taken. All the SEM images of the composites were analyzed from the cross section.

The SEM images in Figure 4.8 were polished with a diamond paste in order to see the particle size and homogeneous distribution of the additives easily. Figure 4.9 shows that the particle size of the all additive materials is in nanoscale. As shown in Figure 4.9, it can be also observed that the distribution of the all additives in PP matrix is uniform. It should be attributed to the good compatibility between the halogen-free inorganic nanoparticles and PP. It is known that this phenomenon contributed to the flame retarding mechanism (M.-J. Chen, Shao, Wang, Chen, & Wang, 2012).

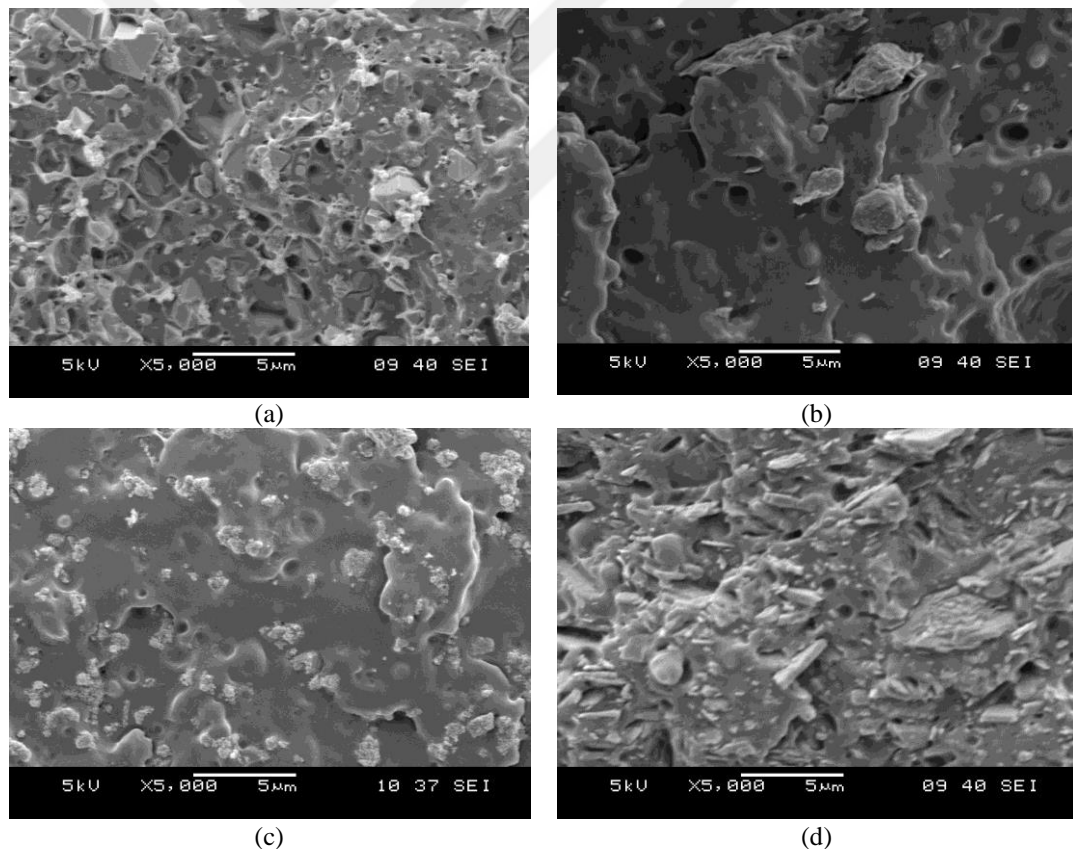


Figure 4.8 SEM micrographs of (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite 30 wt% reinforced composites

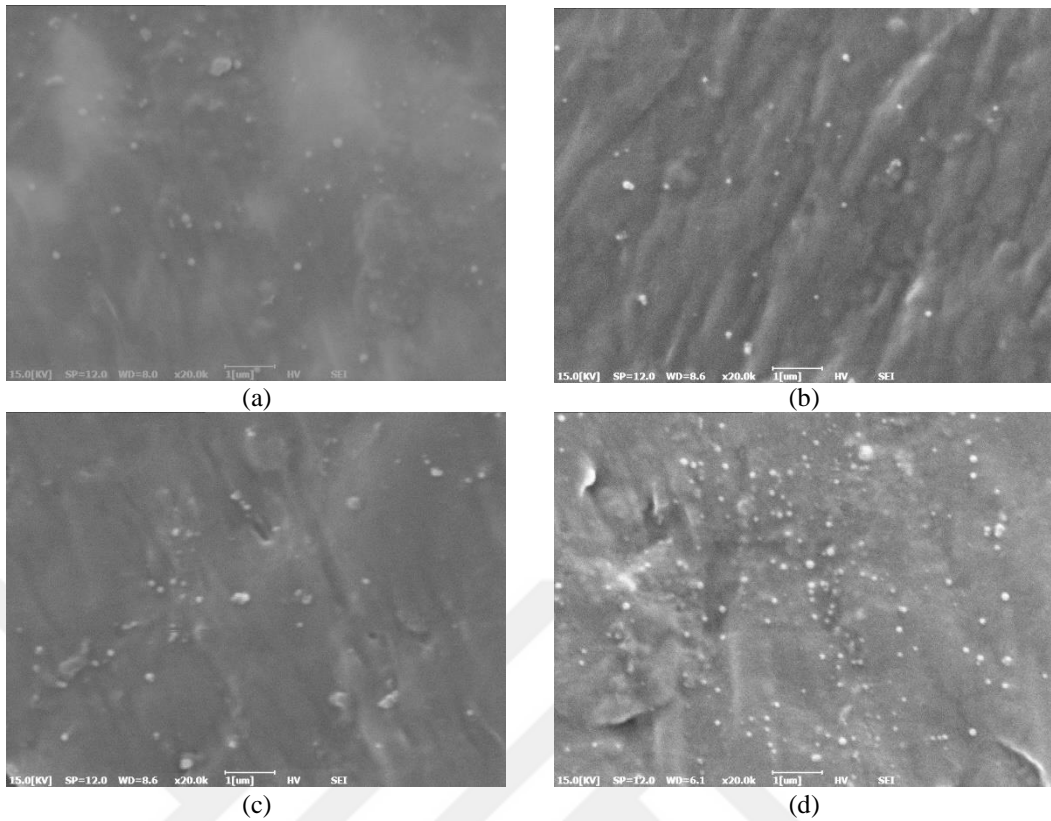


Figure 4.9 SEM micrographs of polished (a) antimony trioxide, (b) bentonite, (c) zinc borate and (d) huntite/hydromagnesite 30 wt% reinforced composites

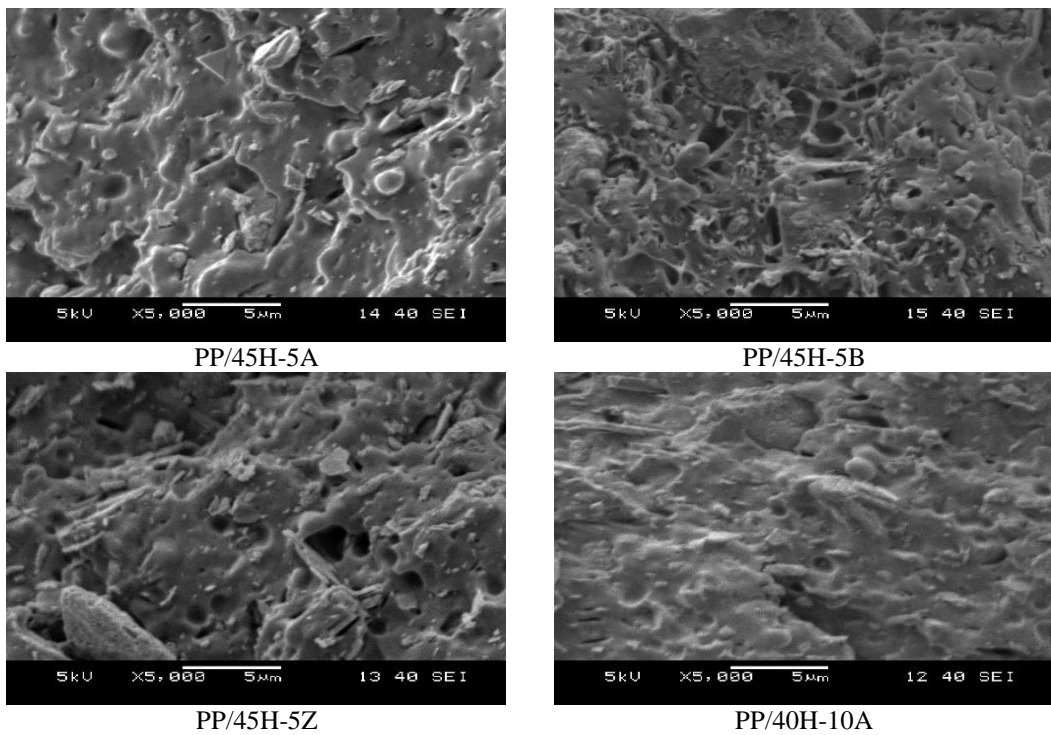


Figure 4.10 SEM micrographs of PP composite specimens reinforced with different additives and different ratio

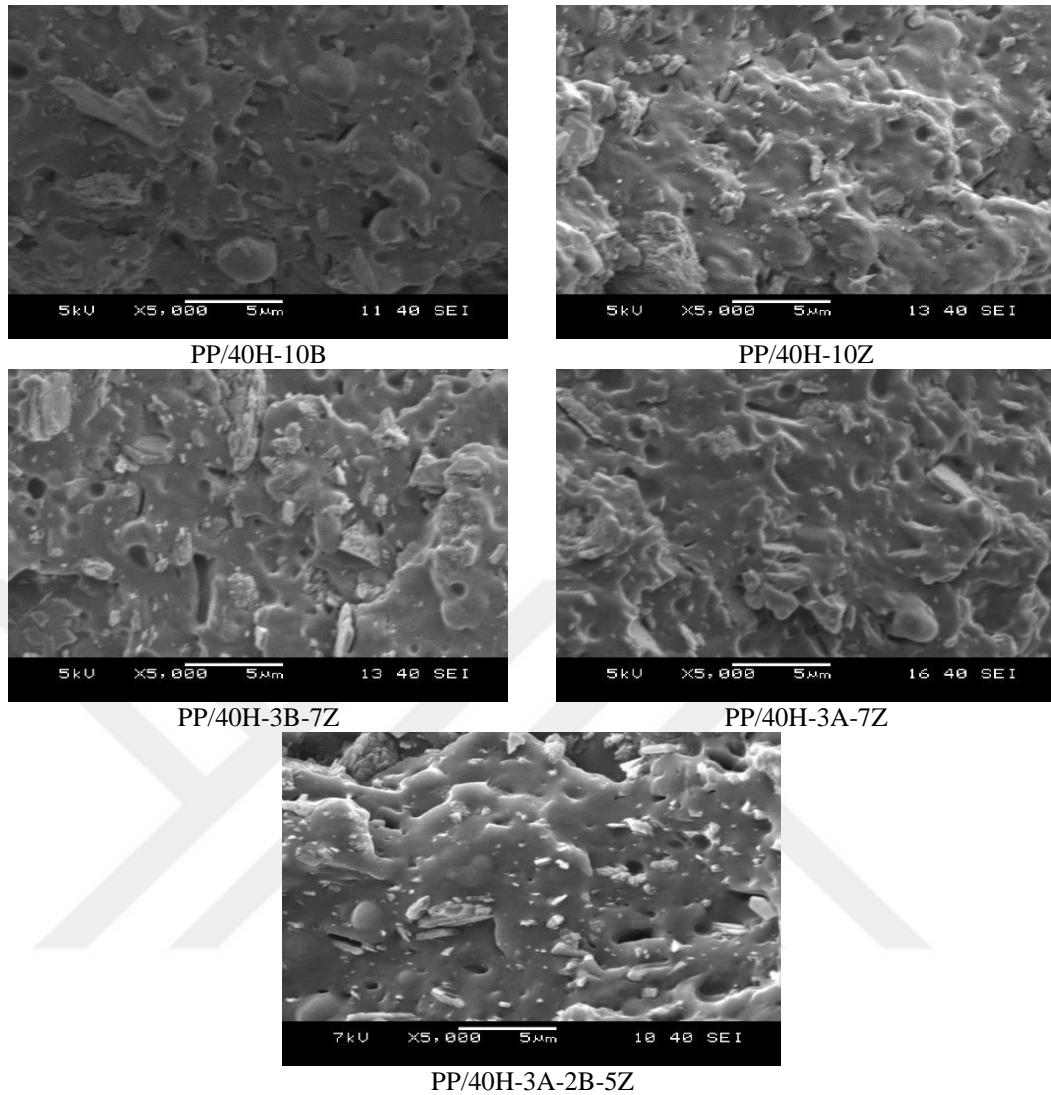


Figure 4.10 Continues

SEM images of multi-additive reinforced PP composites were demonstrated in Figure 4.10. When the microstructures of all composite structures are examined, it is seen that the additives are dispersed homogeneously in the structure successfully. All microstructural studies have been performed from the cross section of the samples. It is also seen that some of the additive materials agglomerate while producing composites.

4.6 Mechanical Properties

Tensile tests were performed to demonstrate the mechanical properties of pure PP and the presence of flame retardant additives in PP composites. Figure 4.11 presents the tensile strength and Young's modulus of PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites. Their mechanical properties are listed in Table 4.1. When PP composites reinforced with 30 wt% of huntite/hydromagnesite, antimony trioxide, bentonite and zinc borate were investigated, PP/30H composite provides an enhancement of Young's modulus approximately 68% from pure PP. It is significantly evolved by adding different flame retardant nanoparticles into polymer matrix since inorganic fillers have much higher stiffness values than the polymer matrix in good agreement with literature (Fu, Feng, Lauke, & Mai, 2008). Although it is generally considered that the addition of flame retardants into polymers can cause a reduction of tensile properties (Fu et al., 2008; Kurt & Mengelöglu, 2011), the drops in tensile strength should not be considered as negative because they are acceptable levels for industrial applications.

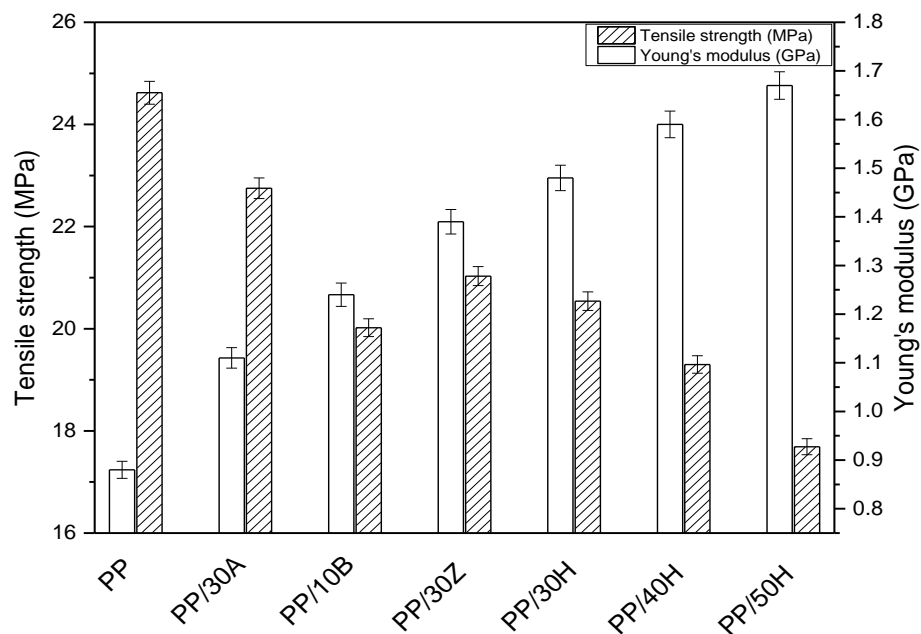


Figure 4.11 Tensile strength and elastic modulus of pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites

Table 4.1 Mechanical properties of pure PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites

Sample code	Tensile strength (MPa)	Young's modulus (GPa)	Hardness (Shore D)
PP	24.62	0.88	67.6
PP/5A	23.08	0.93	67.8
PP/10A	22.51	1.02	69.2
PP/15A	22.53	1.07	68.2
PP/20A	22.39	1.09	66.2
PP/25A	22.41	1.1	68.0
PP/30A	22.75	1.11	66.6
PP/5B	20.02	1.2	69.8
PP/10B	20.00	1.24	68.2
PP/5Z	20.85	0.96	68.1
PP/10Z	20.99	1.1	67.9
PP/15Z	20.92	1.15	68.2
PP/20Z	21.08	1.29	68.5
PP/25Z	20.72	1.35	68.8
PP/30Z	21.03	1.39	68.9
PP/5H	23.08	1.11	67.6
PP/10H	22.16	1.13	67.8
PP/15H	21.62	1.21	67.9
PP/20H	21.37	1.27	68.1
PP/25H	20.54	1.44	68.5
PP/30H	20.01	1.48	68.6
PP/40H	19.31	1.59	68.9
PP/50H	17.69	1.67	69.0

Mechanical properties of PP composites containing 40 and 50 wt% huntite/hydromagnesite were also demonstrated in Figure 4.11. From the results, the PP/40H and PP/50H composites exhibited higher modulus and lower tensile strength if compared to PP/30H composite. The incorporation of flame retardants into polymer decreased the tensile strength of PP by 28%. As expected, the addition of inorganic flame retardant reinforcing materials into PP tended to improve the stiffness but weaken tensile strength. This could be attributed to the poor interaction between the

reinforcing materials and PP which may acted as a formation of crack initiator (Mareri, Bastide, Binda, & Crespy, 1998).

The mechanical results of the multi-additive reinforced composites are given in Table 4.2. Looking at the mechanical results, the elastic modulus and the hardness values of the PP composites are at acceptable levels, while the tensile strengths are slightly lower than those of single additive reinforced composites.

Table 4.2 Mechanical properties of the multi-additive reinforced composites

Sample code	Young's modulus (GPa)	Tensile strength (MPa)	Hardness (Shore D)
PP/45H-5A	1.26	18.45	67.6
PP/45H-5B	1.09	18.55	65.8
PP/45H-5Z	1.05	19.22	69.2
PP/40H-10A	1.18	19.72	68.2
PP/40H-10B	1.20	18.81	66.2
PP/40H-10Z	1.52	21.01	68.0
PP/40H-7Z-3B	1.28	20.49	66.6
PP/40H-7Z-3A	1.51	20.35	69.8
PP/40H-5Z-3A-2B	1.42	20.33	68.2

4.7 Thermal Properties

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) are of great importance as flame-retardant properties are aimed in composites. DTA-TG tests were carried out in air atmosphere with a heating rate of 5 °C / min at 25-600 °C for pure PP and all composites. When the DTA-TG analysis of the pure PP in Figure 4.12 is examined, it is seen that the degradation begins at about 230 °C and that no residue, impurity, etc. remain at 400 °C.

When the DTA-TG results of all the composites shown in Figures 4.13-4.16 are examined, it is observed that the exothermic reaction started at the latest at huntite/hydromagnesite 50% reinforced PP composite. Therefore, it can be

understanding that the best flame retardant property among these samples will be accomplish in this sample

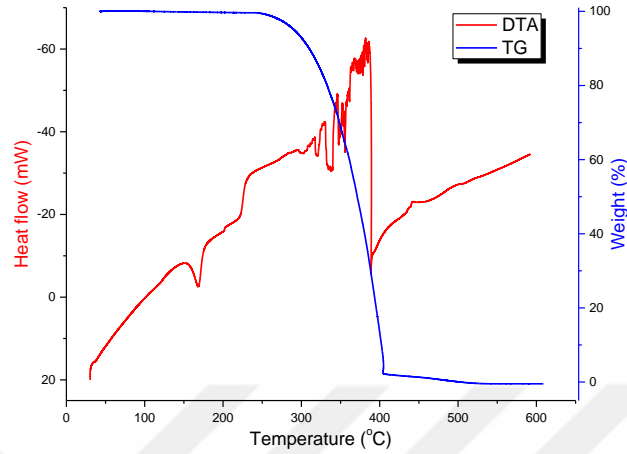


Figure 4.12 DTA-TG curves of pure PP specimen

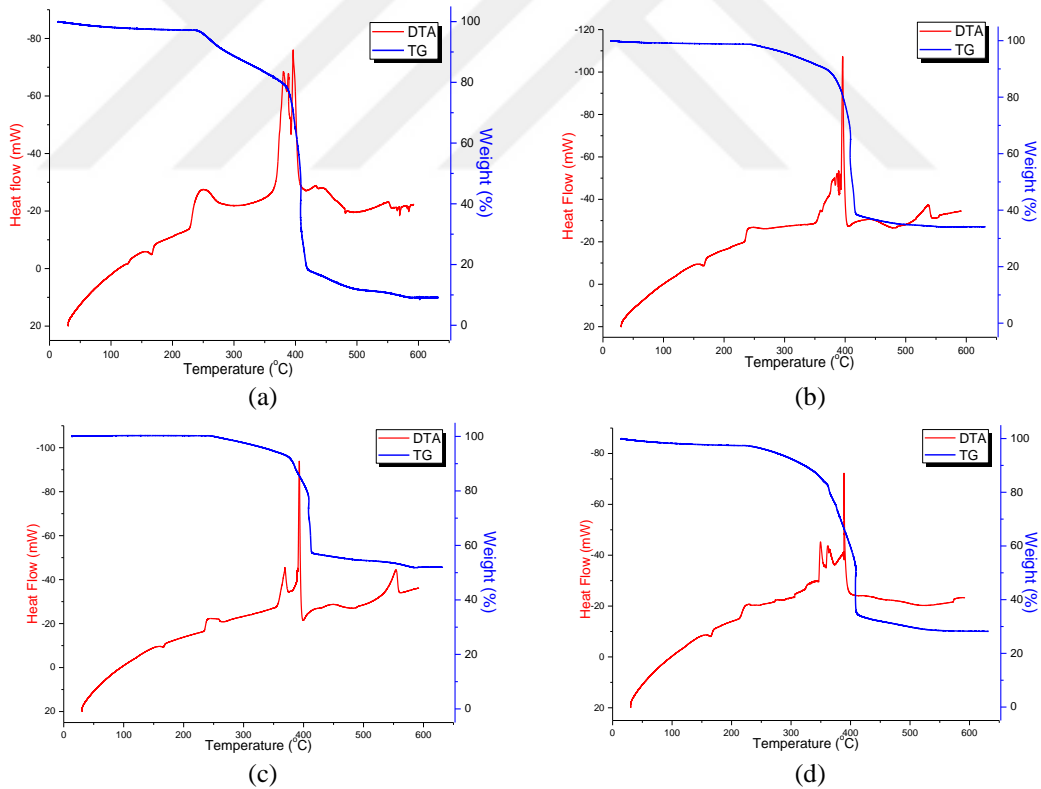


Figure 4.13 DTA-TG curves of a) 5 %, b) 10%, c) 20% and d) 30% antimony trioxide reinforced PP composite specimens

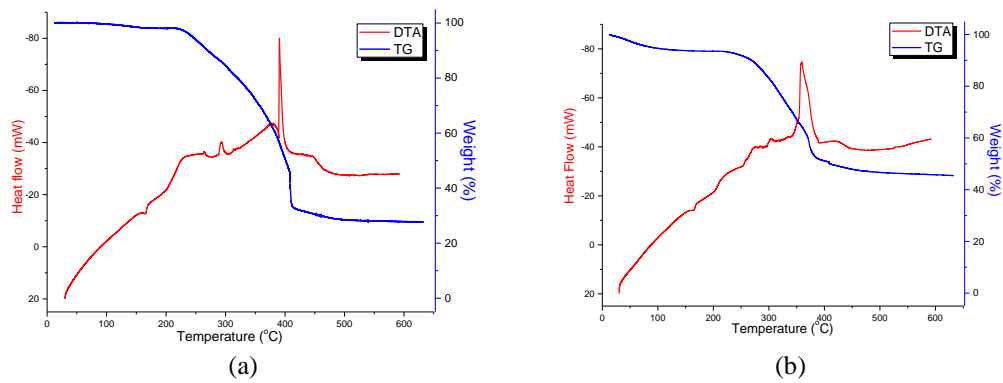


Figure 4.14 DTA-TG curves of a) 5% and b) 10% bentonite reinforced PP composite specimens

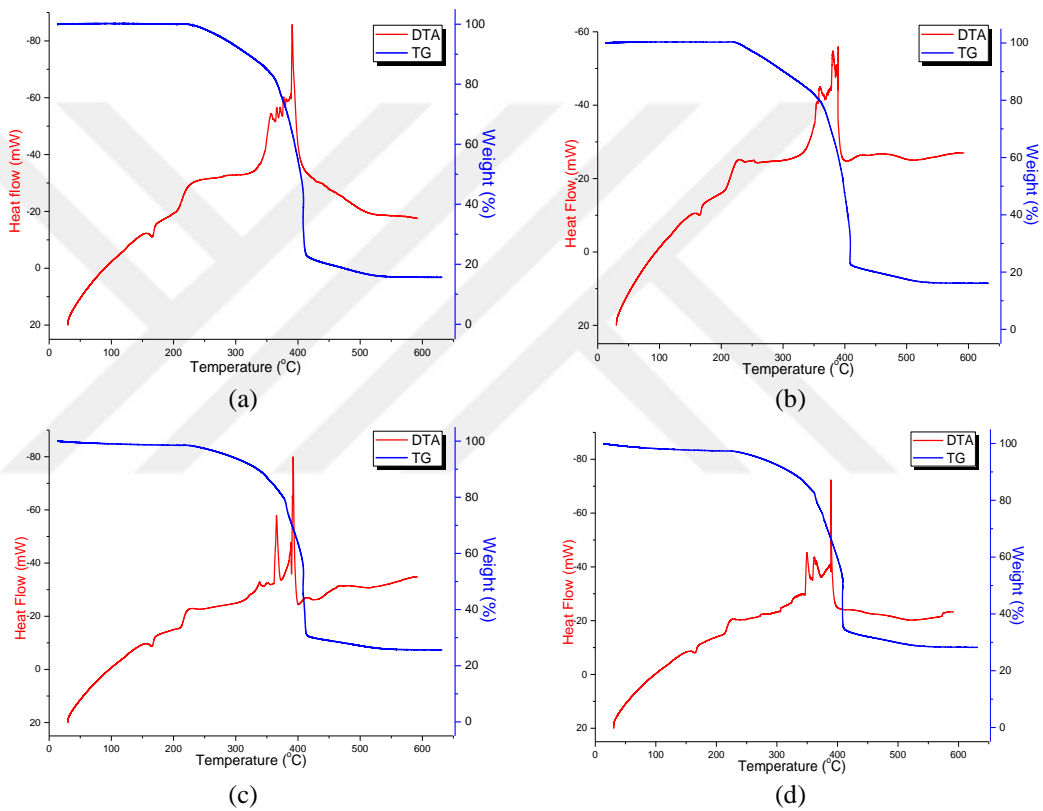


Figure 4.15 DTA-TG curves of a) 5%, b) 10%, c) 20% and d) 30% zinc borate reinforced PP composite specimens

TGA analysis of the antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites was also used to investigate the thermal degradation behavior of pure PP and PP composites in the same figure (Figure 4.17). In addition, derivative TG (DTG) curves of PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites are shown in Figure 4.18.

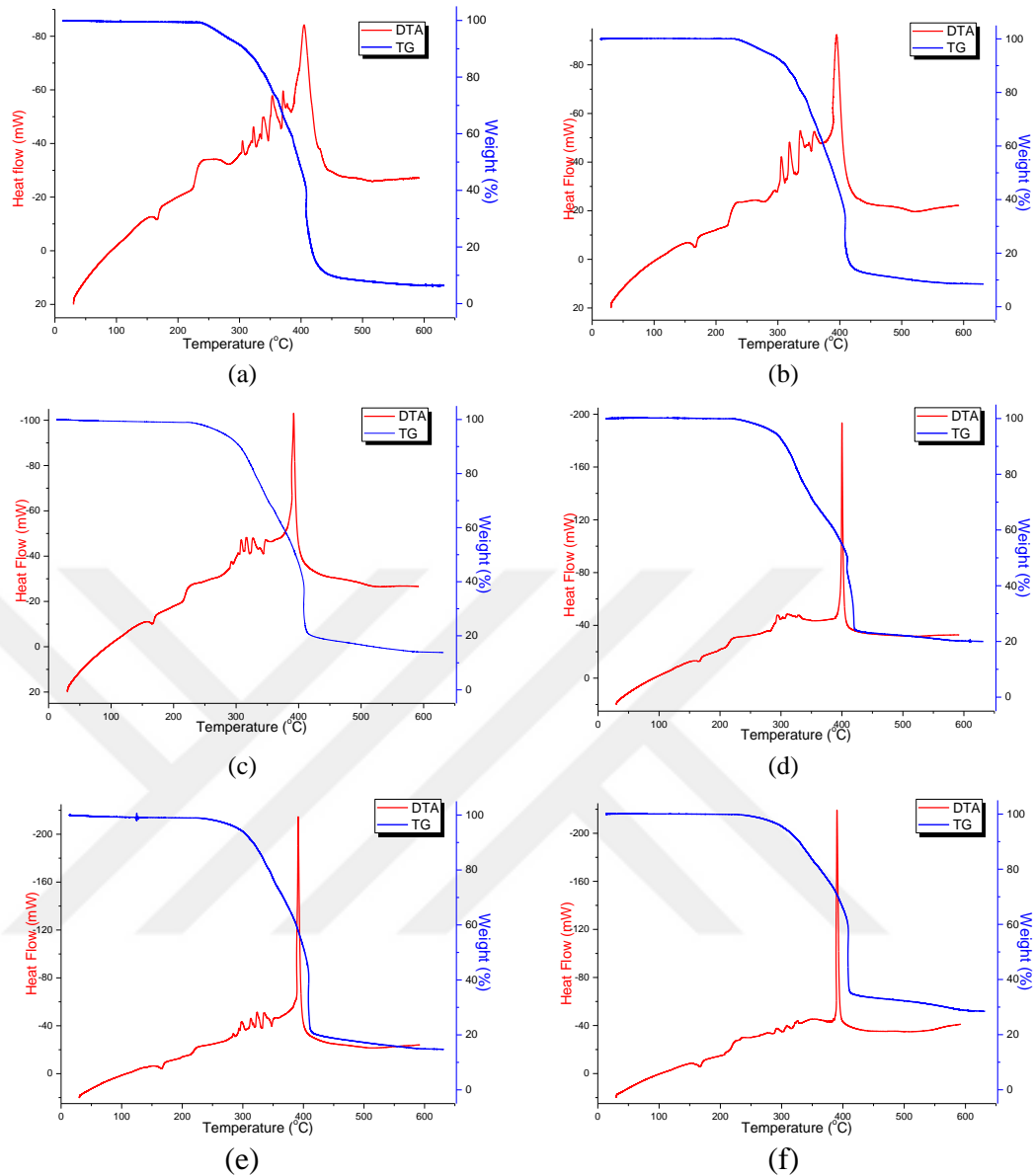


Figure 4.16 DTA-TG curves of huntite/hydromagnesite a) 5%, b) 10%, c) 20%, d) 30%, e) 40% and f) 50% reinforced PP composite specimens

The initial degradation temperature ($T_{5\%}$), the 50 wt% loss temperature ($T_{50\%}$), the maximum decomposition temperature (T_{max}) and the char residue of PP and PP composites at 600 °C are listed in Table 4.3. Thermal decomposition temperatures of PP at $T_{5\%}$ and $T_{50\%}$ are 276 and 356, respectively with no char residue. However, the presence of flame retardant nanoparticles increased $T_{50\%}$ of the pure PP. In order to improve the flame retardant property, it is aimed to produce composites reinforcing two, three and four additions at the same time into the PP structure. All DTA-TG

results of the composites including two, three and four additives in the structure were demonstrated in Figure 4.19.

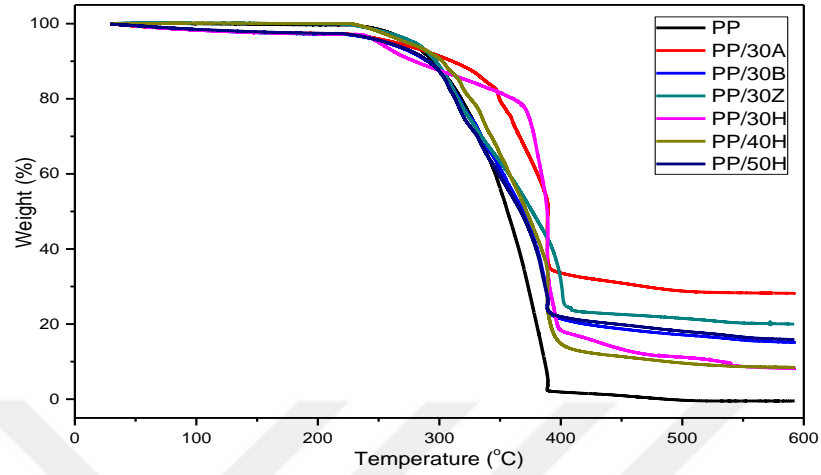


Figure 4.17 TGA curves of PP and PP/30A, PP/30B, PP/30Z, PP/30H, PP/40H and PP/50H composites

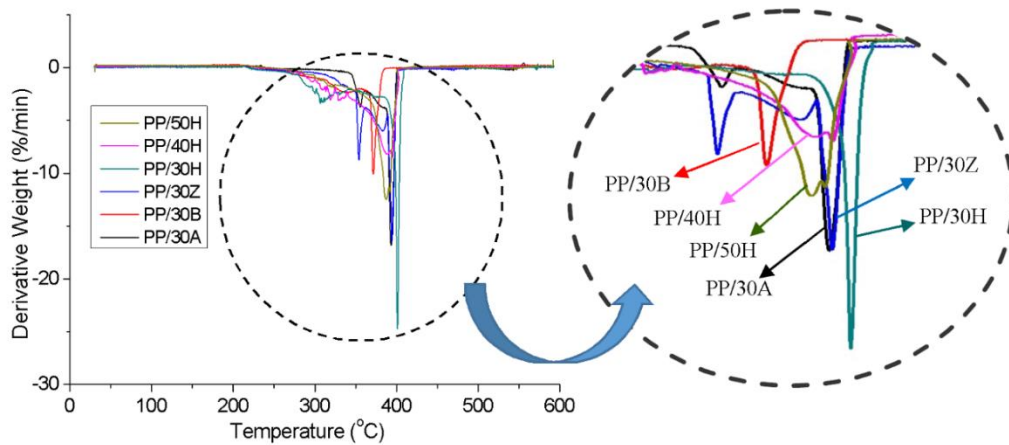


Figure 4.18 DTG curves of PP/30A, PP/30B, PP/30Z, PP/30H, PP/40H and PP/50H composites

Table 4.3 Thermal properties of PP and PP composites

Sample code	T _{5%} (°C)	T _{50%} (°C)	T _{max} (°C)	Char yields at 600 °C (%)
PP	276	356	358	0
PP/30A	263	389	393	28.2
PP/30B	255	368	371	15.1
PP/30Z	279	376	394	19.9
PP/30H	250	388	401	8.1
PP/40H	273	371	389	8.5
PP/50H	256	366	387	15.8

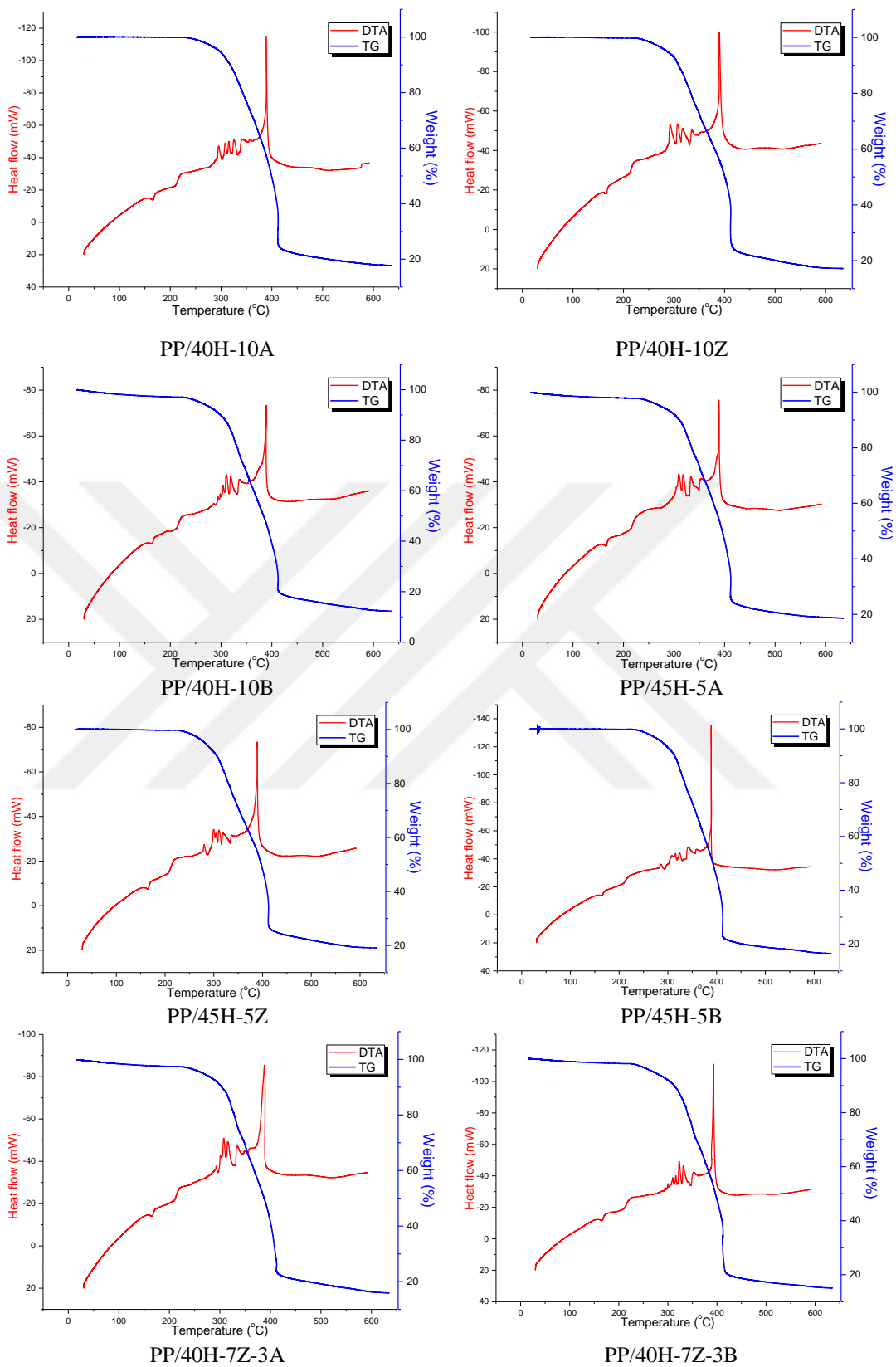


Figure 4.19 DTA-TG curves of PP composite specimens reinforced with different additives and different ratio

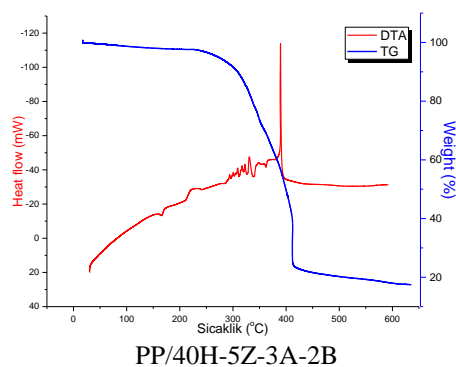


Figure 4.19 Continues

The thermal analysis results of all samples were examined in detail. It can be understood from the Figure 4.17 that the composites reinforced with PP/50H, PP/40H-10Z and PP/40H-5Z-3A-2B specimens were of the maximum degradation temperature. The synergistic effect was seen to be successful in improving the thermal behaviors of multi-additive reinforced composites. The initial values of the combustion temperatures of all composites are given in Table 4.4.

4.8 Flame Retardancy Properties

Table 4.5 presents the UL94-V testing results of PP and antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced composites. Naturally, in the absence of flame retardants, the pure PP burned easily with allowing melt dripping. Considering different types of additives reinforced with 30 wt%, while the results of the PP/30A, PP/30Z and PP/30H correspond to a UL 94 rating of V-1, the PP/30B composite is V-2, indicating that the addition of bentonite into PP did not improve the flame retardant properties sufficiently as much as others. With further increased of huntite/hydromagnesite amount up to 50 wt%, the UL-94 rating could reach V-0. It is noteworthy that in spite of the leading role of additive type in thermal stability, the composites with same or higher huntite/hydromagnesite content performed better in LOI and UL 94 tests compared with the thermally most stable PP/30A sample.

Table 4.4 The initial values of the combustion temperatures of all PP composites

Sample code	Initial value of the combustion temperatures (°C)	Sample code	Initial value of the combustion temperatures (°C)
PP	230	45H-5A	376
PP/5H	290	45H-5B	380
PP/10H	305	45H-5Z	373
PP/20H	320	40H-10A	375
PP/30H	382	40H-10B	372
PP/40H	394	40H-10Z	384
PP/50H	400	40H-7C-3B	366
PP/30Z	338	40H-7C-3A	367
PP/30A	380	40H-5Z-3A-2B	386
PP/10B	346		

On basis of the above discussions, it was concluded that huntite/hydromagnesite reinforced composite exhibited better flame retardant performance than other additive reinforced composites with the same contribution rate. When the effect of the additive ratio was examined, it is seen that the PP/50H composite has superior flame retardant property which is dramatically enhanced with the amount of additive increased by 50 wt%. It is evident that there was a good compatibility between huntite/hydromagnesite and PP at high contribution rates when the LOI and UL94 performances considered. Moreover, some interesting events were occurred during LOI tests.

When the samples were tested with a low oxygen ratio, the intensity of flame diminished and finally disappeared. It was understood from this phenomenon, free radicals produced with quenching effect by the matrix material were adequate to compress the combustion which result in the formation of char barrier that protects the sample from further degradation. The LOI test results of the multi-additive reinforced composites are given in Table 4.6. As can be seen from Table 4.6, the LOI results of multi-additive reinforced composites are not superior to those of single reinforced composites.

Table 4.5 UL 94-V and LOI testing results of PP and PP composites

Sample code	UL 94-V rating	Cotton ignition	LOI (%)
PP	No rating	Yes	17.1
PP/5A	No rating	Yes	17.1
PP/10A	No rating	Yes	17.2
PP/15A	No rating	Yes	17.5
PP/20A	No rating	Yes	17.8
PP/25A	No rating	Yes	18.1
PP/30A	V-1	No	21.3
PP/5B	No rating	Yes	17.2
PP/10B	V-2	Yes	19.2
PP/5Z	No rating	Yes	17.3
PP/10Z	No rating	Yes	17.5
PP/15Z	No rating	Yes	17.6
PP/20Z	No rating	Yes	17.9
PP/25Z	No rating	Yes	18.1
PP/30Z	V-1	No	20.5
PP/5H	No rating	Yes	17.6
PP/10H	No rating	Yes	18.0
PP/15H	No rating	Yes	18.4
PP/20H	No rating	Yes	19.1
PP/25H	V-1	No	22.3
PP/30H	V-1	No	22.7
PP/40H	V-1	No	23.4
PP/50H	V-0	No	25.5

Table 4.6 UL 94-V and LOI testing results of the multi-additive reinforced PP composites

Sample code	UL 94-V rating	Cotton ignition	LOI value (%)
PP/40H-10A	V-1	No	19,0
PP/40H-10B	V-1	No	19,0
PP/40H-10Z	V-1	No	19,0
PP/45H-5A	V-0	No	20,6
PP/45H-5B	V-1	No	19.8
PP/45H-5Z	V-1	No	19.0
PP/40H-7Z-3B	V-1	No	19.8
PP/40H-7Z-3A	V-0	No	19.8
PP/40H-5Z-3A-2B	V-1	No	19.0

4.9 Industrial Applications

There is a wide range of industrial applications where flame retardant composites can be used. In the scope of the thesis, it is envisaged that battery boxes and flaps could be produced from flame retardant additive material reinforced PP composites. All industrial applications were carried out in Nas Plastic (Izmir, Turkey) and Inci GS Yuasa (Manisa, Turkey) companies.

When the production of the PP/50H sample is considered, it is found that the material did not completely fill the mold and the fluidity was not sufficiently well. Therefore, the contribution rate of huntite/hydromagnesite has been reduced to 25 wt%. This battery boxes and flaps were produced using PP/25H sample composition. The products produced with huntite/hydromagnesite reinforced PP composite are shown in Figure 4.20.



Figure 4.20 Industrial application of flame retardant huntite/hydromagnesite reinforced PP composites

4.9.1 Mechanical Properties of Final Products

It was determined whether there was breakage in the boxes by dropping a ball of 1 kg from the height of 15 cm to the bottom side and injection points of the boxes removed from the cooler for samples waiting at -20 °C. The images related to the impact tests are given in Figure 4.21.

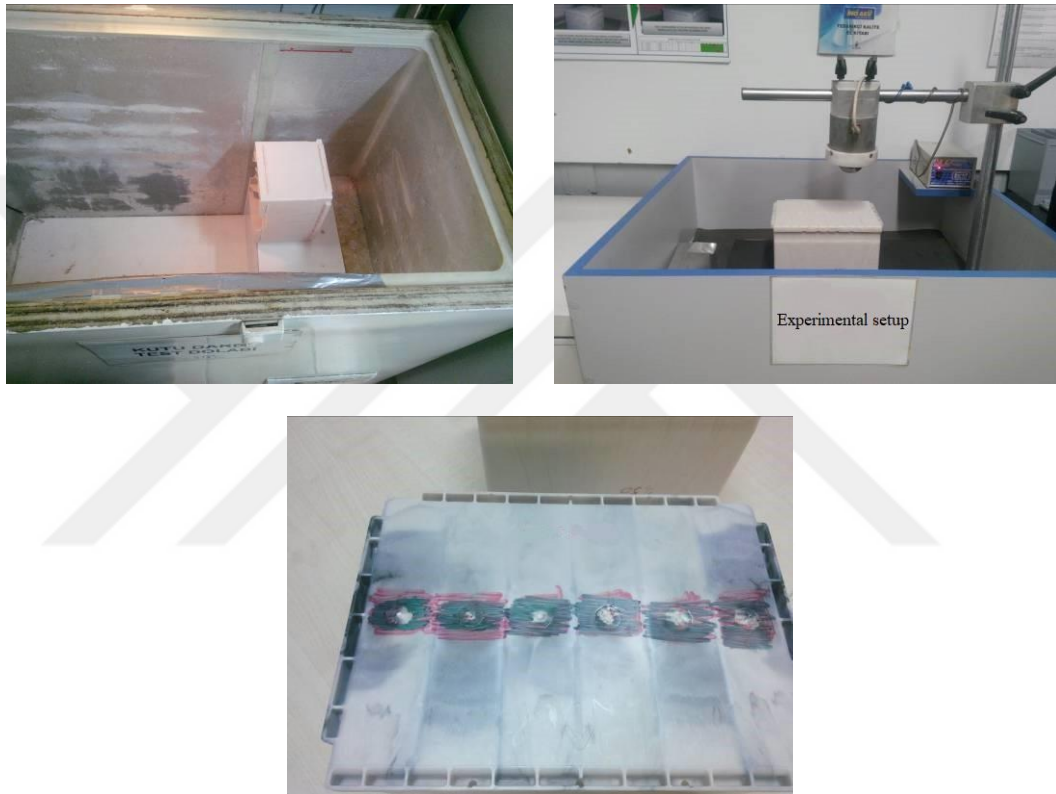


Figure 4.21 Experimental setup of the impact tests for battery boxes

It was understood that the PP/25H sample was not cracked in bottom areas of the boxes as a result of the impact test. The mechanical properties of the boxes were determined to be sufficient for battery production. In the boxes produced with PP/50H composition, the production became very difficult as a result of long struggles, but it was determined that the boxes produced with PP/50H were cracked in the impact tests. PP/25H boxes were manufactured without problems in the production stages and no problems were found in the mechanical tests. The overall evaluation of the tests is given in Table 4.7.

Table 4.7 General test results of the boxes for PP/50H, PP/25H and commercial product

Test	PP/50H	PP/25H	Commercial product
Cover closing	Passed	Passed	Passed
Leakage test	Failed	Passed	Passed
Impact test (25 °C)	Passed	Passed	Passed
Impact test (-18 °C)	Failed	Passed	Passed
Hardness	70.8	71	68.1
Melt flow index (MFI)	1.51 g/10 min	6.05 g/10 min	7.15g/10 min

As a result of the tests carried out, it was determined that the PP/25H sample had passed the cover closing, leakage test, impact test and MFI tests. When the results examined, it was understood that battery components could not be produced using PP/50H sample. The mechanical properties of the commercial product were similar to that of the PP/25H sample. It is known that the PP/25H sample has flame retardant properties, battery components are produced that provide both flame retardant and sufficient mechanical properties.

4.9.2 Performance and Corrosion Properties of Final Products

Produced batteries using in automotive industry have 12 V systems formed by the combination of 6 cells, each of which is 2 V. Each cell works independently within itself. However, the acid solution in cells should not pass from one to another. If this happens, short circuit will naturally occur. Performance (cycle) and corrosion tests were carried out for the battery boxes produced with PP/25H and commercial product. These results were given in Tables 4.8-4.10.

According to the results of the performance tests, the battery produced as commercial product in serial production came to be under 10.5 V at the end of 139 cycles and the battery produced with the PP/25H in 142 cycles. According to these results, the flame retardant additive reinforced boxes does not affect the performance tests of battery.

When Table 4.9-4.10 are examined, it is seen that both batteries have completed 4 cycles successfully according to corrosion test procedure. There is a period of 1 month between the each cycle. Both batteries appear to remain at about 9.70 V when the results of the 4th cycle are evaluated. Therefore, it is understood that the flame retardant additives reinforced boxes does not affect the corrosion tests of the battery. As a result of the performance and corrosion tests, the box produced with PP/25 was passed all the tests.

Table 4.8 Performance (cycle) test results of the commercial product and PP/25H

Test	Commercial product	PP/25H
Capacity	60 Ah	60 Ah
Density before test	1.293 g/cm ³	1.292 g/cm ³
Weight before test	15617 g	15534 g
Weight after test	15375 g	15281 g
Difference	242 mL	253 mL
Water loss	4.0 g/Ah	4.2 g/Ah
Density after test	1.285 g/cm ³	1.280 g/cm ³
Cycle	139	142
Voltage	10.5	10.5
Result	Passed	Passed





Table 4.9 Corrosion test results of the commercial product

Test	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Weight before test	15447 g	15447 g	15447 g	15447 g
Weight after test	15286 g	15378 g	15268 g	15264 g
Difference	161 g	69 g	179 g	183 g
Water added	161 g	69 g	179 g	183 g
Water loss	2.7 g/Ah	1.2 g/Ah	3.0 g/Ah	3.1 g/Ah
U _{30s} ≥ 6 V	10.19 V	9.98 V	9.84 V	9.73 V
t _{6V} ≥ 30 s	30 s	30 s	30 s	30 s
Result	Passed	Passed	Passed	Passed

Table 4.10 Corrosion test results of the box produced with PP/25H

Test	Cycle 1	Cycle 2	Cycle 3	Cycle 4
Weight before test	15590 g	15590 g	15590 g	15590 g
Weight after test	15426 g	15517 g	15410 g	15396 g
Difference	164 g	73 g	180 g	194 g
Water added	164 g	73 g	180 g	194 g
Water loss	2.7 g/Ah	1.2 g/Ah	3.0 g/Ah	3.2 g/Ah
$U_{30s} \geq 6 \text{ V}$	10.23 V	10.10 V	9.80 V	9.71 V
$t_{6V} \geq 30 \text{ s}$	30 s	30 s	30 s	30 s
Result	Passed	Passed	Passed	Passed

Table 4.11 Control of recycling process using crushing products in different ratio

Crushing rate	Result	Images
5 wt%	There was no problem with this contribution rate	
10 wt%	There was no problem with this contribution rate	
15 wt%	The box could be removed from the injection machine. Incomplete filling were seen.	
20 wt%	The box could not be removed from the injection machine. Incomplete filling were seen.	

4.9.3 Recycling Properties of Final Products

Some experiments were carried out to reproduce the boxes for PP/25H sample. In the experiments, the producibility of the products was tested by injecting 5, 10, 15, and 20 wt% of the crushing products together with the PP based granules into the injection machine. The results are given in Table 4.11 together with the images. It was determined that 10 wt% addition rate of the crushing products is optimum value for recycling process. Consequently, it was determined that the recycling process of the boxes produced with PP/25H sample is appropriate.



CHAPTER FIVE

CONCLUSIONS AND FUTURE PLANS

5.1 Conclusions

Summarizing the results of this thesis, flame retardant antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite reinforced PP composites were produced by extrusion and injection molding techniques for the halogen free flame retardant applications successfully. The fire resistance of polypropylene is increased by using flame retardant inorganic nanomaterials. In order to express and summarize this success based on the obtained results; general assessments outlined as follows:

- 1) Prior to production process; flame retardant additives antimony trioxide, bentonite, zinc borate and huntite/hydromagnesite were milled with a nano grinding machine. As a result of milling operations, all additive materials were grinded from micron to nanosclae successfully and adapted into the PP matrix with desired compositions.
- 2) The XRD analyses revealed that pure and reinforced PP composites have a-form PP crystals, hydromagnesite, huntite, antimony trioxide, magnesium hydroxide, zinc borate and bentonite phases. FTIR analysis of composite materials shows O–H stretching mode or =CH₃- structure, the asymmetric and symmetric vibration of C–H in CH₂ and CH₃ and oxygen stretching vibration in oxides. All the data obtained for PP composites by XPS analysis indicated that all additive materials were encapsulated in the PP matrix in accordance with the literature without any chemical and structural changes.
- 3) It was observed from SEM micrographs the particle size of all additives is around 100 nm. These results are consistent with the particle size distribution results. SEM analysis proved that the distribution of the all additives in PP matrix is uniform.

- 4) The TGA analysis showed that antimony oxide and huntite/hydromagnesite enhance the thermal stability of composite and particularly formation of char layer, which protects from heat and flame. The addition of 50 wt% huntite/hydromagnesite into PP exhibit improved flame retardancy due to formed pyrolytic products, prolonged ignition time and impeded dripping. The presence of extinguishing effect can be mentioned as flame retarding mechanism.
- 5) The addition of ceramic based flame retardant reinforcing materials into PP tended to improve the stiffness but weaken tensile strength. The pure PP burned easily with allowing melt dripping. Notwithstanding the leading role of additive type in thermal stability, the composites with same or higher huntite/hydromagnesite content exhibited better in LOI and UL 94 tests compared with the thermally most stable PP/30A sample. It was concluded that huntite/hydromagnesite reinforced composite exhibited better flame retardant performance than other additive reinforced composites with the same contribution rate.
- 6) It was observed from mechanical test results, the presence of more than one additive in the same structure negatively affects the mechanical properties. As the tensile strength of which is less than 20 MPa presents a challenge for industrial applications, PP composites including single additive exhibit better performance.
- 7) Based on UL 94 flammability test results and LOI % values, the PP/50H sample is of the best flame retardant composite composition. Although PP/30H sample exhibited thermal stability, V-0 result of UL 94 vertical test was only achieved with a PP/50H sample. LOI test result of all the multi-additive reinforced PP composites except for the PP/45H-5A sample are below 20 %.
- 8) The production of battery boxes and covers considered to be industrial applications from non-combustible materials has been achieved successfully.

The produced flame retardant composites can be applicable in a wide range of area where one need resistance to fire.

- 9) It can be understood from the results of the mechanical strength, impact tests performed on the manufactured boxes, it was determined that the PP/25H sample passed the cover closing, leakage test, impact test and MFI tests successfully. However, battery components produced with PP/50H sample could not be succeed as well as PP/25H or commercial product. It is known that the PP/25H sample has flame retardant properties; battery components could be produced that provide both flame retardant and sufficient mechanical properties.
- 10) Performance and corrosion tests were carried out for the battery boxes produced with PP/25H and commercial product. When performance and corrosion tests considered, the box produced with PP/25 was passed all the tests. In addition, recycling process of the boxes produced with PP/25H was achieved using 10 wt% of the crushing products with the PP based granules as optimum value. Consequently, it was determined that the flame retardant PP nanocomposites were successfully applied to the industrial applications as battery boxes and covers and passed all the specific tests for the automotive industry.

5.2 Future Plans

Future plans are listed below:

- In the production of composites, various additives or agents may be used to prevent the agglomeration of the additive. Thus, the composites to be produced can be provided with better performance.
- Better structural and mechanical properties can be achieved by working on processing conditions or methods in composite production.

- Flame retardant and mechanical properties can be provided with a lower additive ratio by using the synergistic effect of different additives.
- When industrial applications are considered, single additive reinforced composites with lower additive ratio can facilitate the process.



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