SYNTHESIS AND CHARACTERIZATION OF NANO ZINC BORATE AND ITS USAGE AS A FLAME RETARDANT FOR POLYMERS

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF NANO ZINC BORATE AND ITS USAGE AS A FLAME RETARDANT FOR POLYMERS

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The objectives of this study are to synthesize sub-micron sized zinc borate and to use them with other flame retardant additives in poly(ethylene terephthalate) (PET) based composites.

The study can be divided into two parts. In the first part, it was aimed to synthesize sub-micron sized zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) with the reaction of zinc oxide and boric acid. For this purpose, low molecular weight additives or surfactants were used in the syntheses to prevent the agglomeration and to decrease particle size. Effect of type of surfactant and its concentration; effect of using nano-sized zinc oxide as reactant on the synthesis, properties and morphology of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ were investigated. Synthesized zinc borates were characterized by X-Ray diffraction (XRD), Scanning Electron Microscope (SEM) and Thermogravimetric Analysis (TGA). The results were compared with a commercial zinc borate, Firebrake (FB).

Characterization results showed that at least in one dimension sub-micron size was obtained and synthesized zinc borates did not lose their hydration water until the process temperature of the composites.

In the second part of the study, PET based composites, which mainly included synthesized sub-micron sized zinc borates were prepared by using a co-rotating twin screw extruder and injection molding machine. Synergist materials such as boron phosphate (BP) and triphenyl phosphate (TPP) were also used in the composite preparation. The composites were characterized in terms of flammability and mechanical properties. Flammability of composites was determined by using a Limiting Oxygen Index (LOI) test. Mechanical properties such as tensile strength, elastic modulus, elongation at break and impact strength were also studied.

According to LOI and impact tests, the composites containing 3 wt. % BP and 2 wt. % zinc borate which was modified with poly(styrene-co-maleic anhydride), 2PSMA05/3BP and 2PSMA1/3BP have higher LOI and impact values when compared to neat PET.

Keywords: zinc borate, synthesis, surfactant, sub-micron size, composite, poly(ethylene terephthalate)

ÖZ

NANO ÇİNKO BORAT SENTEZİ, KARAKTERİZASYONU VE POLİMERLERDE ALEV GECİKTİRİCİ OLARAK KULLANILMASI

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Bu çalışmanın amaçları mikron altı boyuta sahip çinko borat sentezlemektir ve bunları diğer alev geciktirici katkı maddeleriyle beraber poli(etilen tereftalat) (PET) bazlı kompozitlerde kullanmaktır.

Çalışma iki bölüme ayrılabilir. İlk kısımda, çinko oksit ve borik asidin reaksiyonuyla mikron altı boyutta çinko borat ($2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$) sentezlemek amaçlanmıştır. Bu amaçla kümelenmeyi engellemek ve parçacık boyutunu düşürmek için sentez sırasında düşük molekül ağırlığına sahip katkı maddeleri ya da yüzey etkin maddeler kullanılmıştır. Yüzey etkin madde çeşidinin; konsantrasyonunun ve reaktant olarak nano boyutta çinko oksit kullanılmasının senteze ve $2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$ ürününün özelliklerine ve morfolojisine olan etkisi incelenmiştir. Sentezlenen çinko boratlar X-Işını kırınımı (XRD), taramalı elektron mikroskobu (SEM) ve termogravimetrik analiz (TGA) yöntemleriyle karakterize edilmiştir. Sonuçlar ticari bir çinko boratla, Firebrake (FB) karşılaştırılmıştır.

Karakterizasyon sonuçları en az bir boyutta mikron altı seviyenin elde edildiğini ve sentezlenen çinko boratların dehidrasyon sularını kompozitlerin proses sıcaklığına kadar kaybetmediklerini göstermiştir.

Çalışmanın ikinci kısmında, esas olarak sentezlenen mikron altı boyuttaki çinko boratları içeren PET bazlı kompozitler çift vidalı ekstruder ve enjeksiyonlu kalıplama cihazlarıyla hazırlanmıştır. Bor fosfat (BP) ve trifenilfosfat (TPP) gibi sinerjist malzemeler kompozit hazırlığında ayrıca kullanılmıştır. Hazırlanan kompozitlerin yanma ve mekanik özellikleri karakterize edilmiştir. Kompozitlerin yanıcılığı Sınırlayıcı Oksijen İndeksi (LOI) testiyle belirlenmiştir. Çekme gerilimi, elastik modülü, kopma anında uzama ve darbe dayanımı gibi mekanik özellikler de çalışılmıştır.

LOI ve darbe dayanımı testlerine göre, ağırlıkça %3 BP ve %2 poli(stiren-ko-maleik anhidrit) ile modifiye edilmiş çinko borat içeren kompozitler, 2PSMA05/3BP ve 2PSMA1/3BP, saf PET ile karşılaştırıldığında daha yüksek LOI ve darbe dayanımı değerlerine sahiptir.

Anahtar Kelimeler: çinko borat, sentez, yüzey etkin madde, mikron altı boyut, kompozit, poli(etilen tereftalat)

To my family

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NOMENCLATURE

$[O_2]$	Oxygen concentration
ΔL	Change in the sample's gauge length when the sample is exposed to elongation
μm	micrometer
A_0	initial cross–sectional area
APP	ammonium polyphosphate
ASTM	American Society for Testing and Materials
ATH	aluminium trihydroxide
BP	boron phosphate
d	distance between parallel lattice planes
DSC	differential scanning calorimetry
DTA	differential thermal analysis
F	force measured during testing
FB	commercial 3.5 mole hydrated zinc borate which was supplied by U.S Borax
F_{NaOH}	factor of NaOH solution and amount of sample
HDPE	high density polyethylene
L_0	initial gauge length of the sample
LDH	layered hydrotalcite
LOI	limiting oxygen index
MDH	magnesium di-hydroxide
n	amount of sample
n	order of a reflection
NIFR	neutralized intumescent fire retardant
NP	zinc borate synthesized without using surfactant
nPAA05	zinc borate synthesized using 0.5% PAA as surfactant and nano sized ZnO
nPEG05	zinc borate synthesized using 0.5% PEG as surfactant and nano sized ZnO
nPSMA05	zinc borate synthesized using 0.5% PSMA as surfactant and nano sized ZnO

θ	Bragg angle
OA05	zinc borate synthesized using 0.5% OA as surfactant
PAA	Poly(acrylic acid)
PAA01	zinc borate synthesized using 0.1% PAA as surfactant
PAA05	zinc borate synthesized using 0.5% PAA as surfactant
PAA1	zinc borate synthesized using 1% PAA as surfactant
$P_{B_2O_3}$	the weight percentage of B_2O_3 in the taken sample
PBS	brominated polystyrene
PC	polycarbonate
PEG01	zinc borate synthesized using 0.1% PEG as surfactant
PEG05	zinc borate synthesized using 0.5% PEG as surfactant
PEG1	zinc borate synthesized using 1% PEG as surfactant
PEG300	poly(ethylene glycol) which has a molecular weight of 300 g/mole
PET	poly(ethylene terephthalate)
PGC	pyrolysis gas chromatography
PP	polypropylene
PSMA	Poly(styrene-co-maleicanhydride)cumene terminated
PSMA01	zinc borate synthesized using 0.1% PSMA as surfactant
PSMA05	zinc borate synthesized using 0.5% PSMA as surfactant
PSMA1	zinc borate synthesized using 1% PSMA as surfactant
PSMA10	zinc borate synthesized using 10% PSMA as surfactant
PSSA	poly(4-styrene sulfonic acid-co-maleic acid)sodium salt
PSSA05	zinc borate synthesized using 0.5% PSSA as surfactant
PU	polyurethane
PVC	poly(vinyl chloride)
PVP	poly(vinyl pyrrolidone)
PVP05	zinc borate synthesized using 0.5% PVP as surfactant
P_{ZnO}	the weight percentage of ZnO in the taken sample
SA	sodium Acrylate
SA05	zinc borate synthesized using 0.5% SA as surfactant
SAXS	small angle X-Ray scattering
SDS	Sodium Dodecyl Sulfate
SDS05	zinc borate synthesized using 0.5% SDS as surfactant
SEI	secondary electron image
TBA	torsional braid analysis

TBBPA	Tetrabromobisphenol A
TEM	transmission electron microscopy
TMA	thermomechanical analysis
TPP	triphenyl phosphate
UREA05	zinc borate synthesized using 0.5% UREA as surfactant
V_{EDTA}	volume of the EDTA used
V_{NaOH}	volume of the NaOH used
WAXS	wide angle X-Ray scattering
XRD	x-ray diffraction
ε	engineering strain
λ	wavelength
σ	engineering stress

CHAPTER 1

INTRODUCTION

Boron is a relatively rare element in the Earth's crust, representing only 0.001%. The worldwide commercial borate deposits are estimated as 10 million tones. Turkey and USA are the world's largest producers of boron. Turkey has almost 72% of the world's boron reserves. Wide spread applications of boron like agriculture, detergents and soap, insulation, flame retardants, nuclear power stations increase its importance every single day [1].

Zinc borate is a multifunctional boron based inorganic compound that is mainly used as flame retardant filler in various types of polymers. There are several studies which aim to synthesize different types of zinc borates which have the molecular formula of $4ZnO \cdot B_2O_3 \cdot H_2O$, $ZnO \cdot B_2O_3 \cdot 1.12H_2O$, $ZnO \cdot B_2O_3 \cdot 2H_2O$, $6ZnO \cdot 5B_2O_3 \cdot 3H_2O$, $ZnO \cdot 5B_2O_3 \cdot 4.5H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and $3ZnO \cdot 5B_2O_3 \cdot 14H_2O$ [2]. The most commonly used ones are $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and anhydrous one, $2ZnO \cdot 3B_2O_3$.

There are several types of approaches about synthesizing nano-sized metal borates like thermal evaporation, a sol-gel process followed by annealing, supercritical ethanol drying technique and chemical vapor deposition. However, high temperatures are needed for these methods and to obtain hydrated nanosized metal borates, new methods have to be developed [3]. Zinc borate is a type of metal borate additives and previous studies include synthesis of zinc borate by the reaction of zinc salts and borate salts or by the reaction of zinc oxide and boric acid [4]. In the second one, several parameters such as B_2O_3/ZnO molar ratio, reaction temperature, reaction time and amount of water have effects on synthesis of zinc borate [5].

There are several studies performed to produce zinc borate. Shi et al. [3, 6, 7] synthesized $4ZnO \cdot B_2O_3$ by using $ZnSO_4$ and $Na_2B_4O_7 \cdot 10H_2O$ as reactants in the presence of PEG300 as surfactant. Aim of the study was to synthesize nano-/microstructures with different morphologies which can be controlled by varying reaction parameters. Gönen et al. [5] synthesized zinc borate both from the reaction of zinc oxide with boric acid and borax decahydrate and zinc nitrate hexahydrate. To eliminate possible interactions between solvent and zinc borate samples, effect of supercritical ethanol drying of zinc borate was also investigated.

Zinc borates can be used as smoke and afterglow suppressant, corrosion inhibitor, anti-tracking agent, lubricant additive, char promoter, preservative in wood composites, flame retardant synergist, modifier of electrical and optical properties and wear resistance [3, 4, 7-10]. It also functions as mildew-stat and tannin-stain blocker for coatings [11].

3.5 mole hydrated zinc borate is the most commercial type of zinc borates. It has an unusual property of holding its hydration water till 290˚C. This thermal stability makes it attractive as a fire retardant additive for plastics. Important attributes of zinc borate including relatively low water solubility and low refractive index (1.58) permits the manufacture of transparent or translucent articles [11].

When comparing with other flame retardants, it is concluded that zinc borates have major advantages when processed with several kinds of polymers. The most crucial advantage is that zinc borates do not produce toxic and corrosive substances upon combustion process. Also, zinc borate is famous with its high dehydration temperature (290˚C) which offers ease for processing at high temperatures [7].

However, zinc borates have some disadvantages. For instance, using very large amount of them causes a difficulty of uniform dispersion in polymeric matrix. This is a remarkable problem that causes the mechanical properties of flame retardant polymeric materials to decrease sharply and flame retardant efficiency to reduce [4, 6, 7].

Recently, the production of nano-sized zinc borate species has been the subject of several studies and particle size of product has become extremely important for most of the applications. Also for industrial scale; the mean particle size of bulk solids governs the behavior of the particulate mass. Speed and type of mixing (high shear/low shear, higher pumping) play an important role in deciding the final size of the precipitated reaction product [5, 12].

Two major challenges occur in the production of nanoparticles; controlling of the particle size in the reaction step and prevention of nanoparticles' agglomeration [5]. Most of the studies in the literature have dealt with synthesizing and characterizing different types of zinc borate with the minimum particle size of final product and there have been limited number of works focus on selection of effective surfactant and its concentration on the reaction medium to decrease particle size [3, 6, 7, 13, 14]. In these studies, several experiments were performed to prevent agglomeration as a result of high surface energy of particles, to increase interaction between filler and the polymer matrix and to enrich resistance to fire without reducing mechanical properties. For instance; Ramazani et al. [15] investigated mechanical properties of polypropylene (PP)/zinc borate composites and they explained the reduction in mechanical properties were due to the lack of compatibility of zinc borate with PP matrix.

In this thesis, it is aimed to synthesize sub-micron sized zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) with the reaction of zinc oxide and boric acid. For this purpose, use of low molecular weight additive in the synthesis is considered so that the additive prevents the agglomeration and leads to a decrease in particle size. In the synthesis procedure, boric acid is dissolved in water and reaction is carried out at 85°C. After complete dissolution of boric acid; zinc oxide, low molecular weight additive and seed crystals of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ are added to this solution at a certain stoichiometric ratio. The reaction continues for a while by mixing, and the zinc borate formed is filtered, washed with hot water-methanol mixture in order to remove of residual boric acid and dried in ambient conditions [13].

This thesis consists of two main parts. As mentioned above, the first part focuses on the investigation of effect of type of surfactant and its concentration on the synthesis, properties and morphology of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$. Additionally, effect of using nano-sized zinc oxide as reactant on the final product is also investigated.

The second part of the study includes the use of synthesized zinc borates in the production of flame retardant poly(ethylene terephtalate) (PET) based composites.

Polymeric materials play an essential role in human life because of the extraordinary range of accessible properties like lightness and easy processing. However, polymers also have high flammability; commonly produce toxic or corrosive gases and smoke during burning. As a consequence, enhancing the flame retardancy is a primary challenge for spreading their applications.

Safety requirements are currently becoming more important in terms of reaction mechanism of polymer to fire and performance against fire while halogenated additives are not preferable because of proven negative effects on environment. Consequently, production and manufacturing of effective and environmentally friendly flame retardant materials for polymeric materials is a hot topic.

Recently, consumption of halogen-free flame retardants is more preferable for its environmental and health safety due to their nontoxic products during combustion. Thus, certain sectors such as aerospace industry, microelectronics, wire and cable manufacture are particularly interested in alternative non-halogenated flame retardants [7, 10].

Literature includes very diverse and efficient methods for enhancing polymer thermal stability and resistance to fire, which primarily depend on chemical specifications of the polymer considered, its decomposition route and the required level of fire safety and also the global or environmental performances of the resulting materials [16].

PET has aromatic groups in its structure and high carbon content that leads to high flammability. According to the literature [17], thermal degradation of PET is initiated by chain scission of the ester linkage, yielding carboxyl and vinyl ester groups. Swoboda et al. [18] investigated the effect of adding a PET chain extender to PET based composites and determined that; adding a chain extender (triphenyl phosphate (TPP)) to the structure enhanced flame retardant properties and increase mechanical properties such as tensile strength and elongation at break.

In the second part of the present study, as mentioned it is aimed to produce flame retardant PET based composites which mainly include sub-micron sized zinc borate which have been synthesized in the first part of the study. Using these sub-micron sized zinc borates, which means less amount in the composite, may provide improved flame retardancy and mechanical properties. PET based composite compositions were prepared by using a co-rotating twin screw extruder with synthesized zinc borates and synergists (boron phosphate (BPO_4) and triphenyl phosphate (TPP)). Composites were molded by injection molding machine. Then, they were characterized in terms of flammability and mechanical properties. Flammability of composites was tested by using a Limiting Oxygen Index (LOI) apparatus. Mechanical properties such as tensile strength, tensile modulus, elongation at break and impact strength were also studied.

CHAPTER 2

BACKGROUND

2.1 Boron and Its Properties

Boron is an element with an atomic number of 5 and having symbol B. The most common form of boron is amorphous boron, a dark powder, unreactive to oxygen, water, acids and alkalis. It has an ability to react with metals to form borides. Boron is a poor electrical conductor at standard temperatures but is a preferable conductor at high temperatures [19].

2.2 Metal Borates

Metal borates can occur in nature as mineral or synthetic form and find extensive industrial use in both mineral and synthetic forms. There are approximately 230 kinds of boron minerals in the nature. Borax (sodium borate decahydrate) and colemanite (calcium borate pentahydrate) are the most common types of natural metal borates. Crystalline metal borates contain different boron, oxygen, metal and hydrogen coordination in their structure. The structure may also include water molecules (in crystal form), non-borate ions and/or hydroxyl groups according to the production reaction. However, development of structure-stability relation is extremely important to synthesize metal borates with desirable properties [5, 20].

Metal borates can also be divided into two sub-branches according to their molecular water content: hydrated and anhydrous. So-called hydrated borates, most common used type in industry, have structures containing B-OH groups and also contain molecular water [11].

2.3 Zinc Borate

2.3.1 Properties of Zinc Borate

Zinc borate is an inorganic boron compound with a chemical composition of $xZnO \cdot yB_2O_3 \cdot zH_2O$. Water is often shown as a water of hydration in formulas for borates; in fact borates are rather complex hydroxide salts. There are various types of zinc borates commercially available, which release different amounts of hydration water. Common examples of zinc borates have following molecular formula: $4ZnO \cdot B_2O_3 \cdot H_2O$, $ZnO \cdot B_2O_3 \cdot 1.12H_2O$, $ZnO \cdot B_2O_3 \cdot 2H_2O$, $6ZnO \cdot 5B_2O_3 \cdot 3H_2O$, $ZnO \cdot 5B_2O_3 \cdot 4.5H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and $3ZnO \cdot 5B_2O_3 \cdot 14H_2O$ [2].

Zinc borates which have a chemical formula of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ are the most commonly used one. $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ holds about 13.5 wt % of its hydration water from 290 to 450˚C and absorbs 503 J/g for dehydration [21].

For 3.5 mole hydrated zinc borate; formation of a protective, cellular and vitreous char layer is promoted by released water and B_2O_3 (softens at 350˚C and flows above 500˚C). This layer acts as a good insulator, protects the underlying polymer or substrate from heat and oxygen and diverts the burning polymer to carbon rather than to fuel for gas phase combustion. Also this layer reduces the release of combustible gases since during burning and combustion of polymers; zinc borates dehydrate endothermically and heat is absorbed by the vaporized water and this vaporized water dilutes oxygen and gaseous flammable components. Zinc species in the condensed phase trigger the production of aliphatic hydrocarbons rather than benzene and other aromatics which cause an increase in crosslinking reactions and results in an increase in both smoke suppression and char formation [16, 21, 22].

There are several benefits (Table 2.1) of using zinc borate in the plastics industry which include use of zinc borate as a flame retardant and smoke suppressant alone or with other additives like antimony trioxide (Sb_2O_3) and aluminium trihydroxide ($Al(OH)_3$) [22]. Zinc borates are commonly used in halogen-containing systems and especially in poly(vinyl chloride) (PVC). Zinc borates significantly increase char formation and react with hydrogen chloride (HCl) which was resulted from the thermal decomposition of PVC. Then zinc chloride catalyzes dehydrohalogenation, promotes crosslinking which leads to an increase in char yield and decrease in smoke formation. Zinc borate also creates a porous ceramic-like residue, which has much better isolative properties than those of pure anhydrous alumina when it is used with aluminium trihydroxide (ATH). Zinc borate also accelerates magnesium hydroxide ($Mg(OH)_2$) dehydration, creates a ceramic-like structure with dehydrated MgO [21].

Table 2.1 Mechanism of action of zinc borate on different polymer matrices [12]

Polymer	**Benefit**
PVC	Smoke suppressant Flame retardant Synergist with Sb_2O_3 Lowers total fire retardant cost Char promoter
Polyolefins	Smoke suppressant Char promoter Afterglow suppressant Improves elongation properties Anti-arcing agent
Polyamides	Anti-tracking agent Synergist of halogen sources Afterglow suppressant Used in both halogen containing and halogen-free systems
Elastomers	Smoke suppressant Afterglow suppressant Char promoter Anti-arcing and anti-tracking agent
Epoxy resins	Smoke suppressant Char promoter Partial or completely replace with Sb_2O_3

2.3.2 Synthesis of 3.5 Mole Hydrated Zinc Borate

Zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$) is generally produced with the reaction between zinc oxide and boric acid. Boric acid is dissolved in water and zinc oxide and seed crystal of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ are added to this solution at a certain stoichiometric ratio related to the reaction given below (2.1). Seed crystal amount, mixing rate, reaction time and reaction temperature are the parameters of the synthesis [12, 16]. The reaction continues for a while by mixing and final zinc borate product is filtered, dried and ground [2]. The synthesis reaction of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ is in Reaction 2.1:

$$6B(OH)_3(aq) + 2ZnO(s) \rightarrow 2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O(s) + 5.5H_2O(l) \qquad (2.1)$$

In the present study same synthesis method was used to produce 3.5 mole hydrated zinc borate by keeping the synthesis parameters constant given above. In addition, nine different low molecular weight additive or surfactants were added to the reaction medium. Among these surfactants, some of them were studied with different concentrations. Besides, using nano-sized zinc oxide as reactant was also considered.

2.3.3 Literature Survey on Zinc Borate Synthesis

Shi et al. [3, 6] aimed easier and flexible hydrothermal route for the synthesis of $4ZnO \cdot B_2O_3 \cdot H_2O$ and successfully synthesized nano and micro structures with different morphologies with a surfactant-assisted hydrothermal method. For $4ZnO \cdot B_2O_3 \cdot H_2O$ synthesis, $ZnSO_4 \cdot H_2O$ and poly(ethylene glycol) 300 (PEG300) were mixed completely and added slowly to $Na_2B_4O_7 \cdot 10H_2O$ and water mixture. Solution was mixed for 20 minutes; sealed and maintained in an autoclave at 100°C for 24 hours. Synthesized final product was washed with distilled water and ethanol, and dried at 80°C for 24 hours. The influence of hydrothermal reaction parameters including the initial pH, reaction temperature and time, quantity of the surfactant (PEG 300)) and concentrations of reactants on the formation of final zinc borate product were investigated. It was observed that surfactant has a crucial effect on the morphology of the final product. Synthesized nanorods have dimensions with 150-800 nm width, 70 nm thickness and few microns length.

In addition; Shi et al. made some preliminary studies about fungistatic and bacteriostatic effect of zinc borate nanocrystals on six different fungis[7]. They also synthesized lamellar-like 2D and 3D $4ZnO\cdot B_2O_3\cdot H_2O$ nanoparticles and by same method. Lamellar-like particles have dimensions which were around several hundred nanometers in diameter and about 30 nm in thickness. The microsphere structures had different diameters, and the secondary structures were made from rod-like particles with different size and morphology. It was also concluded that surfactant ratio, temperature and reaction time directly affect particle size of the final product.

Tian et al. [4, 9] aimed to synthesize three mole hydrated hydrophobic zinc borate nanoplate like structures (with a formula of $Zn_2B_6O_{11}\cdot 3H_2O$) via one-step precipitation reaction to decrease the friction coefficient of base oil. Zinc sulfate heptahydrate ($ZnSO_4\cdot 7H_2O$) was added drop wise to sodium borate decahydrate ($Na_2B_4O_7\cdot 10H_2O$), ethanol and oleic acid (OA) mixture. Then the solution was heated to 70˚C and mixed for 6.5 hours. Final product filtered then washed with ethanol and distilled water and dried at 80˚C. It was found that optimal amount of OA was 1% of weight of zinc borate and when the reactant ratio was 1.5:1 – 2:1; nanoplate like structure with average diameters of 100–500 nm and thickness of 30±5 nm was observed. At the same time, active ratio measurements showed that final hydrophobic zinc borate nanodiscs sharply decreased the friction coefficient of base oil.

Ting et al. [8] prepared a nano zinc borate $ZnO\cdot yB_2O_3\cdot zH_2O$ (y=0.3-0.4, z=1.0-1.4) with netlike amorphous structure with the method called coordination homogeneous precipitation. Influence of reaction time on the morphology was investigated and it was found that fibers had length about hundreds of nanometers and diameter about 15 nm, some of which entangled each other to form dendritic or interconnected networks. Final zinc borate product was used as flame retardant additive for poly(propylene)(PP) and high density poly(ethylene)(HDPE), the residue of carbon ratio of PP and HDPE were 75% and 63% when the sample content was about 12 wt %, respectively.

Shete et al. [14] studied mixing parameters affecting product morphology and conversion of zinc oxide to zinc borate ($2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$) with a fluid–solid reaction. The purpose of their study was to perform experiment to comment on the effect of process variables. Boric acid and zinc oxide were used to synthesize zinc borate. To determine the effects of mixing on the size distribution of a product made in a batch heterogeneous reaction; speed of agitation, impeller type, mean initial particle size of zinc oxide, temperature and initial concentration of boric acid were studied as experimental parameters. As a conclusion of their study; to accelerate conversion and decrease zinc borate particle size; smaller zinc oxide should be used with a impeller which has a higher speed than the minimum suspension speed.

Chang et al. [23] sintered mixed powders which was containing Zn nanoparticles and boron oxide (B_2O_3) in the presence of Ag catalysts in argon gas to synthesize zinc borate (ZnB_4O_7) nanotubes. The nanotubes of ZnB_4O_7 had a diameter of several tens of nanometers and a length of several tens of micrometers. Also solid-phase reaction mechanism of synthesis ZnB_4O_7 nanotubes from crystalline particles was investigated.

Gürhan et al. [13] studied the production of 3.5 mole hydrated zinc borate and investigated the synthesis parameters on the final product properties with considering reaction kinetics. Reaction rate, reaction completion time, composition and particle size distribution of zinc borate product were determined by changing the boric acid to zinc oxide ratio, the particle size of zinc oxide, stirring rate, temperature and the size of seed crystals. It was concluded that high stirring rates (till 800 rpm) decreases particles size of final product whereas particles size of zinc oxide and size of zinc borate seed have no significant effect on the crystal dimensions of final zinc borate product.

Gönen et al. [5] obtained zinc borates either from zinc oxide and boric acid ($2ZnO\cdot 3B_2O_3\cdot 3H_2O$) or borax decahydrate and zinc nitrate hexahydrate ($ZnO\cdot B_2O_3\cdot 2H_2O$) with supercritical ethanol drying method. It was concluded that both products decomposed into nano zinc oxide, particle size decreased from 10µm to 2µm. Furthermore, critical temperature and ethanol drying played an important role in decomposition of zinc borate products.

Savrık et al. [24] synthesized zinc borate both by inverse emulsion and precipitation technique and used it as lubricating oil additive to examine the effect of final product on friction coefficient of base oil. Different morphologies were observed in both synthesis methods. These particles were transformed as nano-sized zinc borate species by supercritical ethanol drying which decreased surface energy. According to four-ball wear test results, final zinc borate products improved the lubricant properties of base oil.

Mergen et al. [25] synthesized zinc borates with liquid emulsion method to observe the effect of different reaction temperature, time and effect of addition of phosphoric acid (D_2EHPA) to reaction medium. As a result of their studies, three mole hydrated zinc borate having different morphologies were synthesized. However, agglomeration could not be prevented because of high surface energies of nanoparticles.

Köytepe et al. [26] developed polyimide–zinc borate (PI/zinc borate) hybrid nanocomposite films from the poly(amic acid) of 2,6-diaminopyridine and different weight percentages (1, 5, 10 wt%) of zinc borate. They also used sorbitan monododecanoate (span 80), propanol-2 and kerosene as surfactants. It was concluded that thermal stability of the composite films increased with homogeneous dispersion of zinc borate in the polymer.

2.3.4 Experimental Techniques for Material Characterization

In this section, theoretical informations about the methods used for characterizing zinc borate particles are given. Solid zinc borate particles were characterized by X-Ray Diffractometer (XRD) to comment on the crystalline structure of zinc borate. Thermal gravimetric analyses (TGA) were performed for thermal stability and scanning electron microscope was used to investigate the morphology of zinc borate particles.

2.3.4.1 X-Ray Diffraction (XRD) Analysis

X-ray diffraction is a widely used tool which can provide the information about both the crystalline and amorphous states for almost all solids under the right conditions. X-ray diffractometers generally analyze single crystal or powder. Single-crystal studies allow the absolute configurational determination of polymeric materials that have high degrees of crystallinity. Powder X-ray spectroscopy can employ smaller crystalline samples from one to several hundred nanometers. These crystallites have broadened peak profiles as a result of incomplete destructive interference at angles near the Bragg angle defined as:

$$n\lambda = 2d \sin \theta \tag{2.2}$$

where n is the order of a reflection, λ is the wavelength, d is the distance between parallel lattice planes, and θ is the angle between the incident beam and a lattice plane known as the Bragg angle. This broadening allows determination of crystallite size and size distribution. There are two types of X-Ray scattering; wide angle X-Ray scattering (WAXS) is used for the investigation of small scale structures, small angle X-Ray scattering (SAXS) is used to study large scale morphological structures [27, 28]. XRD equipment which was used in this study is shown in Figure 2.1.

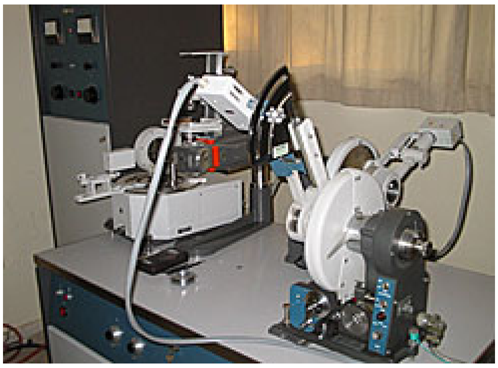


Figure 2.1 XRD equipment [29]

2.3.4.2 Thermogravimetric Analysis (TGA)

Major instrumentation involved with the generation of thermal property behavior of materials includes thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), differential thermal analysis (DTA), torsional braid analysis (TBA), thermomechanical analysis (TMA), and pyrolysis gas chromatography (PGC) [27]. Thermogravimetry (TG) is a type of thermal analysis which examines the mass change of a sample as a function of temperature [30].

In TGA the mass loss of the sample is recorded with respect to increasing temperature. The basic instrumental requirements are simple: a precision balance, a programmable furnace, and a recorder. Modern instruments, however, tend to be automated and include software for data reduction. Most TGA devices are configured for vacuum and/or variable atmospheres like air, nitrogen, or oxygen [30, 31]. Usual sample sizes for commercial instruments are in the range from 0.1 mg to 10 g with heating rates from 0.1 to 50˚C/min. The most commonly employed heating rates are 10, 15, 20, 25, and 30˚C/min [27].

In a single classic TGA system, specimen powder is placed in a platinum refractory pan. The pan, which is in the hot zone of the furnace, is suspended from a high sensibility balance. A thermocouple encloses proximity to the specimen but not in contact, so as not to interfere with the free float of the balance. The balances are electronically balanced so that the specimen pan does not move when the specimen gains or losses weight. The balances associated with TGA are highly sensitive, with resolutions down to 1 µg [31].

Thermal actions such as glass transition or melting may not change the mass of the sample but in TGA there are some very crucial exceptions which include desorption, absorption, sublimation, vaporization, oxidation, reduction and decomposition. The onset of volatilization is proportional to the boiling point of the liquid. The residue remaining at high temperature represents the percent ash content of the sample. Figure 2.2 shows scheme of the TGA instrument [30, 32].

Sample purity, identification, solvent retention, reaction rate, activation energy, heat of reaction, polymer decomposition temperature, thermal stability in inert atmospheres, oxidative stability, compositional analysis of rubbers and elastomers and ash, inert filler, moisture, residual solvent, plasticizer of polymer can be determined by TGA [27, 33].

Characteristic of TGA curves directly influenced by the shape and nature of the sample holder, mass, volume and physical form of the sample, the nature and pressure of the atmosphere in the sample chamber and the scanning rate [32].

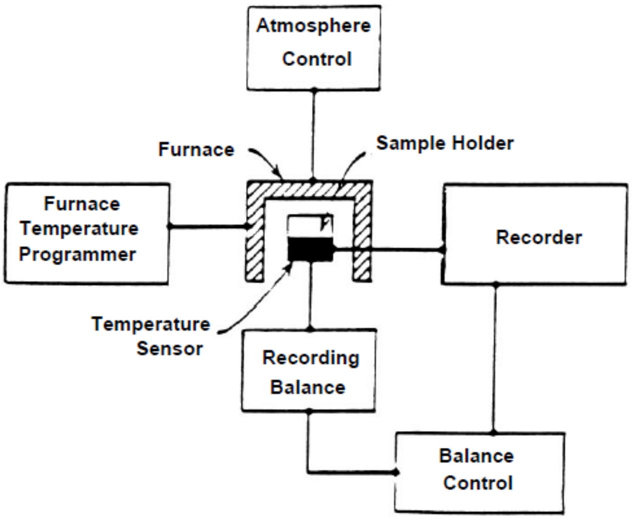


Figure 2.2 Scheme of the TGA Instrument [32]

2.3.4.3 Scanning Electron Microscopy (SEM)

When the domain size is in the range from < 1 µm to 10 nm, scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM) are necessary. Samples in the SEM can be examined for general morphology, as freeze fractured surfaces or as microtome blocks of solid bulk samples. The color difference in the image is determined by the sample morphology and this contrast can be achieved by any one or combination of the following methods: i) Solvent etching; ii) Osmic acid (O_5O_4) staining; iii) Ruthenium tetroxide (RuO_4) staining [32].

Figure 2.3 SEM Instrument [34]

SEM is generally used to observe surfaces of materials. Usually, a SEM micrograph is formed by an electron beam which is scanned across the surface of a sample in a series of lines and frames at any given moment; the specimen is bombarded with electrons over a very small area. These backscattered electrons are elastically reflected with no loss of energy however they may be absorbed and increase: i) secondary electrons of very low energy; ii) visible light emission and iii) electric currents within the specimen [35]. This secondary electron image (SEI) gives information about the topography of the sample surface.

Removing the surface layer of the material is crucially important during investigation of the morphology of the material. Only when adhesion between the phases is poor, that reflects the bulk morphology can be created by fracturing the sample. Sample is first annealed in liquid nitrogen and then fractured when adhesion between the phases is poor to prevent plastic deformation.

Etching is another method of removing the surface layer. This process may be carried out by chemical etching, solvent etching and ion beam etching [36]

Samples suitable for SEM measurements include most solids which are stable under vacuum (metals, ceramics, polymers, minerals). Carbon or gold is used for coating of Non-conducting samples to prevent electrostatic charging.

2.4 Poly(ethylene terephtalate) (PET) and Its Properties

Poly(ethylene terephthalate) (PET) is a thermoplastic polymer resin of the polyester family which can be used in synthetic fibers; beverage and liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber since 1966.

The production of these polymers takes place in two stages:
1. Esterification of dimethyl terephthalate with ethylene glycol
2. Polycondensation

Typical properties of PET are:

- high hardness, stiffness, strength, abrasion resistance and dimensional stability
- good toughness and creep resistance even at low temperatures
- low friction and water absorption and high
- white in the semi-crystalline state and transparent in the amorphous state
- good electrical insulating properties
- high tracking resistance
- resistant to water at room temperature, dilute acids, neutral and acidic salts, alcohol, ethers, oils, fats, percolated, aromatic and aliphatic hydrocarbons but not resistant to alkalis, superheated steam, ketones, phenols, esters, oxidizing acids and chlorinated hydrocarbons
- resistant to stress cracking, weathering and hot air
- burns with black smoke with a sweet aromatic smell

PET can be used in applications such as bottles, audio tapes, shrink packaging, rollers, wheels, switches, pump parts, valves.

2.5 Thermal Decomposition

The thermal decomposition of a polymer is a process which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms (200–400 kJ/mol for most C–C polymers). Weakest bonds and presence or absence of oxygen in the solid and gas phases are main factors affecting the decomposition mechanism. Non-oxidizing thermal degradation and oxidizing thermal degradation can be distinguished between each other since thermal decomposition is the result of a combination of heat and oxygen [37].

There are four chemical mechanisms directly related to thermal decomposition of polymers: i) random chain unzipping; ii) chain-end unzipping, in which the polymer depolymerizes from the chain ends; iii) elimination of pendant groups without breaking of the backbone; iv) crosslinking [21].

Non-oxidizing thermal degradation usually starts with chain unzipping under the simple effect of temperature (pyrolysis). This unzipping includes changing degrees of material depolymerization. The unzipping depends on several factors: the presence of oxygen atoms in the structure, former residues of oxidation, chemical defects in polymer chains and the existence of weak bonds along the chain which can initiate unzipping reactions.

Chain unzipping can occur in two ways:

- free radical formation
- hydrogen atom migration and the formation of two stable molecules one of which has a reactive double bond between carbon atoms.

The polymeric material reacts with oxygen in the air and generates a variety of low molecular weight products like carboxylic acids, alcohols, ketones, aldehydes, etc in oxidizing thermal conditions. Hydrogen atoms from the polymer chains control the propagation rate of the degradation process. C–H bond energy is the main factor affects on oxidation stability of polymer. Polymer degradation is occurred via non-oxidizing thermal decomposition only if combustion temperatures are above

300°C. As a conclusion of thermal decomposition low molecular weight compounds results oxidation occurs in the gas phase.

2.6 Polymer Combustion Process and Burning Concept

Polymers can be used in wide-spread structural applications due to their long-term resistance to mechanical loads, elasticity, and temperature resistant attributes. But as a result of high carbon and oxygen constitution, polymers are highly combustible materials. Polymers are used in widespread applications like buildings, various engineering applications such as electrical, computer or mining and other industries so this scope makes flame retardancy an important requirement for many of them [10, 26].

Burning process of polymers starts with an ignition event when a source of heat contacts with a fuel which was occurred as a result of heating of the polymer. This event starts a flow of flammable degradation products which react with oxygen from the air to produce flame and heat. Some of the heat is transferred back to the surface of the fuel, maintaining the flow of flammable volatile degradation products [21, 38].

Ignitability is associated via time to ignite or minimum time for ignition and also directly related with how quickly the surface can be raised to the temperature of ignition. Unlike other materials, polymers melt before thermal decomposition. Usually, at lower heat rates, melting causes ignition and also causes dripping of polymer which removes heat from the surface. This phenomenon is important for flame retardancy of uncharrable polymers. On the contrary, at a higher heat rates, ignition may occur before the surface is heated to sufficient depth for the melted material to flow and this means that the material is easy to ignite.

To burn a polymeric material, thermal energy (heat) must be added to the material to raise its temperature. This thermal energy can be obtained from; i) external source; ii) adjacent flame as energy feedback in the case of flame spreading. The heat absorbed by a polymeric material during the burning process depends on characteristic of flux, absorption characteristic of polymer, surface reflectance of polymer [22].

Char formation is another concept when burning of a polymer is considered. Char formation for polymeric materials proceeds through four stages: i) crosslinking; ii) aromatization; iii) fusion of aromatics; iv) graphitization. Although many polymers tend to crosslink at thermal decomposition firstly, char is formed when crosslinked polymer contains aromatic fragments and/or conjugated double bonds and is inclined to aromatization during the thermal decomposition [21].

The combustion process involves: i) reducing agents and ii) oxidizing agent (generally the oxygen in the air). Combustion usually occurs with an increase in the temperature of the polymer due to a heat source that causes polymer bond separation. A combustible gaseous mixture named “fuel” occurs as a result of the volatile fraction of the polymer compositions formed and diffused into the air. This gaseous mixture ignites when the auto-ignition temperature is reached or else the fuel can also ignite at flash point (lower temperature) during reaction with an external source of intense energy (spark, flame, etc.) There are a lot of heat transfer processes during combustion and burning in polymer surface.

2.7 Flame Retardancy Concept

Each year fires leading to thousands of injuries, deaths and billion dollars financial lose. Especially personal losses occur mostly from flammable wall coverings, curtains and furnitures in residences or from fires and explosions occurred as a result of accidents in transportation vehicles.

To increase protection and escape time from fires, methods to enhance the flame retardancy of consumer goods have been developed. Flame retardants are additives for both natural and synthetic materials, intended to stop or to inhibit the polymer combustion process. Chemicals that are used as flame retardants can be in inorganic, organic, mineral, halogen-containing, phosphorous-containing, nitrogen-containing, silicon-containing, boron-containing structure [22].

Nowadays, many countries demand comprehensive safety identification on new compounds and materials for their effect on human and environmental before they are allowed to be put in the market. To determine potential hazards of flame retardants on human and environment; data about toxicity, biodegradability and bioaccumulation potential, combustion products and stability of the product at the processing temperature are needed [22].

There are many parameters and long list of processing factors to select consistent type of flame retardant for a suitable type of polymeric material before a material can be accepted for use. Flame retardants are generally recommended for use with those plastics with which they are expected to be effective in improving fire performance without excessive loss of other characteristic properties. It is important to be effective in certain plastics also with an acceptable cost. So development of a polymeric material that meets all of these requirements involves finding the optimum combination of polymers, flame retardants, synergists, stabilizers, processing aids and all other additives. This requires a great deal of time, effort and expense [22].

Accordingly ideal flame retardant material has [39]:

- a high resistance to ignition and flame propagation
- a low rate of combustion
- to decrease smoke generation
- to produce non-toxic gases during burning
- acceptability in appearance and properties for specific end-uses
- little or no economic penalty
- to be efficient in small amounts
- to require no unusual processing conditions
- to be applicable in commercial equipments
- to be reproducible

Approaches to the flame retardation of a polymeric material are based on [39]:

- chemical and physical properties of the polymer and flame retardant additive
- polymer degradation phases
- polymeric materials combustion mechanism and its dependence on the nature of the degradation products

2.8 Types of Flame Retardants

There are eight types of flame retardants which can be used for various types of polymer composites:

- Mineral Flame Retardants
- Halogenated Flame Retardants
- Phosphorus-Based Flame Retardants
- Nitrogen-Based Flame Retardants
- Silicon-Based Flame Retardants
- Boron based Flame Retardants
- Intumescent Flame Retardants
- Nanometric particles

Metal hydroxides and hydroxycarbonates are the most widespread used mineral flame retardants. These inorganic fillers show physical mode of action. Increasing temperature causes these fillers to decompose endothermically and therefore to absorb energy. Aluminium tri-hydroxide (ATH) and magnesium di-hydroxide (MDH) are two most common used metal hydroxides. However, ATH containing flame retardant polymers are preferable at high loading levels. ATH is generally used for polymers having with low processing temperatures due to its low decomposition temperature [16].

Figure 2.4 shows the consumption of flame retardants across Europe in 2005. Highest percent belongs to aluminium tri-hydroxide with 51%.

Halogen-containing flame retardants are the most widespread class of retardants. But nowadays, because of toxicological and environmental affects, halogen flame retardant additives are not preferable and replaced with non-halogenated flame retardants exhibiting enhanced efficiency of flame retardancy [7, 16].

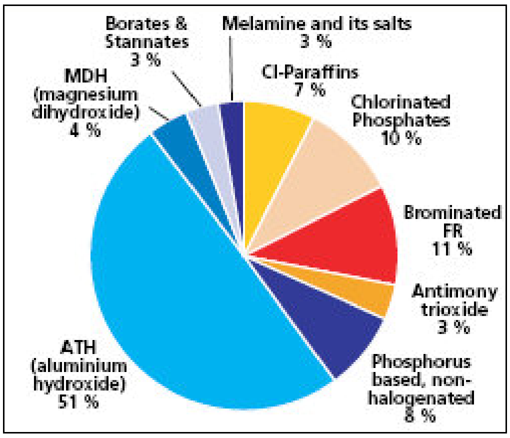


Figure 2.4 Consumption of flame retardants in Europe (2005) [40]

Effectiveness of halogen-containing flame retardants depend on releasing halogen radical or halogen halide below the decomposition temperature of the polymer [21]. Type of halogen is the other factor changes effectiveness of flame retardant. It was concluded that halogens and halogen compounds do not affect the oxidation of carbon into CO_2. Moreover, they essentially inhibit the oxidation of CO and CO_2 and the formation of formaldehyde during combustion of methane [22].

Fluorine and iodine-based compounds seldomly used in polymer composites because they do not interfere with the polymer combustion process. In contrast, bromine and chlorine take part in the combustion process since they are easy to release because of their low bonding energy with carbon atoms. Tetrabromobisphenol A (TBBPA) is the most widely used halogenated flame retardant. It is a reactive flame retardant mainly incorporated with epoxy resins for printed circuit boards [16].

Phosphorus-based flame retardant products are another common type including phosphates, phosphonates, phosphine oxides, phosphinates and red phosphorus. Phosphorus-based flame retardants act most of its flame retardant function in the condensed phase (including both the solid and liquid phases, because various degrees of melting are involved at fire temperatures) and perform effectively in oxygen- or nitrogen-containing polymers which could be either heterochain polymers or polymers with these elements in pendant groups. Phosphorous containing compounds increase the amount of carbonaceous char formed by one or both of these two mechanisms: i) reduction of the chemical reactions involved in decomposition in favor of reactions yielding carbon rather than CO or CO_2; ii) formation of protective char layer on the surface [22].

Red phosphorus is the most commonly used source of phosphorus-based flame retardant. Using less than 10%, it is highly effective in polymers such as polyamides, polyesters and polyurethanes. However, it can release highly toxic phosphine (PH_3) through reaction with moisture because of its poor thermal stability throughout the melting process. Another type of phosphorus-based flame retardants; ammonium polyphosphates (APP) are known to be stable and non-volatile compounds. Decomposition temperature of short chain APP is 150˚C while decomposition temperature of long chain APP is 300˚C. Therefore it is crucially important to select the suitable type of APP for polymer [16].

Melamine is a thermally stable crystalline nitrogen-based flame retardant that has a melting point of 345˚C, sublimation point of 350˚C and contains 67 wt% nitrogen atoms. During sublimation, high energy is absorbed that decrease the temperature [16]. Their common advantages are low toxicity and lack of toxic combustion products during burning process as well as their low evolution of smoke. Today, nitrogen-based flame retardants (melamine compounds) are preferred in several applications such as polyurethane flexible foams, nylons, polyolefins, intumescent paints, textiles and wallpapers [22].

Silicon-based flame retardants (silicones, silicas, organosilanes, silsesquioxanes and silicates) can also be effective in small amounts and improve flame retardancy when they are added to polymers. They can be also used such as; i) additives incorporated to polymer; ii) copolymers or iii) the main polymer matrix [16].

Boron additives have also synergistic effect with other flame retardants and attractive because of lower cost than other synergists like antimony oxide. Zinc borate, is used as flame retardant additive instead of antimony oxide in unsaturated polyesters, polypropylene and flexible PVC. Boron compounds are also used to decrease and eliminate afterglow in halogen-containing compositions. Especially for zinc borate; low specific gravity, low toxicity and nearly same refractive index with polymers are factors making this compound preferable. Boron-based flame retardants act in two different mechanism: i) redirecting the decomposition route of carbon formation rather than CO or CO_2 and forms char ; ii) forms a protective layer on the surface and prevents the diffusion through the surface which causes oxidation of polymer matrix [22].

Main aim to produce intumescent systems is to protect fabrics, wood and coatings from burning. Intumescence means formation of a carbonized layer on the surface of the polymer during thermal degradation. This cellular insulating barrier having foam-like structure (whose density decreases with respect to temperature), reduces heat transfer between the heat source and the underlying polymer surface. It blocks fuel and mass transfer between polymer, stops the flame formation, prevent the diffusion of oxygen into the material. Intumescent systems require three main components: i) carbonizing agent; ii) acid source (promotes dehydration of the carbonizing agent; iii) blowing agent [16, 21].

Nanometric particles are materials that cause an enhancement in thermal, mechanical and flame retardancy properties when dispersed uniformly in polymer matrices. They cause a reduction of the loading rate of filler since the interfacial area between the polymer and the addtive is hugely increased. Also nanometer particles have some special properties such as low melting point, low density and high surface area [43]. Nanoparticles can be investigated as: i) layered materials (2D nanoparticles); ii) fibrous particles (1D nanoparticles); iii) particulate materials (0D nanoparticles). Uniform distribution of nano-particles in polymer matrix during process cause a considerable decrease in flammability, increase in thermal stability and limiting oxygen index (LOI) value.

As a conclusion, in order to select the suitable type of flame retardant and to enhance flame retardancy properties; following criteria must be considered:

- processing conditions of polymer
- compatibility of additive flame retardant with polymer
- cost

- environmental concerns

2.9 Flame Retardant Mechanism

Although flame retardants have varying characteristic structures, general mechanism of actions is applicable for most of polymers. But difference comes from gaseous and condensed phase active flame retardants [16].

Gaseous phase active flame retardants perform primarily capturing free radicals which cause branching of radical chain reactions in the flame. Other types dehydrate endothermically moreover the hydrate water vaporizes, absorbs heat and dilute oxygen and flammable compounds in gaseous state. This decreases the rate of combustion and extinguishes the flame [41].

Charring is the most general condensed phase mechanism. It could be promoted by: i) chemical interaction between flame retardant and polymer; ii) physical retention of the polymer in the condensed phase or iii) catalysis or oxidative dehydrogenation. Gas phase and condensed phase actions during burning is shown in Figure 2.5.

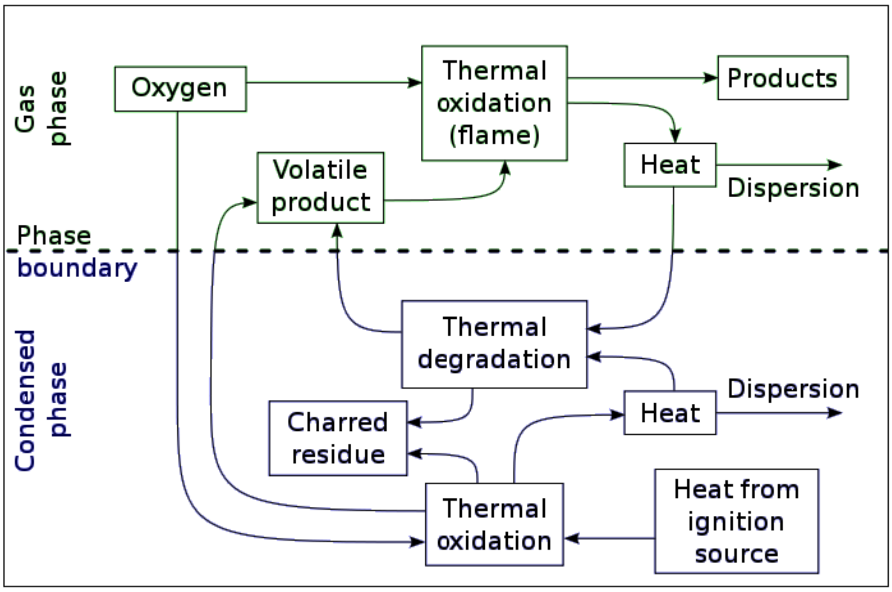


Figure 2.5 Gas phase and condensed phase actions during burning [42]

Flame retardant systems can either act physically or chemically. They can be related with the various processes involved in polymer combustion (ignition, heating, pyrolysis, propagation of thermal degradation). Modes of actions for flame retardants in polymer composites can be divided into two parts as physical action and chemical action.

The endothermic decomposition of some flame retardant additives induces a temperature decrease by heat consumption. This involves cooling of the reaction medium below to the polymer combustion temperature. Some flame retardants show physical mode of action like magnesium hydroxide [$Mg(OH)_2$] and aluminum trihydrate [$Al(OH)_3$] which holds water vapor till approximately 200 and 300˚C, respectively.

In addition, some flame retardant additives accelerates formation of a protective solid or gaseous layer between the gaseous phase and polymer surface where thermal degradation occurs and this layer limits the transfer of combustible volatile gases and oxygen. As a result, quantity of decomposition gases produced is decreased while combustion process was occurred because of the separation of oxygen.

Chemical mode of action can be observed in either the gas or the condensed phase. In the gaseous phase, coordination of flame retardant additives that release specific radicals (e.g. Cl・ and Br・) stops the free-radical mechanism of the combustion process. These specific radicals can react with highly reactive species (such as H・ and OH・) to form less reactive or inert molecules. This modification causes a decrease in the heat given during the reaction which leads to a reduction in temperature and therefore a decrease in the fuel produced.

In the condensed phase, two types of flame retardancy mechanisms are possible: first one, flame retardants quicken breaking of polymer chains so that polymer can drip and move away from burning zone. Second one, flame retardant carbonizes a layer at the polymer surface which performs as a physical insulating layer between the gas and the condensed phase.

Flame retardants can also be classified as:

- *Additive flame retardants*: are macromolecules like hybrids, mineral fillers or organic compounds which generally incorporated during the transformation process and do not react with the polymer but only interact when the fire starts.
- *Reactive flame retardants*: are generally introduced into the polymer during synthesis (usually as monomers) or in a post-reaction process and integrated in the polymer structure [16].

2.10 Flame Retardant Synergism

There is any kind of flame retardant that will act in an exact flame retardant behaviour. The concept of synergism is used to define flame retardant formulations and increase efficiency of single flame retardant. Chemical materials or flame retardants are always accompanied by one or several other additives, most commonly performs endothermically. This combination is called synergism [21]. Synergists have achieved great importance nowadays because they are less expensive than a single flame retardant moreover they increase flame retardancy efficiency without decreasing other properties [22].

Nanoparticles alone are proven to be insufficient for enhancing fire resistance to meet the required standards. However, their combination with other flame retardants such as phosphorous-based or boron-based compounds may be a very effective approach to increase flame retardancy [16].

Two most common examples to flame retardant synergism are halogens with antimony compounds and phosphorous with nitrogen compounds. Apart from antimony oxide, halogen-containing flame retardants can be synergistic with bismuth oxide (Bi_2O_3), tin oxide (SnO_2), molybdenum trioxide (MoO_3), iron (III) oxide (Fe_2O_3), zinc borate, zinc sulfide and zinc oxide. In some flame retardant compositions these compounds can be replaced partially by Sb_2O_3. In many occasions these metal oxides also enhance smoke suppression properties [21].

Fontaine et al. [44] observed the performance of different types zinc borates and synergistic effect of them with neutralized intumescent fire retardant (NIFR) in polypropylene (PP) composites. The selection of zinc borate type was directly related to the processing temperature of the polymer. Small addition of zinc borate leaded to a considerable improvement in fire retardant properties and this was explained by the intumescent layer on the flammable surface.

2.11 Literature Survey on Flammability of PET

There are several studies based on flammability of PET composites. In this section; flammability studies including both zinc borate and PET based composites are discussed.

Kılınç et al. [2] synthesized 3.5 mole hydrated zinc borate (with reaction of zinc oxide and boric acid) and boron phosphate then prepared PET based flame retardant composites which mainly included synthesized products. In zinc borate synthesis they investigated effects of reaction parameters (seed amount, presence of baffle, stirring rate and particle size of zinc oxide) on reaction kinetics and final product size. In the characterization part of the polymer composites, according to LOI results; 5% triphenyl phosphate (TPP) and 5% boron phosphate increased LOI value of neat PET from 21% to 36%. Moreover, mechanical properties of pure PET increased with addition of flame retardant additives especially when they were used with TPP.

Swoboda et al. [18] worked on flame retardancy properties of recycled PET blends containing polycarbonate (PC) and triphenyl phosphite (TPP). PET and PC first melt blended with a catalyst of transestherification allowing the compatibilization of the blend, before adding TPP. TPP was used to stop the transestherification reaction between PET and PC, avoiding chain breaking. TPP acts as a chain extender in PET matrix. TPP was also acted as a flame retardant in pure PET, pure PC and their different formulations. In addition, compositions of PET/PC/TPP increased tensile modulus of neat recycled PET by 30%.

Wang et al. [45] used modified nano-hydrotalcite as flame-retardant fillers for PET based composites. A flame-retardant composition was prepared from layered hydrotalcite (LDH) dispersed in brominated polystyrene (PBS) solution and then solvent evaporation from the dissolved PBS samples. Inorganic flame retardant LDH was favorable for this study not only it released its chemically combined water of hydration to cool the system, thereby delaying or inhibiting the ignition of PET but also it had a low cost compared to other flame-retardants. In addition, it is easy handling and relatively nontoxic. Especially, magnesium oxide (MgO) and alumina oxide (Al_2O_3), occurred as a result of decomposition of LDH, can absorb toxic gases that were released from the halogenated flame-retardant and this was another factor for selecting LDH. Surface treatment of LDH was also crucial because in this way high surface tension of nano-LDH particles was reduced and the large size agglomerates can be prevented into a certain extent They have objected that LDH was an effective flame retardant and there were no obvious decrease in mechanical properties of LDH/PBS based PET.

Ramazani et al. [15] studied the effects of filler compositions of zinc borate and aluminum hydroxide on properties of polypropylene (PP). They also used maleic anhydrate grafted polypropylene and calcium stearate to increase the interaction between filler and polymeric matrix. ATH containing polypropylene increased mechanical properties of composites but it slightly decrease limiting oxygen index (LOI) value. Increasing zinc borate amount, in all samples resulted a reduction in tensile strength and elongation at break and increase in tensile modulus. Zinc borate addition to ATH-containing composites caused an increase in LOI.

Bourbigot et al. [10] aimed to study the effect of zinc borate on flame retardant properties of halogen-free ethylene vinyl acetate - ATH (EVA- ATH) and EVA-magnesium hydroxide ($Mg(OH)_2$) flame-retardant composites. The first part of the work was based on determination of the fire performances and the second part of the work concerned about the thermal behavior of flame retardant compositions. It was observed that the decomposition of ATH and zinc borate to Al_2O_3 and B_2O_3, respectively, during the heating of the polymer resulted in an increase of the ignition time and yielded char production.

Yıldız et al. [46] prepared polyurethane zinc borate composites to enhance the flame retardancy of the pure polyurethane (PU) which was produced for artificial leather. Zinc borate was added into PU matrix by the amount of 0.5–7 percent by weight and it did not decrease mechanical properties of PU sharply while flame retardancy and oxidative stability increased.

Agrawal et al. [47] prepared water-insoluble complexes by reaction of boric acid, pentaerythritol, and metal salts while studying the effect of zinc-borate complex with respect to gel time, exotherm peak temperature, tensile strength, elongation at break, nitroglycerine absorption and flame retardancy. In addition synthesis, characterization, and evaluation of a zinc-pentaerythritol-boric acid complex as a flame-retardant filler for unsaturated polyester was investigated. Further, it was observed that the zinc-borate also acted as a synergist with antimony trioxide (Sb_2O_3) similar to other metal oxide based fillers. They concluded that zinc-borate complex is an efficient flame-retardant additive for unsaturated polyesters.

Motivation of the present study is to synthesize 3.5 mole hydrated zinc borate particles having sub-micron particle size and to prevent agglomeration of synthesized zinc borate particles by adding water-soluble low molecular weight additives or surfactants to reaction medium. It is expected that, these surfactants may cover the surface of zinc borates during reaction and prevent crystal growth. After synthesis of zinc borate, the preparation and characterization of flame retardant PET based composites which include synthesized zinc borate with/without other flame retardant synergists are also performed. The composites are characterized in terms of flame retardancy and mechanical properties.

2.12 Processing and Preparation of Flame Retardant Composites

Polymer processing can be divided into two broad areas. The first one is the processing of the polymer into pellets or powder form. The second one describes the process of converting polymeric materials into useful standardized shapes. The choice of a particular processing technique is determined by part design, choice of material, production requirements and cost–performance considerations [48]. In this section, theoretical information about process equipments used for composite preparation is given.

2.12.1. Extrusion

Extrusion is a processing technique for converting thermoplastic materials in powdered or granular form into a continuous uniform melt, which is shaped into items of uniform cross-sectional area by forcing it through a die. Extrusion end products include pipes for water, gas, drains, and vents; tubing for garden hose, control cable housings, soda straws; profiles for construction, automobile, and appliance industries; film for packaging; filaments for brush bristles, rope and twine, fishing line, tennis rackets; parisons for blow molding. Extrusion is perhaps the most important plastics processing method today [48].

A simplified sketch of the extrusion line is shown in Figure 2.6. It consists of an extruder into which polymer is poured as granules or pellets and where it is melted and pumped through the die of desired shape. The molten polymer then enters a sizing and cooling trough or rolls where the correct size and shape are developed. From the trough, the product enters the motor-driven, rubber-covered rolls (puller), which essentially pull the molten resin from the die through the sizer into the cutter or coiler where final product handling takes place [48].

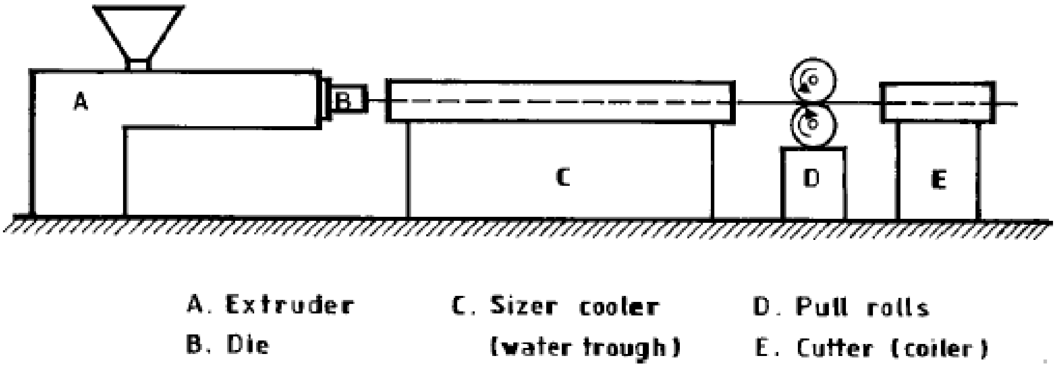


Figure 2.6 Sketch of an extrusion line

Twin-screw extruders are commonly in use especially where additive and ingredient mixing is required. Multiscrew extruders are also are generally preferred for specialized applications for which the single screw is not enough to mix ingredients. Twin-screw extruders are able to produce blends and alloys with desired properties. They (Figure 2.7) are often classified as tangential or intermeshing ones with the intermeshing being further divided into counter-rotating or co-rotating [27].

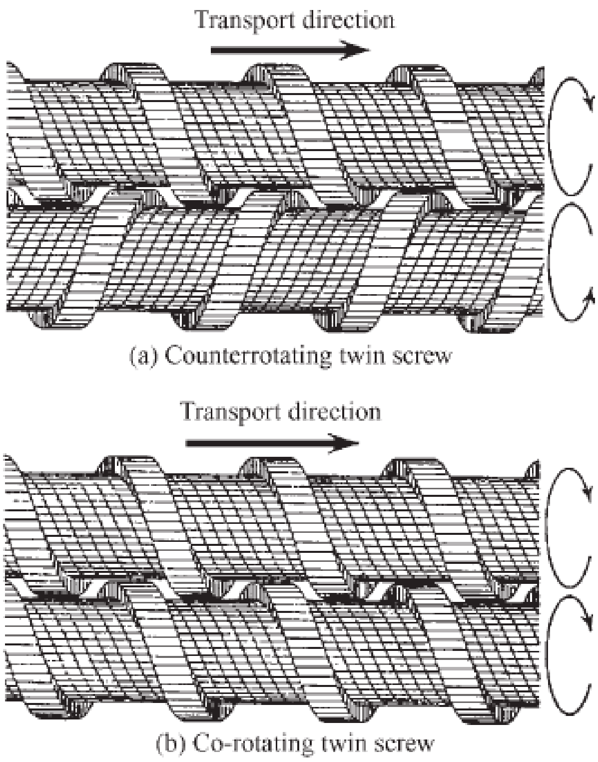


Figure 2.7 Types of twin screws [49]

2.12.2 Injection Molding

Injection molding is one of the most common processing techniques for converting thermoplastics and thermosets from the pellet or powder form into useful standardized products. Forks, spoons, computer, television, and radio cabinets, to mention just a few, are some of these products. Basically, injection molding consists of heating the pellet or powder until it melts. The melt is then injected into and held in a cooled mold under pressure until the material solidifies. Lastly, the mold opens and the product is ejected.

Injection molding machines have two principal components to perform the repeating steps in the molding process. These are the injection unit and the clamp unit [48].

2.13 Characterization of Flame Retardant Composites

There are different characterization techniques for polymer blends based on their flammability and mechanical properties.

2.13.1 Flammability Tests

Combustion of polymers is similar to the combustion of many other solid materials but tendency of polymers to form flame away from fire source differs since many polymers melt and drip. Therefore, it is extremely crucial to test the flammability of polymeric compounds under standardized conditions [21].

The fire characteristics of a material are characterized by ease of ignition, contribution to flame spread, and heat release, as well as other factors generally associated with fires, including smoke density and toxicity and corrosiveness of the combustion by-products [33]. Depending on the application of the polymeric material, at least one of these flammability factors of the material must be determined with standardized flammability tests [16]. Fire behaviour, however, cannot be considered as a material property because it is markedly affected by both material and environmental factors. These include the distribution of material in the room, material geometry and other physical factors, temperature history, thermal conductivity, intensity and type of ignition source, exposure time to the ignition source, integration of the material, and ventilation effects [33].

There are several types of flammability tests, changing due to the scale of the production, used in industrial or laboratories for determining the behavior of product before development or manufacturing. Small-scale horizontal flame tests have been used to estimate the flammability of solid (ASTM D-635), cellular (ASTM D-1692–74), and foamed polymers (ASTM D-1992), but these tests are useful for comparative purposes only. Large-scale tunnel tests (ASTM E-84) and corner wall tests are more significant, but they are also more expensive than laboratory tests. One of the most useful laboratory flammability tests is the limiting oxygen index (LOI) test (ASTM D-2043 and ASTM D-2863) [27].

2.13.1.1 Limiting Oxygen Index (LOI) Test

The value of the limiting oxygen index (LOI) is defined as the minimal oxygen concentration needed to ignite the specimen for 3 minutes or consumes a length of 5 cm of the sample, with the sample placed in a vertical position (ASTM D 2863). Although this test is phased-out nowadays because of new technologies however it is still one of the most considerable screening and quality control methods used in the plastics industry. Table 2.2 lists LOI values for various polymers.

Table 2.2 LOI values for different polymers [22]

Polymer	LOI, % value
Acrylonitrile-butadiene-styrene (ABS)	18 - 39
Cellulose	19
Epoxy (unfilled)	18.3 - 49
High density polyethylene (HDPE)	16 - 18
Nylon-6	31.8
Nylon-6,6	31.2
Low density polyethylene (LDPE)	16 - 18
Polybenzimidazole (PBI)	38 - 43
Polybutadiene	18.3
Polycarbonate	22.5 - 28
Polyethersulfone (PES)	38
Polyethylene terephtalate (PET)	20
Polyimide	18.6
Polymethyl methacrylate (PMMA)	16.6 - 18.2
Polypropylene (PP)	17.5 - 18
Polystyrene (PS)	18.3 - 19
Teflon (PTFE)	>95
Polyurethane (PU)	16.5
Polyvinyl chloride (PVC) (rigid)	21.6
Polyvinyl chloride (PVC) (flexible)	35.5
Silicon rubber	25

Limiting Oxygen Index (LOI) value is expressed as follows:

$$LOI = 100\,[O_2] / ([O_2] + [N_2]) \qquad (2.3)$$

In this equation; $[O_2]$ and $[N_2]$ show oxygen and nitrogen concentration in the oxygen/nitrogen mixture, respectively.

LOI is measured on specimens, with certain dimensions given in ASTM D2863, which are placed vertically at the center of a glass chimney. The mixture of gases flows upstream through this chimney and is homogenized by being passed through the sample in the glass. After 30 seconds purge of the column, the top of the specimen is ignited like in Figure 2.8. LOI values above 21 are classified as ‘‘self-extinguishing’’ which cannot be ignite at ambient temperature without an external energy contribution. Higher the LOI means better the flame retardant property [16]. Schematic presentation of LOI equipment is shown below in Figure 2.8.

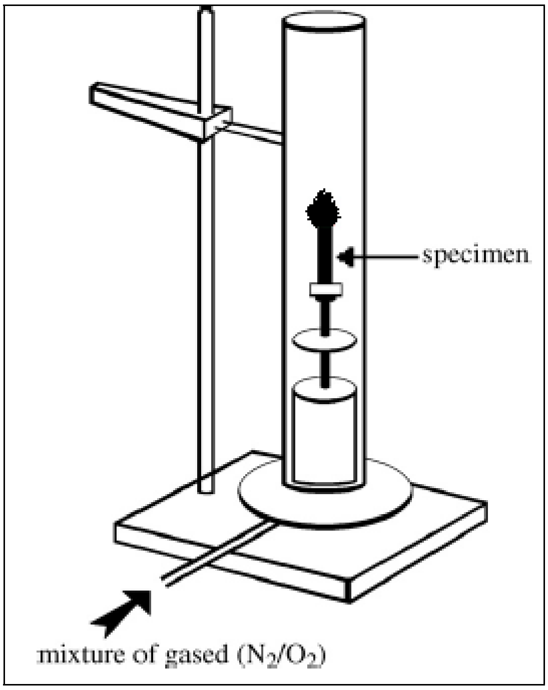


Figure 2.8. LOI measurement set-up

2.13.1.2 Smoke Density Measurement Test

Device used in this test, consists of a measuring unit which is mounted to the top of the LOI chamber. Measuring unit consists of a light source and an optical sensor which measures the light coming from the light source. Light emitted by the light source passes through the gases evolved from the burning sample in the LOI chamber and the transmitted light falls on the sensor. Device transforms this data to the recorder unit and recorder records the smoke density of the samples in terms of percent light transmittance.

2.13.2 Mechanical Tests

Polymeric materials are processed under hard mechanical, chemical, thermal and electrical conditions according to the requirements of a specific application. Polymer components may fail to perform their intended functions in specific applications as a result of:

1. Excessive elastic deformation
2. Yielding or excessive plastic deformation
3. Fracture

The determination of the mechanical characteristics of a polymer directly related to the usefulness and applicability of the material in industry. Although some methods of investigation yield data that are not only useful for engineering practice, but also allow deductions about composition and structure of the polymeric material [35].

Failure of polymers in certain applications to carry design loads or occasional accidental overloads may be due to excessive plastic deformation resulting from the inadequate strength properties of the polymer. For the quantification of such failures, the mechanical property of primary interest is the yield strength and the corresponding strain. The ultimate strength, along with the associated strain, also provides useful information [48].

Polymers show excessive elastic deformation, particularly in structural, load bearing applications, due to inadequate rigidity or stiffness. For such failure, the controlling material mechanical property is the elastic modulus. Elastic modulus of some polymers is subject to some measure of control through appropriate structural modification [48].

Polymers can be used in a variety of end-use situations. Therefore, to ensure their successful performance in these applications, it is necessary to clearly understand their mechanical behavior under a variety of stress conditions. Particular consideration must be taken of the relatively high sensitivity of polymer failure modes to temperature, time, and loading history. For good design, it is important to be able to relate design load and component dimensions to some appropriate material property that defines the limits of the load-bearing capability of the polymer material. A variety of test methods exist for predicting mechanical performance limits under a variety of loading conditions. These range from simple tension, compression, and shear tests to those designed to test complex stress states and polymer time–temperature response [48].

2.13.2.1 Tensile Test

Stress–strain experiments have traditionally been the most commonly used mechanical test. Because of the viscoelastic nature of polymeric materials, the test only gives idea about how a polymer will perform in a finished product. In stress–strain tests the specimen is deformed (pulled) at a constant rate, and the stress required for this deformation is measured simultaneously.

Polymers exhibit a wide variation of behavior in stress–strain tests, ranging from hard and brittle to ductile, including yield and cold drawing. The utility of stress–strain tests for design with polymeric materials can be greatly enhanced if tests are performed over different temperatures and strain rates [48]. To investigate and to understand the specifications of a polymeric material it is required to have the tests at several different temperatures, rates of testing and other conditions [36].

Usually the tensile response is plotted as engineering stress (σ) versus engineering strain (ε) as shown in Figure 2.9.

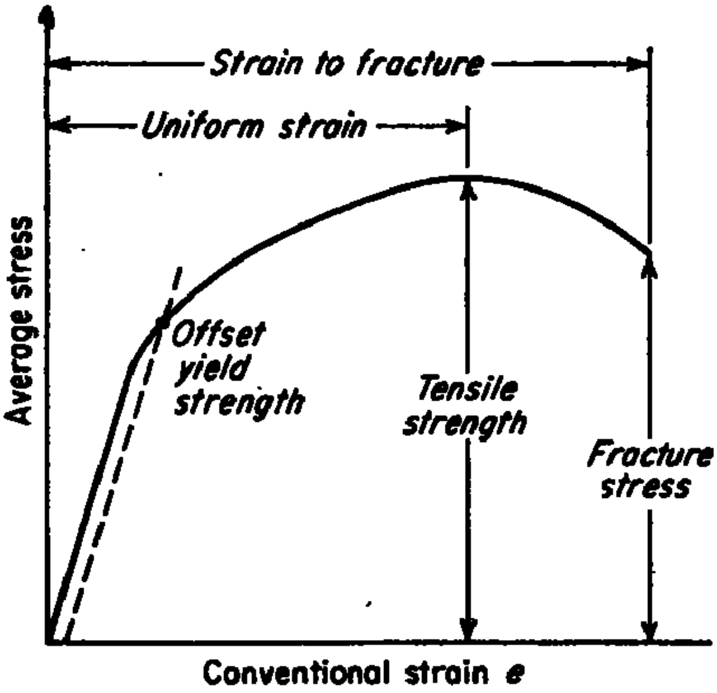


Figure 2.9 Stress-strain curve for a typical material [50]

Engineering stress can be calculated from the following relation;

$$\sigma = \frac{F}{A_0} \tag{2.4}$$

where, F is the force measured during testing and A_0 is the initial cross–sectional area of the specimen. Engineering strain can be calculated from Equation 2.5;

$$\varepsilon = \frac{\Delta L}{L_0} \tag{2.5}$$

where ΔL is the change in the sample's gauge length when the sample is exposed to elongation and L_0 is the initial gauge length of the sample [28].

Elastic (Young's) Modulus is the slope of the initial portion of the stress versus strain curve and gives idea about stiffness.

Four types of materials can be discussed in terms of the stress-strain relationship [27, 36]:

1. Brittle materials. $E = \sigma/\varepsilon$ is constant, independent of strain, ε.

2. Semi-ductile materials. $E = \sigma/\varepsilon$ decreases with strain, ε.

3. Ductile materials. They initially show similar trend with semi-ductile materials. However, these materials deform further, cause yield point. The rupture takes place at lower values than the yield stress.

4. Ductile materials with flow. These materials have greater deformability capacity than typical ductile materials. Initially, the stress-strain dependence resembles that described for ductile resin, but before the rupture there is a zone of deformation where the stress remains about constant. Within this zone there is "flow" of material that usually leads to molecular alignment and/or to changes to the crystalline structure (viscoelastic deformation of polyolefins) [36].

2.13.2.2 Impact Test

Polymers can be preferable for a particular application since the ability to resist the inevitable sharp blows and drops met in day-to-day use is often one of the most considerable characteristic properties. However, they may fail because of rapid stress loading. The primary aim of impact testing should be to give a reliable guide to brittleness and toughness of the material [33].

Various test methods have been proposed for assessing the behaviour of a polymeric material to resist impact loads. Impact strength is a measure of the energy needed to break a sample. Toughness is typically employed in describing the impact strength of a material. Toughness does not have a distinct definition but is often described as the area under stress—strain curves [27].

Impact tests may provide useful information in the selection of a polymer for a specific application, such as determining the suitability of a given plastic as a substitute for glass bottles or a replacement for window glass. Table 2.3 gives examples on values of impact energies for some polymers [48].

Table 2.3 Impact energies for various polymers

Polymer	Grade	Impact Energy (kJ/m^2)
Polystyrene	General purpose	0.34–0.54
	Impact	0.68–10.80
Poly(vinyl chloride)	Rapid	0.54–4.07
	Plasticized	1.36–20.33
Polypropylene	Unmodified	0.68–2.71
Poly(methyl methacrylate)	Molding	0.41–0.68
	High impact	1.9
Polyoxymethylene		1.90–3.12
Nylon 6,6		1.36–3.39
Nylon 6		1.36–4.07
Poly(propyleneoxide)		6.78
Polycarbonate		16.26–24.39
Polyethylene	Low density	21.70
	High density	0.68–27.10
Polyethylene terephtalate		16
Polytetrafluoroethylene		4.07
Polypropylene		0.68–2.71

Methods for impact strength determination include measurement of the cross-sectional area under the stress–strain curve in the high-speed (rapid) tensile test; the measurement of the energy required to break a specimen by a ball of known weight released from a predetermined height, the so-called falling ball or dart test; and the Izod and Charpy tests. The most popular of these tests methods are the Izod and Charpy impact tests. Essentially, the Izod test involves the measurement of the energy required to break a notched cantilever specimen that is clamped rigidly at one end and then struck at the other end by a pendulum weight. In the case of the Charpy test, a hammer-like weight strikes a notched specimen that is rigidly held at both ends. The energy required to break the standardized sample is obtained from the loss in kinetic energy of the hammer [48].

For this purpose, the test specimen is broken by a pendulum and then the energy to break the specimen is measured. The impact strength of a material can be calculated by the ratio of the fracture energy to the cross-sectional area. Specimens can be notched in a V-shape before the test thereby impact can be concentrated at a notched point on the test specimen [35].

CHAPTER 3

EXPERIMENTAL

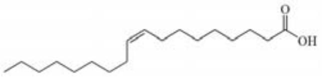
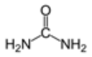
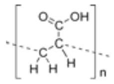
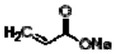
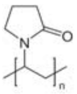
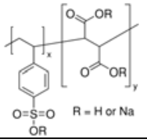
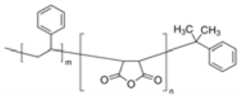
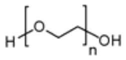
Experimental section of this thesis can be divided into four main parts: i) synthesis of 3.5 mole hydrated zinc borate; ii) characterization experiments for synthesized zinc borates; iii) production and processing of flame retardant PET composites and iv) characterization of flame retardant PET composites.

3.1 Synthesis of 3.5 Mole Hydrated Zinc Borate

3.1.1 Materials Used

Throughout the synthesis of 3.5 mole hydrated zinc borate, two different chemicals were used as reactants. First reactant is boric acid (H_3BO_3) with 99.9% purity which was supplied by Eti Mine Works. Other reactant is zinc oxide (ZnO). Two different types of zinc oxides with average particle size <1μm and <100 nm were used to determine the effect of zinc oxide size on properties of final product. Zinc oxides having 99.9% purity were obtained from Aldrich. Commercial 3.5 mole hydrated zinc borate (FB) was used as seed crystal and was supplied by U.S Borax (with 37.4% ZnO and 48% B_2O_3 content). Distilled water was obtained by distilling the tap water using a water distillation apparatus (Nüve NS 108) at METU BOREN Research Laboratory. Nine different surfactants were used in 3.5 mole hydrated zinc borate synthesis in order to examine their effects on the product. Name of the surfactants and their chemical structures are listed in Table 3.1.

Table 3.1 Surfactants used in zinc borate synthesis

Sample Code	Surfactant	Manufacturer	Structure
SDS	Sodium Dodecyl Sulfate	Aldrich	
OA	Oleic Acid	Merck	
UREA	Urea	Aldrich	
PAA	Poly(acrylic acid)	Aldrich	
SA	Sodium Acrylate	Aldrich	
PVP	Poly(vinyl pyrrolidone)	Aldrich	
PSSA	Poly(4-styrene sulfonic acid-co-maleic acid)sodium salt	Aldrich	
PSMA	Poly(styrene-co-maleic anhydride)cumene terminated	Aldrich	
PEG	Poly(ethylene glycol)	Aldrich	

3.1.2 Synthesis of 3.5 Mole Hydrated Zinc Borate

In this study, zinc borate was synthesized by the reaction (Reaction 3.1) of boric acid and zinc oxide:

$$6B(OH)_3(aq) + 2ZnO(s) \rightarrow 2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O(s) + 5.5H_2O(l) \quad (3.1)$$

Experimental set-up includes 4 liters stainless steel batch reactor, a mechanical stirrer, a heating jacket, a thermocouple, a temperature control unit and a vacuum pump. Photograph of the experimental set-up is given in Figure 3.1.

Figure 3.1 Photograph of Experimental Set-Up

Mechanical stirrer (Heidolph RZR 2041) was used to mix the slurry in the reactor. The mixing rate of the stirrer was seen on the monitor of the stirrer.

The reaction temperature was controlled by a temperature controller unit. This unit consisted of a thermocouple, a temperature controller and heating jacket. The reaction temperature was kept constant at desired temperature (85˚C) by adjusting a set point on the temperature controller.

A 50 ml syringe, which was attached to a glass pipe, was used to take the sample from the reactor. Final products, zinc borate and the water, were separated by use of vacuum filtration. This unit consisted of a vacuum pump (KNF NO22, Germany) connected to a flask and a funnel was placed on top of flask. Filter paper (Blue band filter paper) was placed on the funnel and solid particles were collected on the filter paper on the other hand the solution was collected in the flask.

Zinc borate production experiments were carried out by first dissolving the required amount of boric acid in 3 liters distilled water. Reactor was heated to 85°C. For all cases, H_3BO_3:ZnO mole ratio was kept constant as 5:1. After boric acid was completely dissolved in water, zinc oxide was added to make H_3BO_3:ZnO mole ratio 5. An excess amount of boric acid was used to ensure the formation of $2ZnO^{\cdot}3B_2O_3^{\cdot}3.5H_2O$ [2]. Water soluble low molecular weight surfactant was also added to reaction medium with desired amount (0.1%, 0.5%, 1%, and 10% by weight of water used in reaction). Commercial zinc borate (FB) (about %1.5 of the used boric acid in the solution), which acted as seed crystals in the production reaction, was also added. This mixture was reacted through stirring at 85°C for 3.5 hours. Samples were taken at a time interval of 30 minutes from reactor to perform chemical analysis to determine the change of ZnO and B_2O_3 amounts in the solids during synthesis. After 3.5 hours, slurry in the reactor was filtered and washed with hot distilled water-methanol mixture to remove excess boric acid in the system. After filtration process, final product was dried on filter papers for 24 hours at room temperature.

In order to determine the effect of surfactant and its concentration on particle size and properties of the final product, a comprehensive set of experiments were performed. In addition, one set of experiment without using any type of surfactant

(NP) was done for comparison. In addition, commercial zinc borate (Firebrake, FB) was also used as a reference material to the synthesis.

For 3.5 mole hydrated zinc borate synthesis; stirring rate (580 rpm), reaction temperature (85˚C) and reaction time (3.5 hours) are fixed parameters. Table 3.2 shows variable parameters of these experiments.

Table 3.2 Variable Parameters of Zinc Borate Synthesis

Zinc Borate Code	**Surfactant**	**Surfactant Concentration (%)**	**ZnO Particle Size**
SDS05	Sodium Dodecyl Sulfate	0.5	< 1μm
OA05	Oleic Acid	0.5	< 1μm
UREA05	Urea	0.5	< 1μm
PAA01	Poly(acrylic acid)	0.1	< 1μm
nPAA05		0.5	<100 nm
PAA05		0.5	< 1μm
PAA1		1	< 1μm
SA05	Sodium Acrylate	0.5	< 1μm
PVP05	Poly(vinyl pyrrolidone)	0.5	< 1μm
PSSA05	Poly(4-styrene sulfonic acid-co-maleic acid) sodium salt	0.5	< 1μm
PSMA01	Poly(styrene-co-maleic anhydride) cumene terminated	0.1	< 1μm
nPSMA05		0.5	<100 nm
PSMA05		0.5	< 1μm
PSMA1		1	< 1μm
PSMA10		10	< 1μm
PEG01	Poly(ethylene glycol)	0.1	< 1μm
nPEG05		0.5	<100 nm
PEG05		0.5	< 1μm
PEG1		1	< 1μm
NP	-	0	< 1μm

3.2 Characterization Experiments for Synthesized Zinc Borates

Synthesized zinc borates were characterized in terms of chemical content analysis (ZnO% and B_2O_3%), X-Ray Diffraction (XRD) Analysis, Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy (SEM).

Comprehensive set of zinc borate syntheses were performed during this study, however the aim of this study is to produce sub-micron sized 3.5 mole hydrated zinc borate so characterization results of products which have 3.5 mole hydrated crystalline structure are given in Results and Discussion part. Other products having different crystalline structures are mentioned in APPENDIX A.

3.2.1 Chemical Content Analysis

Chemical analysis and content determination of final product with titration method is extremely important in order to understand whether the product has desired molecular structure or not. These analyses were performed on the samples which were taken from the reactor during synthesis in 30 minute time intervals. Results of chemical content analyses are given in APPENDIX B.

3.2.1.1 Determination of Zinc Oxide in Final Zinc Borate Product

In this analysis, zinc oxide content is determined by ammonia buffer solution, EDTA and erichrome Black T indicator. Their preparation procedure is given below:

Preparation of Ammonia Buffer Solution: The solution was prepared by dissolving 33.75 grams of ammonium chloride in 460 ml of ammonia solution.

Preparation of 0.05M EDTA: The solution was prepared by dissolving 18.613 grams of A.R Disodium dihydrogen ehtylenediaminetetra – acetate dehydrate, accurately weighed in distilled water and diluted to 1 litre in a standard volumetric flask with distilled water [51].

Preparation of Erichrome Black T Indicator: The indicator was prepared by dissolving 0.2 grams of the dyestuff in 15 ml of triethanolamine and 5 ml of absolute ethanol [51].

This analysis was applied to the solid part of the sample. 0.2-0.21 gram of the sample weighted and dissolved by using 1 ml of hydrochloric acid (with purity of 37%). To make pH 9.5, 15-20 ml of ammonia buffer solution was added to the system. The final solution was titrated with 0.05M EDTA solution by adding 3-4 drops of Erichrome Black T indicator. Titration was performed with the help of micropipettes (Finpipette, Thermo Labsystems) and continued until the color changed from the purple to blue. The volume of EDTA used in the titration step was noted for calculation [13]. ZnO% in the solid sample was calculated from the Equation 3.2:

$$P_{ZnO} = V_{EDTA} \cdot (a) / n \tag{3.2}$$

where P_{ZnO}, V_{EDTA} and "n" are the weight percentage of ZnO in the taken sample, volume of the EDTA used and amount of sample, respectively.

In Equation 3.2, the constant "a" is the weight of ZnO in the sample resulting from the addition of 1 ml of 0.05M EDTA. The value of the "a" is 0.004069 g/l. It was calculated from the basic EDTA analyses principles.

Weight of metal complex can be calculated by multiplying volume of EDTA used (ml) with molarity of EDTA (0.05 M) and with atomic weight of the metal ion (Zn^{+2} ions detected in the analyses but since it was in the form of ZnO for simplicity the atomic weight of ZnO was taken, 81.37 g/mole) [13].

3.2.1.2 Determination of Boric Acid in Final Product

The determination of boric acid in the solid sample was performed as follows: 0.2-0.21 gram solid sample was weighed and dissolved with 1 ml of hydrochloric acid (with purity of 37%). Before titration begins, necessary EDTA solution (10 ml excess of EDTA determined in zinc analysis) should be added to prevent any mistakes that might be caused by the existence of Zn ions. After EDTA addition, 1 N NaOH solution was used for titration until pH 7 was obtained. At this step an automatic titrator (Mettler Toledo LD 50) involving a magnetic stirrer and pH-meter was used to get accurate results. After reaching the pH of 7, 10-15 gram mannitol was added to the solution. Lastly, solution was again titrated with 1 N NaOH until the pH of the solution became 7. The volume of NaOH used in the second titration step was noted for calculation [13]. Boric acid percentage in the liquid sample was calculated from Equation 3.3.

$$\begin{aligned} P_{B_2O_3} &= [(V_{NaOH} * F_{NaOH} * 0.1) / n] * (69.6202/2) * (100/1000) \\ &= 0.348101 * (V_{NaOH} * F_{NaOH}) / n \qquad (3.3) \end{aligned}$$

where $P_{B_2O_3}$, V_{NaOH}, F_{NaOH} and “n” are the weight percent of B_2O_3 in the taken sample, volume of the NaOH used, valence for NaOH solution and amount of sample, respectively.

3.2.2 X-Ray Diffraction (XRD) Analysis

In this study, X-ray diffraction (XRD) patterns of crystalline zinc borate samples were obtained with a twin tube X-ray diffractometer (100 kV Philips (PW/1050)) providing CuKα radiation (λ=0.15418 nm) at 40 kV and 40 mA. Characteristic XRD patterns of reactants and surfactant (PSMA) are given in APPENDIX C for comparison purpose.

3.2.3 Thermogravimetric Analysis (TGA)

The thermal stability and hydration water releases of zinc borate samples were investigated with Thermogravimetric Analysis (TGA) by using a Shimadzu DTG-60/DTG-60A thermal analyzer. The temperature range of the analysis was from 0°C to 700°C. Analyses were performed with 10°C/min heating rate in N_2 atmosphere. TGA graphs of synthesized zinc borates and pure PSMA are also shown in APPENDIX D.

3.2.4 Scanning Electron Microscopy (SEM)

Morphological analyses of the zinc borate samples were performed by using a Scanning Electron Microscope (SEM) (QUANTA 400F Field Emission). Before all analysis, dry zinc borate samples were coated with palladium-gold (Pd-Au) by spin coater to impart conductivity.

Particle sizes of final zinc borate products were measured by image analysis software (Image J). SEM micrographs and particle dimensions were analyzed for each sample and minimum ten zinc borate discs which were clearly seen were taken into account to determine the dimensions.

In addition to the SEM micrographs of reactants given in APPENDIX E, dry method particle size analyses were also performed on some synthesized zinc borates to understand product morphology (APPENDIX F).

3.3. Experimental Procedure of Production and Processing PET Based Flame Retardant Composites

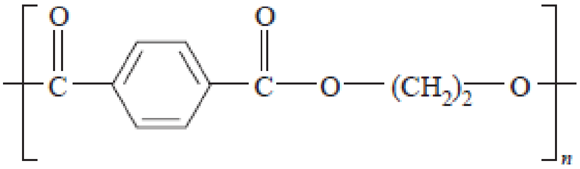
In this section, five parts in PET based flame retardant composites will be introduced: i) materials used; ii) composite formulations; iii) preparation of composites; iv) experimental procedure of processing composites and v) characterization of flame retardant PET based composites.

3.3.1 Materials

3.3.1.1 Amorphous Poly(ethylene terephthalate) (PET)

Throughout processing and preparation of flame retardant polymer composite formulations, amorphous PET was used. Some information on PET are given below in Table 3.3.

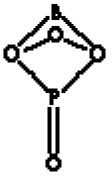
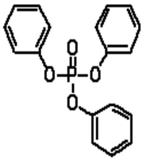
Table 3.3 Properties of Amorphous PET

Type	Amorphous
Trade name and Supplier	Melinar; AdvanSA (Turkey)
Properties	Melting Temperature = 255°C Density = 1.4 g/cm^3
Structure	

3.3.1.2 Flame Retardant Additives

Synthesized zinc borate products were mainly used in the polymer composites produced in this study. However, other flame retardant additives which are considered to affect flame retardancy and mechanical properties [52] were used as well. In this manner, in addition to synthesized zinc borates, boron phosphate (BPO_4) and triphenyl phosphate (TPP) were used in flame retardant formulations Also, commercial zinc borate (Firebrake, FB) was added to flame retardant composite formulations for comparison purposes. Properties of commercial zinc borate, boron phosphate and triphenyl phosphate are given in Table 3.4.

Table 3.4 Properties of Flame Retardant Additives

Flame Retardant Additive	**Manufacturer**	**Formula**	**Structure**	**Properties**
Boron Phosphate (BP)	Synthesized in METU Chemistry Department	BPO_4		T_m = 1400˚C, SG=2.67 g/ml at 25˚C
Triphenyl phosphate (TPP)	Acron Organics	$C_{18}H_{15}O_4P$		T_m= 47-53˚C, BP=370˚, %98 purity
Commercial Zinc Borate (Firebrake, FB)	US Borax	$2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$		SG=2.77, RI=1.58

3.3.2 Flame Retardant Formulations

Synthesized 3.5 mole hydrated zinc borate, triphenyl phosphate and boron phosphate were the selected flame retardant additives which were used for PET based flame retardant composites. In this study, after preparing and processing flame retardant formulations, the composites were characterized to comment on flame retardancy and mechanical properties. Main goal of this part was to prepare and select the successive flame retardant composite formulation, to enhance flame retardancy and to generate less smoke during burning without reducing mechanical properties of pure amorphous PET. Formulations of flame retardants are given in Table 3.5.

Table 3.5 Formulations of Flame Retardant Composites

Code	PET(%)	ZB(%)						TPP(%)	BP(%)
		PAA05(%)	PSMA05(%)	PSMA1(%)	PSMA10(%)	NP(%)	FB(%)		
100P	100	0	0	0	0	0	0	0	0
90 P/5 TPP/5 PAA05	90	5	0	0	0	0	0	5	0
90 P/5 TPP/5 NP	90	0	0	0	0	5	0	5	0
90 P/5 TPP/5 FB	90	0	0	0	0	0	5	5	0
95 P/5 FB	95	0	0	0	0	0	5	0	0
95 P/5 BP	95	0	0	0	0	0	0	0	5
95 P/5 PSMA05	95	0	5	0	0	0	0	0	0
90 P/5 TPP/5 PSMA05	90	0	5	0	0	0	0	5	0
95 P/2 PSMA05/3 BP	95	0	2	0	0	0	0	0	3
95 P/5 PSMA1	95	0	0	5	0	0	0	0	0
90 P/5 TPP/5 PSMA1	90	0	0	5	0	0	0	5	0
95 P/2 PSMA1/3 BP	95	0	0	2	0	0	0	0	3
95 P/5 PSMA10	95	0	0	0	5	0	0	0	0
90 P/5 TPP/5 PSMA10	90	0	0	0	5	0	0	5	0
95 P/2 PSMA10/3 BP	95	0	0	0	2	0	0	0	3

3.3.3 Processing and Preparation of Flame Retardant Composites

Processing of PET based composites includes three stages: i) grinding of PET; ii) twin screw extrusion and iii) injection molding. Figure 3.2 shows the flow chart of processing and characterization of PET based composites. Synthesis and characterization of zinc borates were mentioned before. As seen from the flow chart, characterized zinc borates and PET were dried before processing in the extruder; the composites and neat PET were dried before molding in the injection molding machine. After the extrusion process and the injection molding, composites and neat PET were characterized in terms of flame retardancy and mechanical properties.

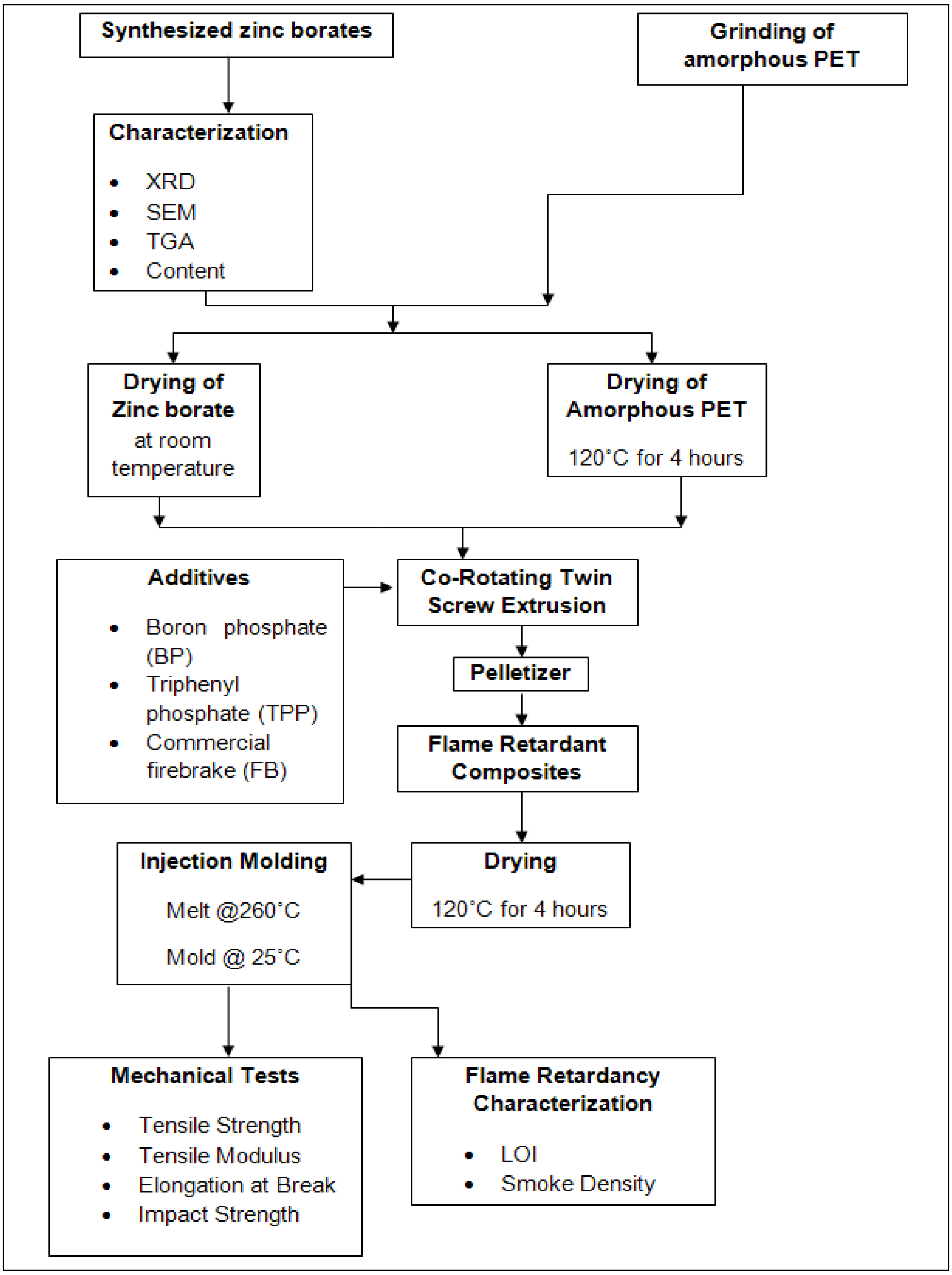


Figure 3.2 Flow chart of processing and characterization of flame retardant composites

3.3.3.1 Grinding of PET

Before extrusion processes, PET pellets were ground into powder form by using a Wiley mill intermediate model grinder (Arthur H. Thomas Co., Philadelphia) to prevent sedimentation during mixing process (Figure 3.3).

Figure 3.3 A photograph of the grinder

3.3.3.2 Twin Screw Extrusion

During flame retardant composite preparation, PET pellets were compounded with zinc borate and other additives in a co-rotating twin screw extruder (Thermo PRISM TSE-16-TC, L/D = 24) shown in Figure 3.4.

Figure 3.4 A photograph of the co-rotating twin screw extruder

Twin screw extrusion process was performed with the temperature profile of 235-240-250-250-255ºC and 100 rpm screw speed. PET powder and flame retardant additives were prepared with weight percentages given in Table 3.5 and fed from the main feeder of the extruder. Moisture control is crucially important for polymers which can influence molecular weight during extrusion [45]. Before the extrusion and molding processes, PET powder and vacuum oven was used for 4 hours at 120º C to dry composite pellets.

3.3.3.3 Injection Molding

Injection molding machine (DSM Xplore, 12 ml Micro Injection Molding Machine) (Figure 3.5) was used to prepare specimens of composites for tensile and impact testing. Samples were molded at 14 bar, 25°C mold temperature and 260°C piston temperature.

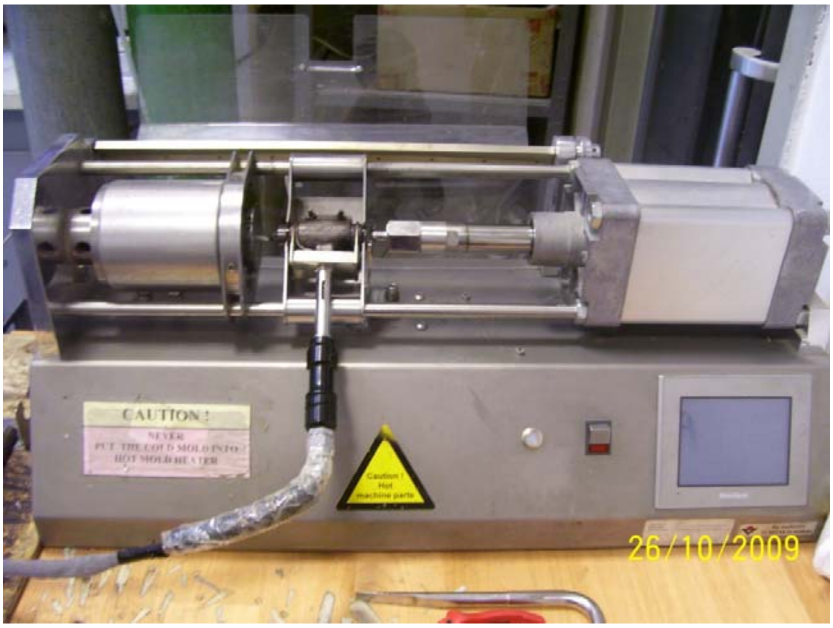


Figure 3.5 A photograph of the injection molding device

3.4 Characterization of Flame Retardant Composites

Characterization of prepared PET based composites were done in terms of flame retardancy and mechanical properties.

3.4.1 Characterization of Flammability

3.4.1.1 Limiting Oxygen Index (LOI) Test

LOI measurements were performed according to ASTM D 2863 standard with molded samples having dimensions of 10 mm width, 4 mm thickness and 80 mm length using a Dynisco Limiting Oxygen Index Test machine (Figure 3.6c).

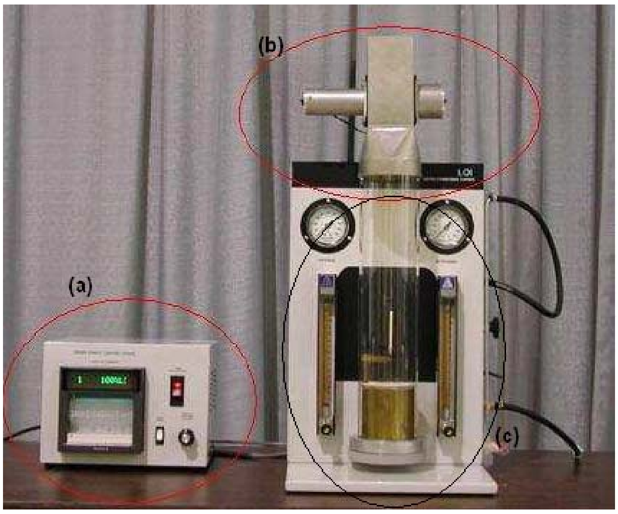


Figure 3.6 Limiting Oxygen Index Testing Machine and Smoke Density Measurement; (a) Recorder, (b) Smoke Density Measuring Unit, (c) Limiting Oxygen Index Machine

3.4.1.2 Smoke Density Measurement Test

Smoke density measurements were performed by using a Dynisco optical smoke detector. Photograph of the smoke detector is given in Figures 3.6a and 3.6b [2].

3.4.2 Characterization of Mechanical Properties

3.4.2.1 Mechanical Tests

The tensile strength, elastic modulus and elongation at break values were determined by Shimadzu Autograph AG-100 KNIS MS universal tensile testing machine (Figure 3.7) at room temperature. Injection molded tensile specimens had a thickness of 2 mm, a width of 4 mm and a gauge length of 30 mm. According to the gauge length and a strain rate of 0.1 min^{-1}, the crosshead speed of testing instrument was selected as 3 mm/min. According to the ASTM D638-10, after stress versus strain diagrams from the measurements were obtained; tensile strength, tensile modulus and elongation at break values can be calculated by taking averages of results of five specimens with standard deviations. However, for some composite formulations tensile properties could not be calculated by averages of five specimens because of lack of enough specimens due to molding difficulties of PET and high fragility of prepared composites. Tensile results of flame retardant composites were listed in APPENDIX G, Tables G.1-G.3.

Figure 3.7 Tensile Testing Machine (Shimadzu Autograph AG-100 KNIS MS)

3.4.2.2 Impact Test

Charpy Impact tests were performed by using a Ceast Resil Impactor 6967 impact testing device (Figure 3.8), instrumented with a 7.5 J hammer, at room temperature. Dimensions of the unnotched samples had a thickness of 4 mm, a width of 10 mm and a length of 80 mm. According to ASTM D 5942-96 standard averages of 5 specimens should be reported with standard deviations. However, for some composite formulations impact strength values could not be calculated by averages of five specimens because of reasons mentioned above. Impact strength results of flame retardant composites were listed in Appendix G, in Table G.4.

Figure 3.8 Impact Testing Machine (Ceast Resil Impactor 6967)

CHAPTER 4

RESULTS AND DISCUSSION

This chapter gives results of characterization experiments in two branches: Characterization results for synthesized 3.5 mole hydrated zinc borate and characterization results for flame retardant PET composites. In the first part XRD, TGA, ZnO and B_2O_3 content analysis and SEM were performed to determine the properties of final zinc borate product. Synthesized zinc borates were compared to commercial zinc borate (FB). In the second part, flammability and mechanical properties were determined and effect of synthesized zinc borate together with other additives on PET based composites were discussed.

4.1 Characterization of Synthesized Zinc Borate Products

Characterization results of synthesized zinc borates which have similar final product properties with commercial zinc borate (FB) were discussed in this section. Characterization results of other products which do not have 3.5 mole hydrated zinc borate structure were given in APPENDIX A. Furthermore, it must be mentioned that none of the zinc borate synthesis experiments has been repeated and reproducibility test has not been carried out in this thesis. But, the comparison for synthesized zinc borate without using surfactant (NP) was made according to the results of our previous study on zinc borate synthesis [2].

4.1.1 Effect of Surfactant Type on the Production of Zinc Borate

In this part; to determine effect of surfactant type on final product properties, especially particle size of final zinc borate product, XRD, TGA, ZnO and B_2O_3 content and SEM analyses were performed and compared to the commercial one

(FB). In each set of experiment, surfactant was added as 0.5 wt. % of water used in reaction. The effect of surfactant type on the production of zinc borate was studied by keeping reaction temperature (85ºC), H_3BO_3:ZnO ratio of 5:1 and type of zinc oxide particles (average particle size <1µm) constant during the synthesis.

XRD analyses were performed on final zinc borate products to determine the final product have same structure with 3.5 mole hydrated commercial zinc borate (FB). Peaks of the final zinc borate product were compared to the commercial one to decide whether final zinc borate product successfully synthesized or not. XRD plot of FB is given in Figure 4.1. Characteristic peaks of commercial zinc borate are observed between 15-70° 2θ ranges.

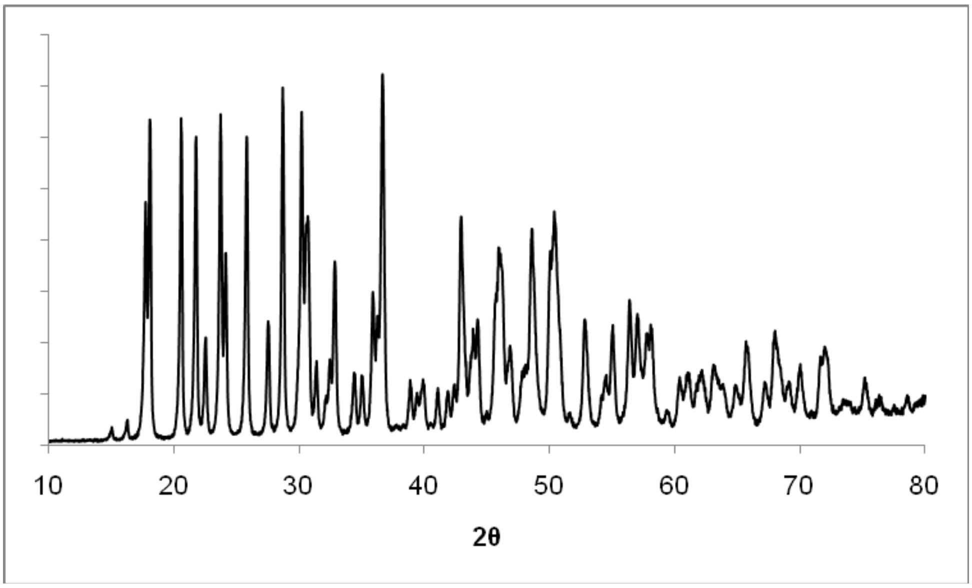


Figure 4.1 XRD pattern of 3.5 mole hydrated commercial zinc borate

XRD patterns of zinc borates which were synthesized with four different surfactants, namely; Poly(acrylic acid), Sodium Acrylate, Poly(vinyl pyrrolidone) and Poly(styrene-co-maleic anhydride) are shown in Figure 4.2. As seen in Figure 4.1, main characteristic XRD peaks of commercial FB draw attention between 18-38 and 42-58° 2θ ranges. In Figure 4.2, peaks of all products match with the characteristic XRD peaks of 3.5 mole hydrated commercial zinc borate. These consistent peaks show that zinc borates were successfully synthesized with the same crystalline structure of FB.

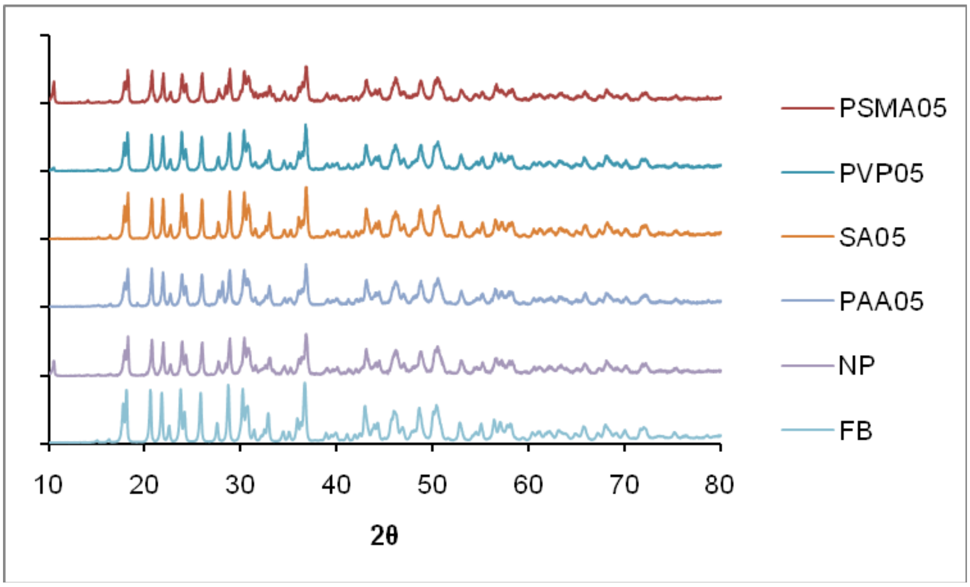


Figure 4.2 XRD peaks of zinc borates which were synthesized by different types of surfactants

TG analyses give information about the thermal stability and weight loss of the zinc borate samples with respect to time. For flame retardant purposes it is crucially important that hydrated water of zinc borate should retain in the structure until high process temperatures. Especially, this hydrated water should not be released until processing temperatures of plastics so that zinc borate can act as flame retardant additive. TG analyses of produced zinc borates are given in Figure 4.3.

According to TGA curves given in Figure 4.3; all samples retain their hydration water till 340˚C. This dehydration temperature is acceptable for flame retardant additives because PET based composites are processed at 260˚C. So synthesized zinc borates keep their hydration water during polymer processing. In this way, they are expected to enhance flame retardant properties. Weight loss of zinc borates shown in Figure 4.3 varies between the range of 14%-16.5%. Highest weight loss occurred in PAA05 product with 16.5% where lowest weight loss was observed in PVP05 with 14%.

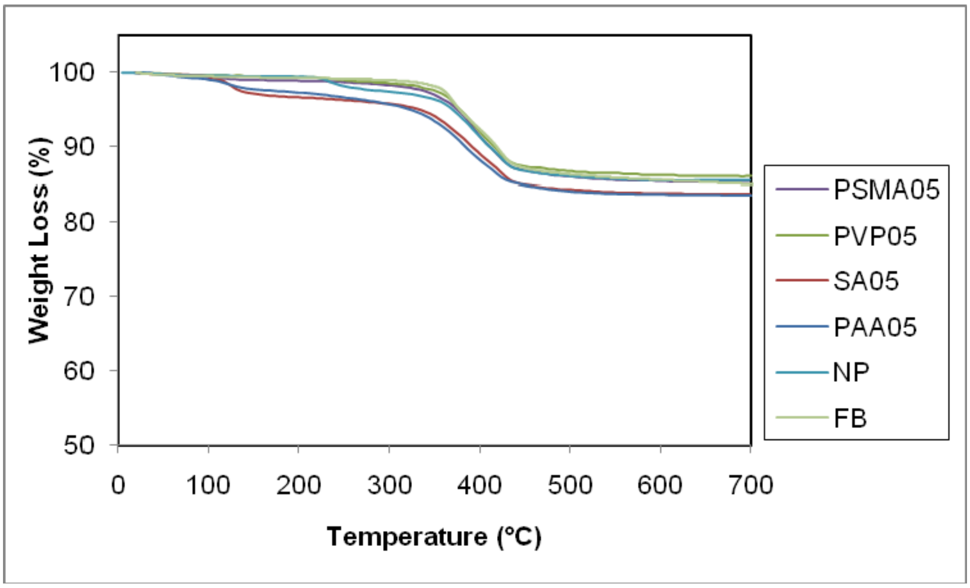


Figure 4.3 TGA curves of zinc borates synthesized by different types of surfactants

In order to understand whether the 3.5 mole hydrated zinc borate synthesized or not; chemical content of ZnO% - B_2O_3% of final product was determined. So analytical analyses were performed on the solid products taken from the reactor in every 30 minutes. The results of chemical content analysis are given in Table 4.1.

TGA graphs can also be used to determine water content of synthesized zinc borate product. The weight difference occurs near 300°C-400°C gives the weight percent of hydration water in zinc borate structure and this calculation provides easier comparison between the experimental values and theoretical values of B_2O_3

content in the final zinc borate product. “B_2O_3% from TGA” values were calculated by subtracting the ZnO% value and H_2O% values from 100%.

When compared to the commercial product, FB, all products have similar B_2O_3 and ZnO content. Insufficient washing of final product may cause higher %B_2O_3 values than the commercial one. This problem can be prevented by optimizing the quantity of water – methanol mixture to remove excess boric acid. Similar contents with commercial zinc borate (FB) show that zinc borate was successfully synthesized in terms of molecular formula of 3.5 mole hydrated zinc borate ($2ZnO\cdot 3B_2O_3\cdot 3.5H_2O$). Experimental mistakes in EDTA and NaOH titration (such as adjusting the quantity of EDTA) may cause higher %B_2O_3 values than the calculated %B_2O_3 values from TGA as seen in Table 4.1.

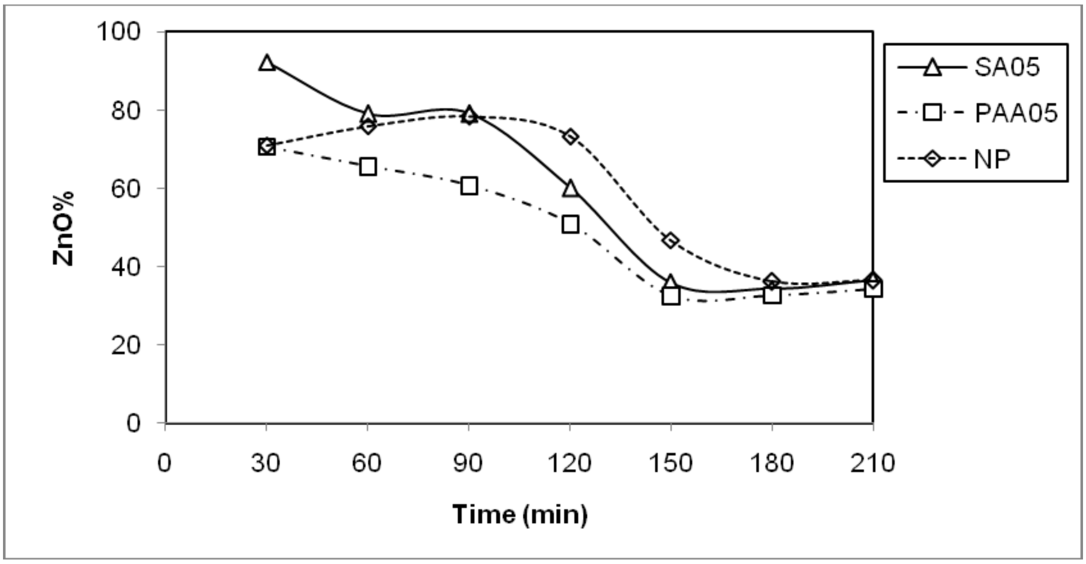
Table 4.1 Final ZnO and B_2O_3 content of synthesized zinc borates by different types of surfactants

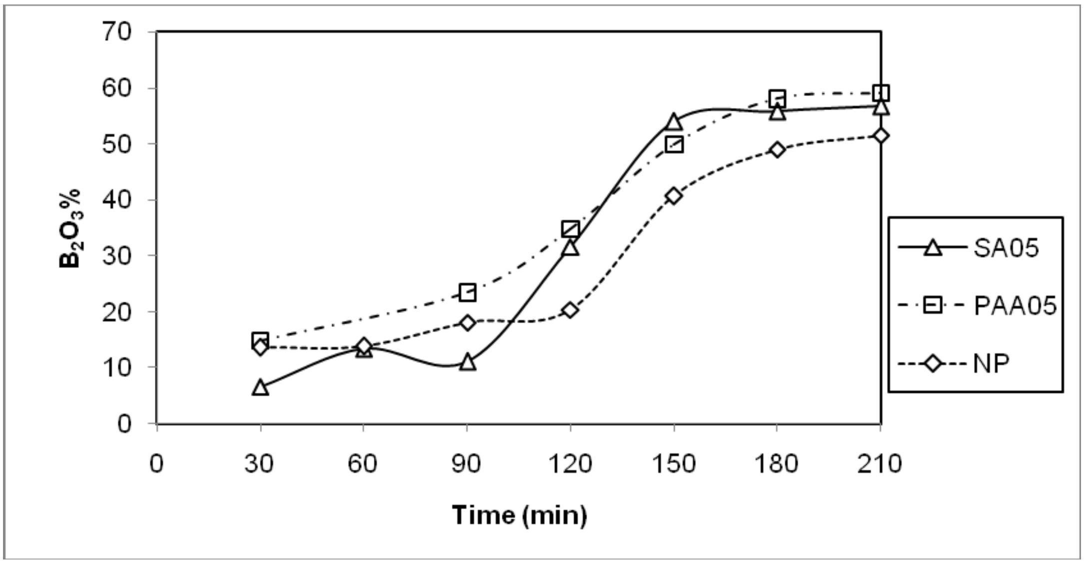
Sample Code	ZnO%	B_2O_3%	H_2O% from TGA	B_2O_3% from TGA
FB	37.4	48.0	13.8	48.8
NP	36.0	52.0	11.8	51.8
PAA05	34.3	59.1	13.6	52.1
SA05	36.4	56.7	12.6	51.0
PVP05	39.2	54.5	13.3	47.5
PSMA05	38.4	52.6	13.3	48.3

Figures 4.4 and 4.5 show change of ZnO% - B_2O_3% content with respect to time for zinc borates synthesized with different surfactants. For comparison, titration results for NP were also given. Figures 4.4 and 4.5 also show the zinc oxide conversion for each zinc borate production. Sample calculation of ZnO conversion is shown in APPENDIX H.

From Figures 4.4 and 4.5 it can be concluded that; ZnO% - B_2O_3% contents in the synthesized zinc borates reached to stability and production reaction was completed between 150-210 minutes. Reaction was completed for the zinc borates synthesized in the presence of 0.5% PAA, SA, PVP and PSMA at the reaction time of 180, 150, 180 and 180 minutes, respectively.

ZnO conversion graphs showed that without using surfactant; conversion of zinc oxide to zinc borate started after 120 minutes and took nearly 90 minutes to achieve complete conversion. However, addition of SA and PSMA decreased the time of conversion of zinc oxide from 90 minutes to 60 minutes. So it can be asserted that SA and PSMA addition increased the reaction rate of zinc borate production. However, addition of PAA and PVP did not increase reaction rate when compared to NP.





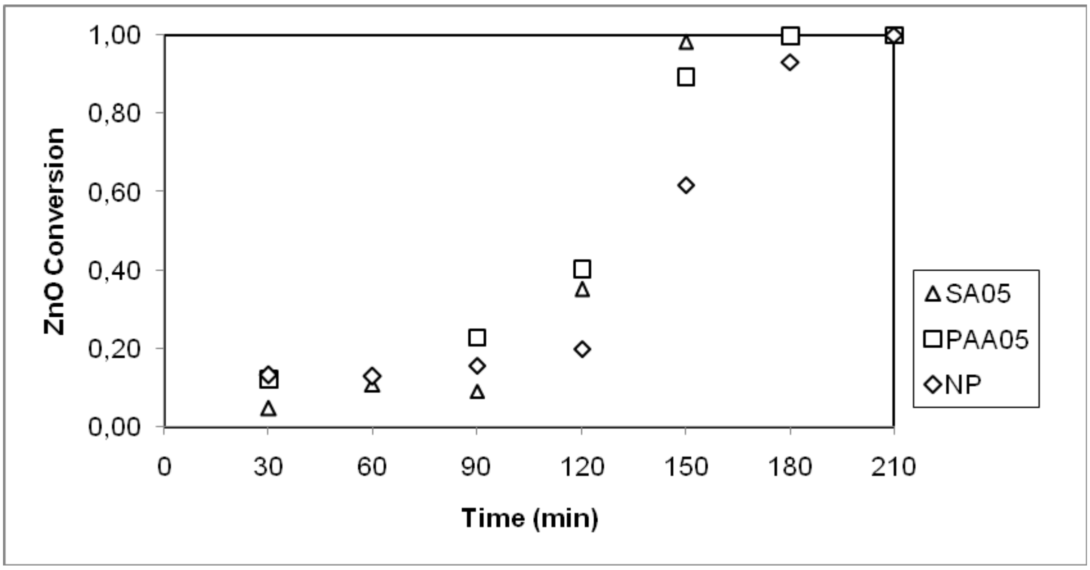
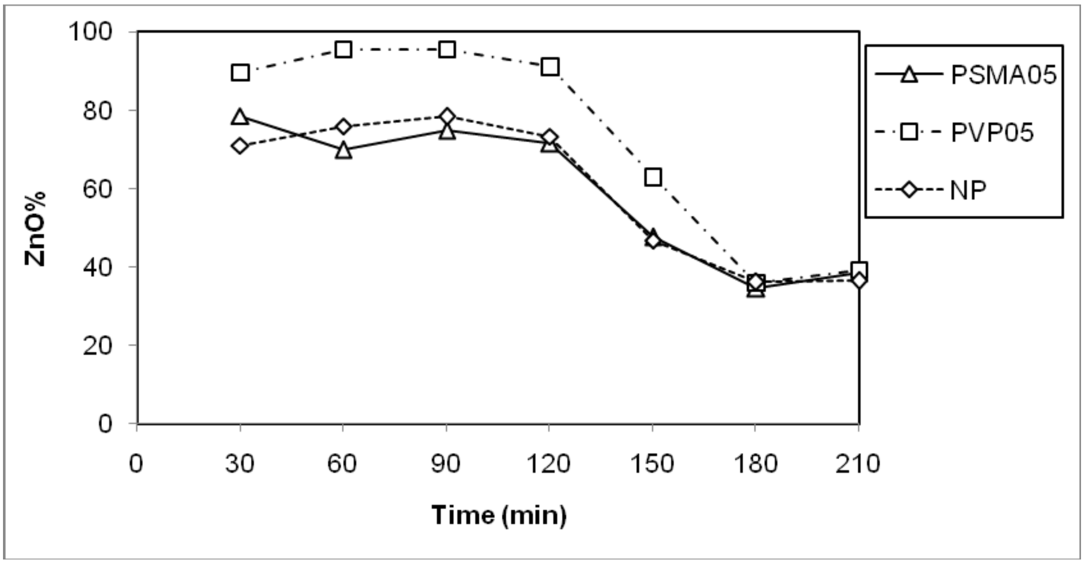
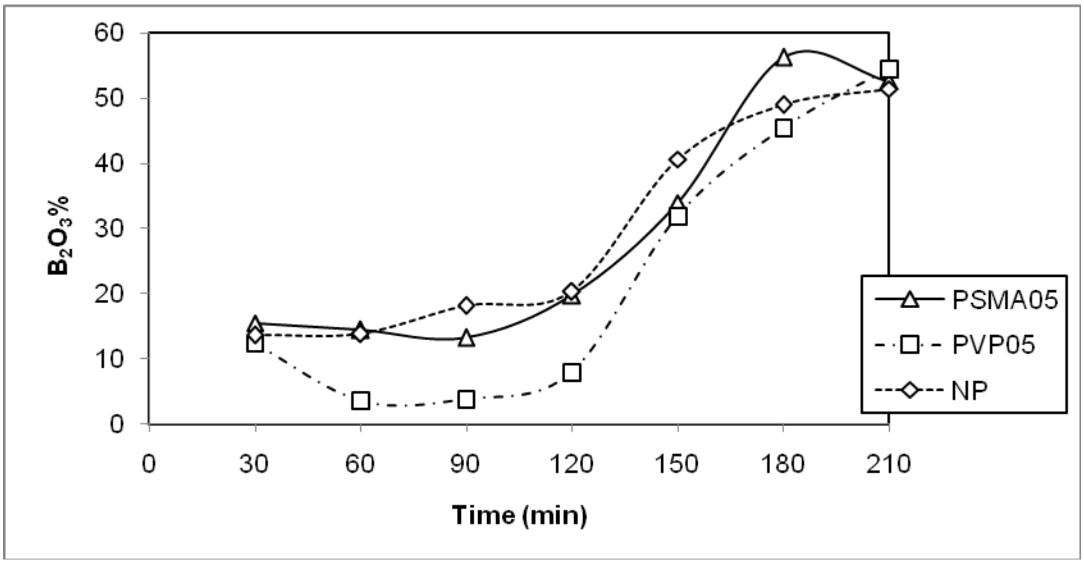


Figure 4.4 Effect of surfactant type (PAA05 and SA05) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1 and average particle size of zinc oxide (<1μm) were constant)


ZnO%
Time (min)
0
20
40
60
80
100
0
30
60
90
120
150
180
210
PSMA05
PVP05
NP


B2O3%
Time (min)
0
10
20
30
40
50
60
0
30
60
90
120
150
180
210
PSMA05
PVP05
NP

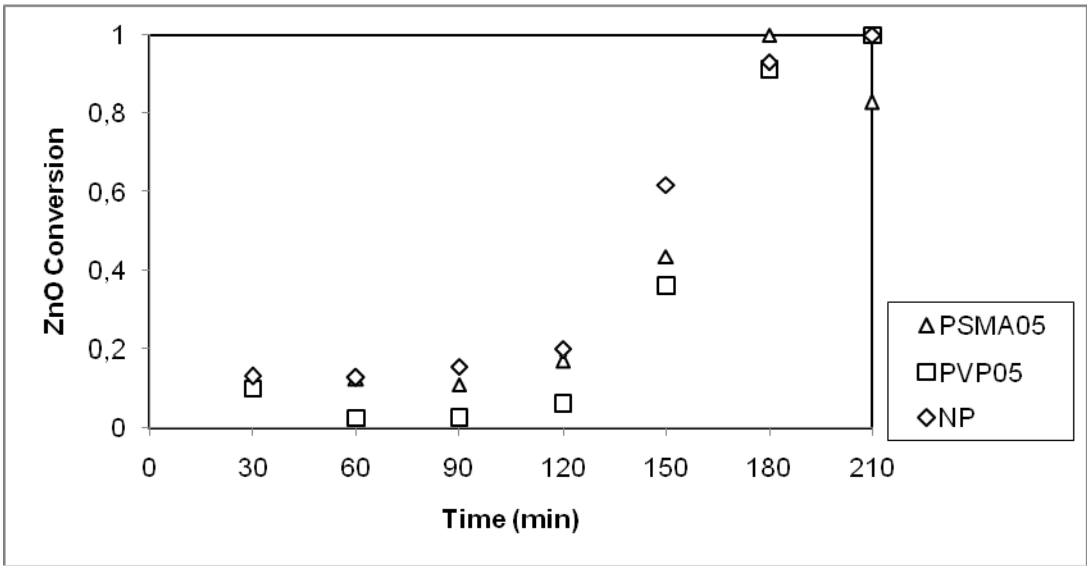
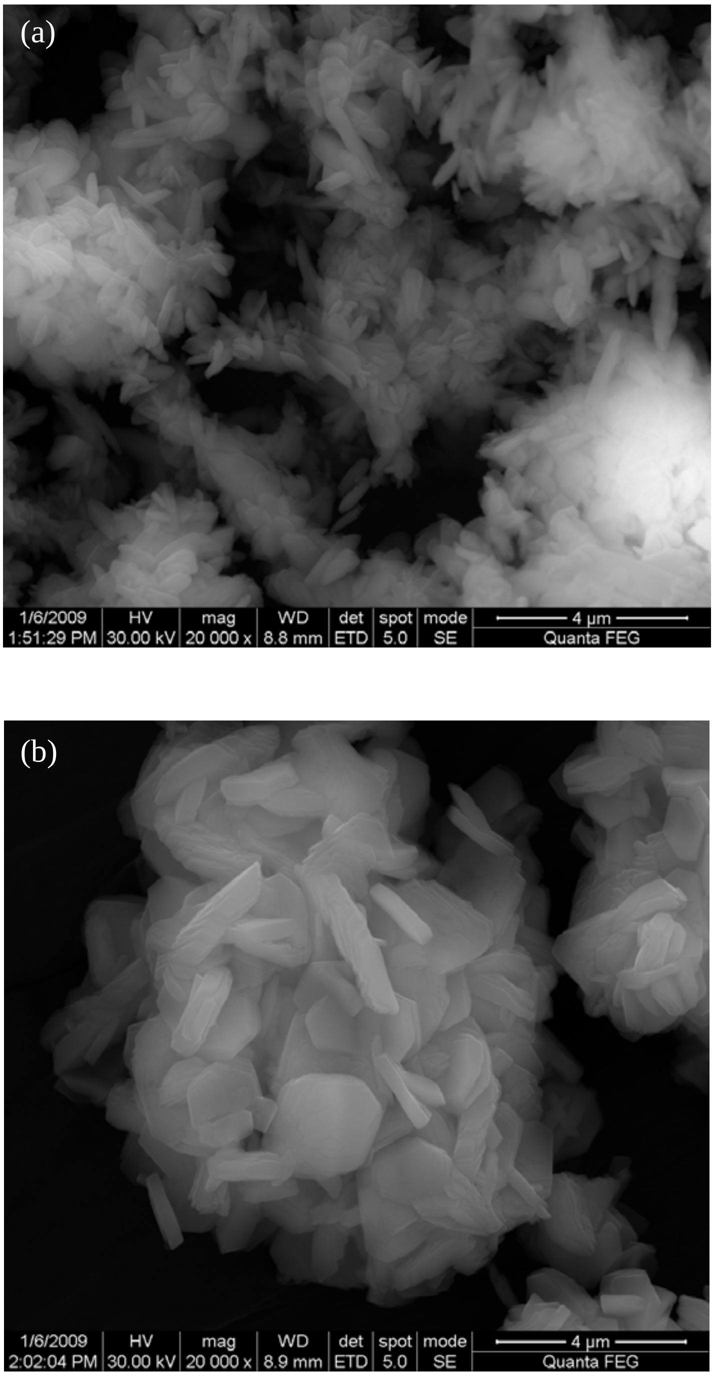


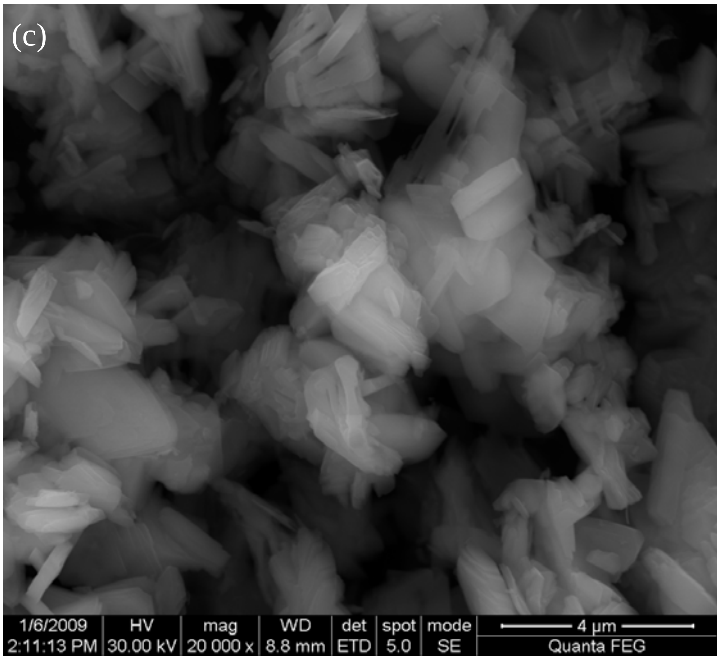
Figure 4.5 Effect of surfactant type (PVP05 and PSMA05) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1 and average particle size of zinc oxide (<1μm) were constant)

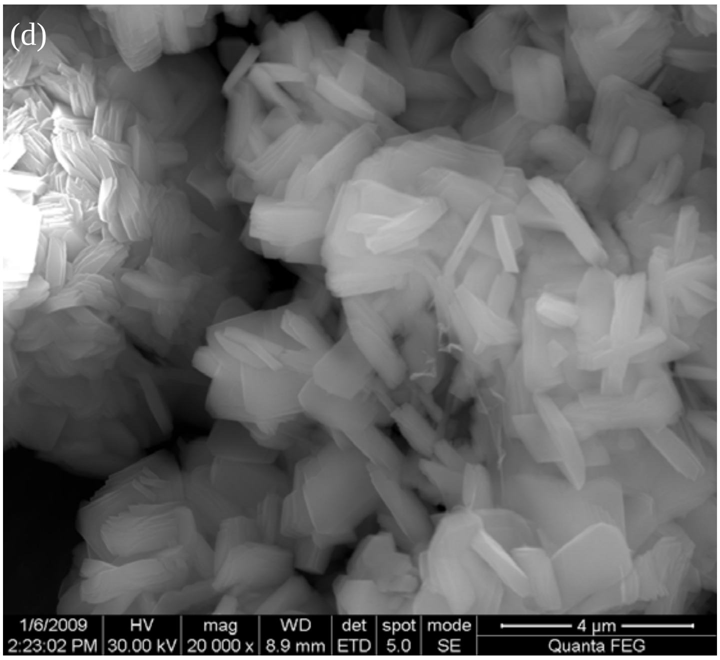
Lastly, SEM analyses were performed to characterize the morphology and to investigate crystal growth on zinc borate product. As mentioned before, particle size of additives is crucially important for polymer composites since smaller size and high surface area for interaction increase the compatibilization between polymer matrix and additive. But high surface energy of small particles causes agglomeration. Preventing agglomeration of zinc borates and providing homogeneous dispersion in polymeric matrix may help to increase mechanical properties such as tensile strength and tensile modulus values and also enhance flame retardancy. In this study, different types of surfactants were used to prevent crystal growth of zinc borate crystals and final zinc borate product particle size.

SEM micrographs of zinc borates, which were synthesized in the presence of Poly(acrylic acid), Sodium Acrylate, Poly(vinyl pyrrolidone) and Poly(styrene-co-maleicanhydride), are given in Figure 4.6 with 20000 magnification.

As seen from Figure 4.6; all synthesized zinc borates are in agglomerate form. All of the particles in the samples have disc-like structure. Dimensions of zinc borates, which were measured by ImageJ programme, are listed in Table 4.2. Among synthesized zinc borates; smallest particle size belongs to PAA05 with the average radius of 0.84 μm and thickness of 140 nm.




(c)
1/6/2009 2:11:13 PM
HV 30.00 kV
mag 20 000 x
WD 8.8 mm
det ETD
spot 5.0
mode SE
4 μm
Quanta FEG


(d)
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HV 30.00 kV
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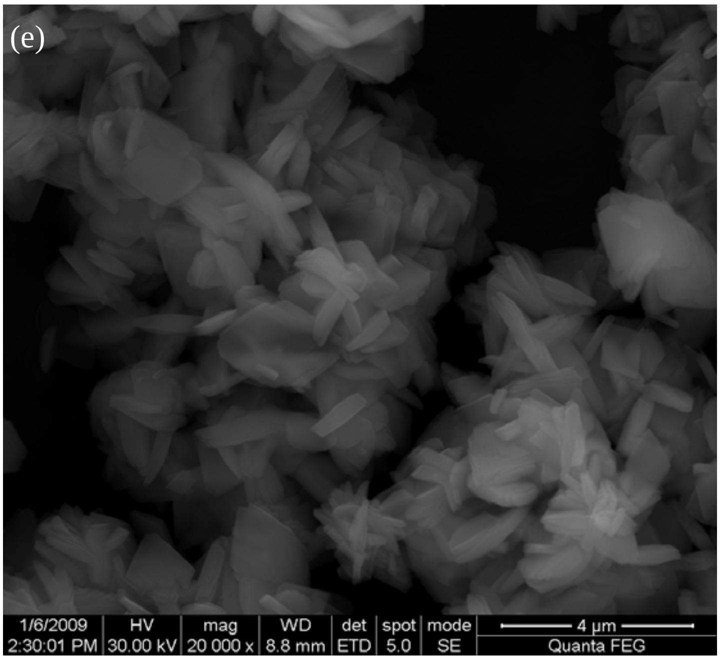


Figure 4.6 SEM micrographs of final zinc borate products: (a) PAA05, (b) SA05, (c) PVP05, (d) PSMA05, (e) NP with 20000 magnification.

Table 4.2 Dimensions of zinc borate particles synthesized by different types of surfactants

Sample Code	Radius (μm)	Thickness(nm)
PAA05	0.84±0.15	140±45
SA05	1.7±0.3	300±40
PVP05	1.4±0.2	370±80
PSMA05	1.2±0.2	350±50
NP	1.1±0.2	280±60

According to Table 4.2, radii of final zinc borate products vary between 0.84 μm to 1.7 μm and thickness changes in the range of 140-370 nm. It can be said that at least in one dimension sub-micron sized zinc borates are obtained through the synthesis.

To sum up; synthesized zinc borates have similar chemical structure with the commercial zinc borate (FB). They release their hydration water after 340˚C and have nano size at least in one dimension. Since PAA05, PSMA05 and NP have smaller particle sizes than the other synthesized zinc borate products; the effect of concentration of PAA and PSMA is studied in upcoming parts of this study.

4.1.2 Effect of Surfactant Concentration on the Production of Zinc Borate

In this part; XRD, TGA, ZnO% and B_2O_3% content and SEM analyses were performed to determine the effect of concentration of two surfactants (PAA and PSMA) on the synthesis of zinc borate and its particle size. Characterization results were compared to the commercial one (FB). In each set of experiment, surfactant ratios were varied as 0.1%, 0.5% and 1%. However synthesis of zinc borate with 1% PAA could not be completed because at this concentration PAA which is capable of absorbing water caused a flood in the reactor.

XRD peaks of zinc borates which were synthesized by different concentrations of surfactants are shown in Figure 4.7. The peaks of the commercial zinc borate (FB) and the synthesized zinc borates were consistent with each other. The same peaks were observed at the same 2θ values. These consistent peaks which matched with the characteristic peaks of commercial zinc borate (FB) indicated that the 3.5 mole hydrated zinc borate was successfully synthesized.

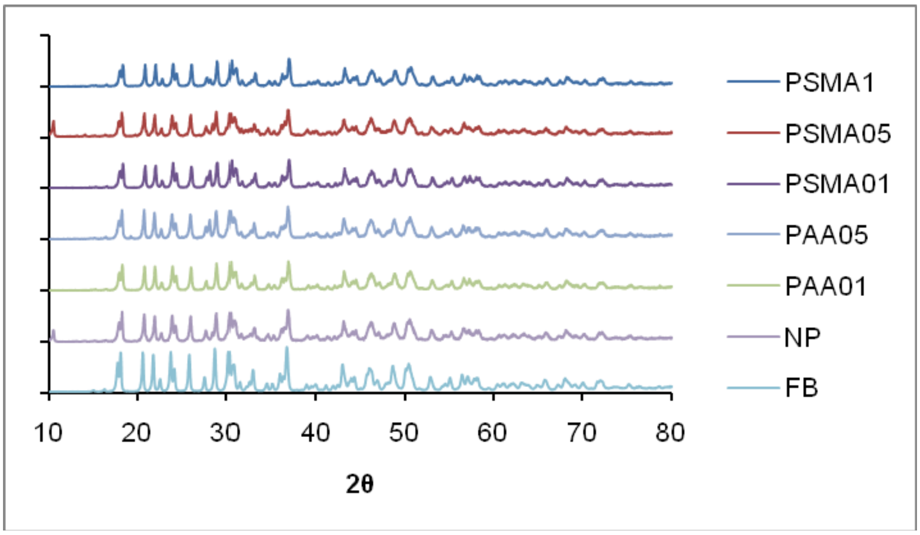


Figure 4.7 XRD patterns of zinc borates synthesized by different concentrations of surfactants

TGA was performed in range of 0-700˚C with 10˚C/min heating rate in N_2 atmosphere. Figure 4.8 shows that when zinc borate samples were compared to the commercial one; all samples retained their hydration water till 335˚C. 14% weight loss was determined for the zinc borates shown in Figure 4.8 except for PSMA1. Additionally, 10% weight loss was observed for PSMA1 at approximately 100˚C. This was attributed to the water which was retained in the sample as a result of insufficient drying of PSMA1.

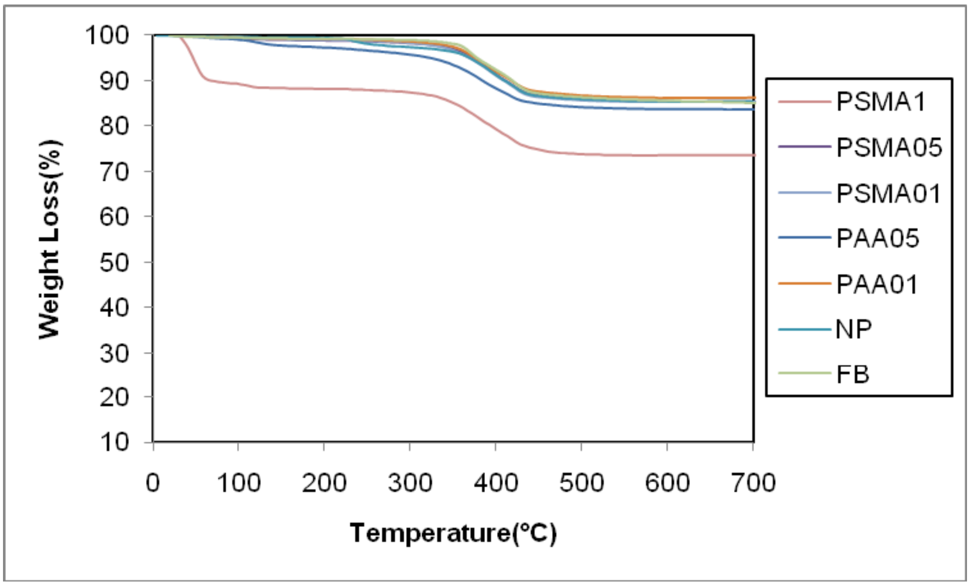


Figure 4.8 TGA curves of zinc borates synthesized by different concentrations of surfactants

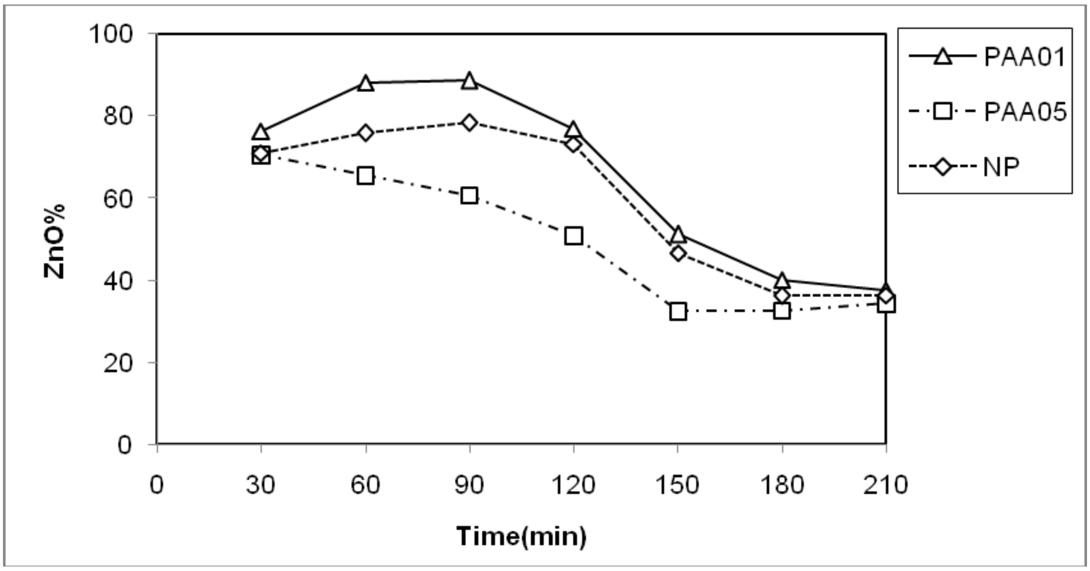
The results of chemical content analyses of final solid zinc borate products are given in Table 4.3. When all of the products, except PSMA1, are compared to the commercial product (FB), they have similar B_2O_3 and ZnO content. For PSMA1, lower percent of ZnO and higher percent of B_2O_3 show that 3.5 hours of reaction time was not enough to convert all ZnO and produce 3.5 mole hydrated zinc borate. On the other hand, for PSMA1, high values of B_2O_3% may be occurred due to the unreacted boric acid which remained as a result of insufficient washing of final product with hot methanol-water mixture. Other zinc borate products have nearly same ZnO and B_2O_3 content with the commercial one.

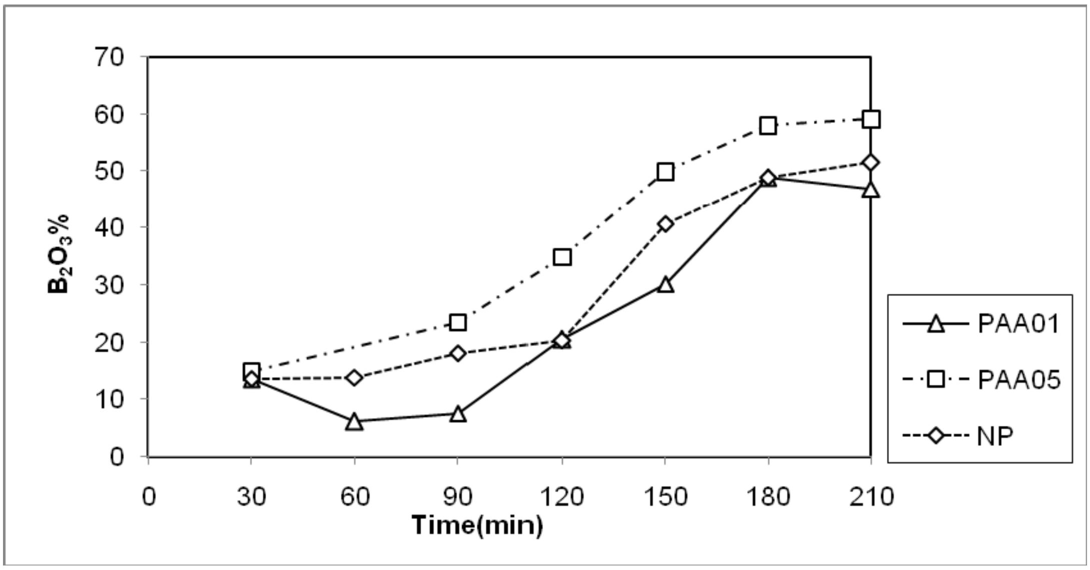
Table 4.3 Final ZnO and B_2O_3 content of synthesized zinc borates by different concentrations of surfactants

Sample Code	ZnO%	B_2O_3%	H_2O% from TGA	B_2O_3% from TGA
FB	37.4	48.0	13.8	48.8
NP	36.4	51.5	11.8	51.8
PAA01	37.7	46.9	13.1	49.2
PAA05	34.3	59.1	13.6	52.1
PSMA01	37.3	56.4	13.7	49.0
PSMA05	38.4	52.6	13.3	48.3
PSMA1	29.3	51.1	14.6	56.1

Figures 4.9 and 4.10 show the ZnO% - B_2O_3% content and ZnO conversion with respect to time in terms of concentration of surfactant in zinc borate production. For comparison, titration results for NP are also given in Figure 4.9.

As mentioned before, ZnO conversion graphs showed that without using surfactant; conversion of zinc oxide to zinc borate started after 120 minutes and took nearly 90 minutes to achieve complete conversion. For instance; increasing PAA percent from 0.1% to 0.5% decreased the time of conversion of zinc oxide to zinc borate from 120 minutes to 90 minutes and initial time to start conversion from 120 minutes to 90 minutes. On the other hand, increasing the PSMA concentration from 0.1% to 0.5% increased the reaction rate from 90 minutes to 60 minutes. However, increasing PSMA concentration from 0.5% to 1% did not have any significant effect on reaction rate but decreased the time to start conversion from 120 minutes to 60 minutes. Consequently, when effect of surfactant concentration on zinc oxide conversion was considered, addition of 1% PSMA to the reaction medium may be efficient in terms of ZnO conversion since it decreased the time of ZnO conversion from 90 minutes to 60 minutes moreover it decreased the time to start conversion from 120 minutes to 60 minutes when compared with NP.


100
80
60
40
20
0
ZnO%
0
30
60
90
120
150
180
210
Time(min)
PAA01
PAA05
NP


70
60
50
40
30
20
10
0
B_2O_3%
0
30
60
90
120
150
180
210
Time(min)
PAA01
PAA05
NP

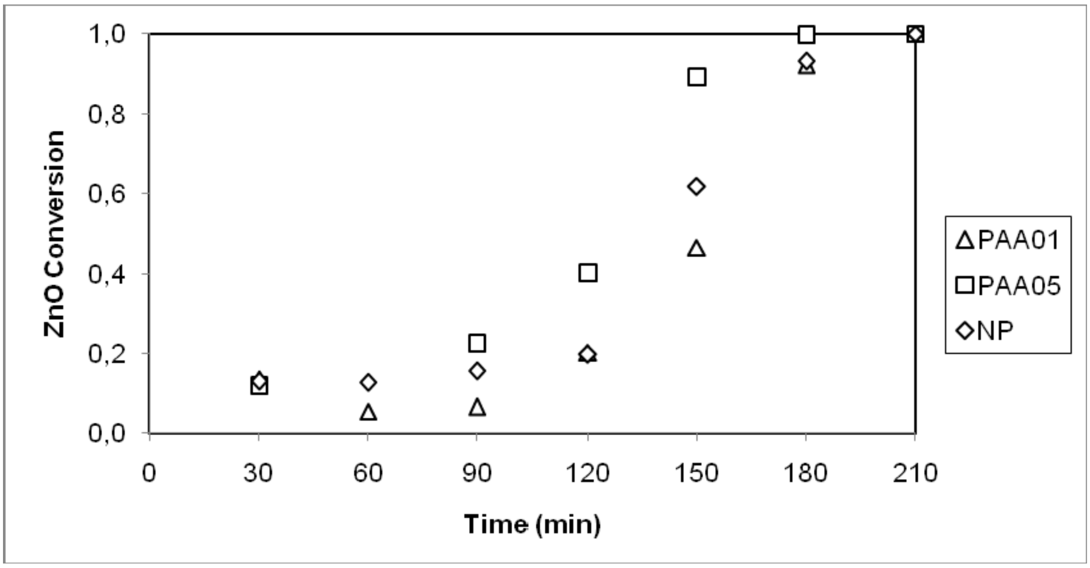
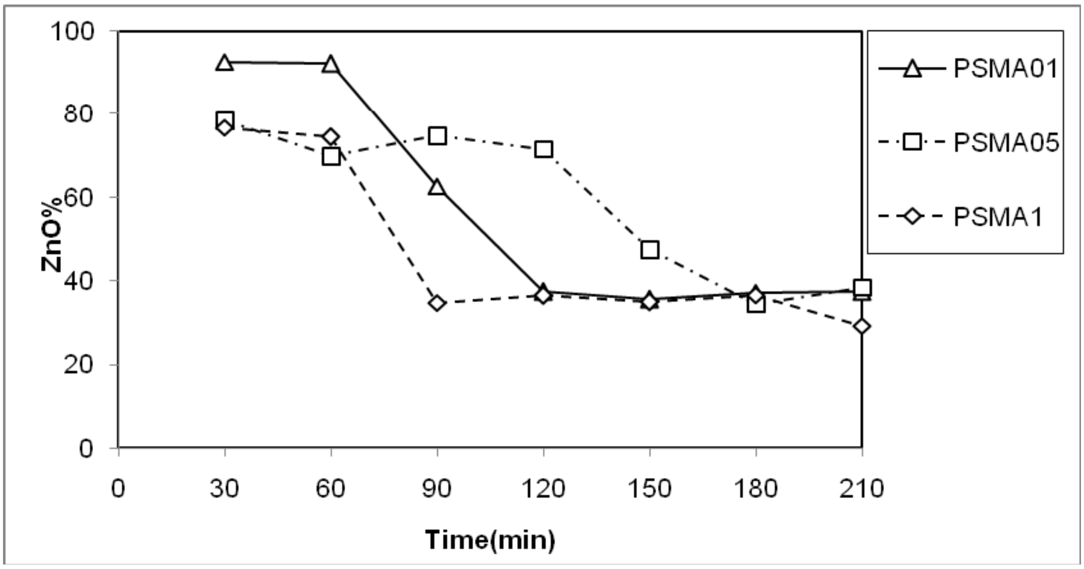


Figure 4.9 Effect of surfactant concentration (PAA01 and PAA05) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1 and average particle size of zinc oxide (<1μm) were constant)



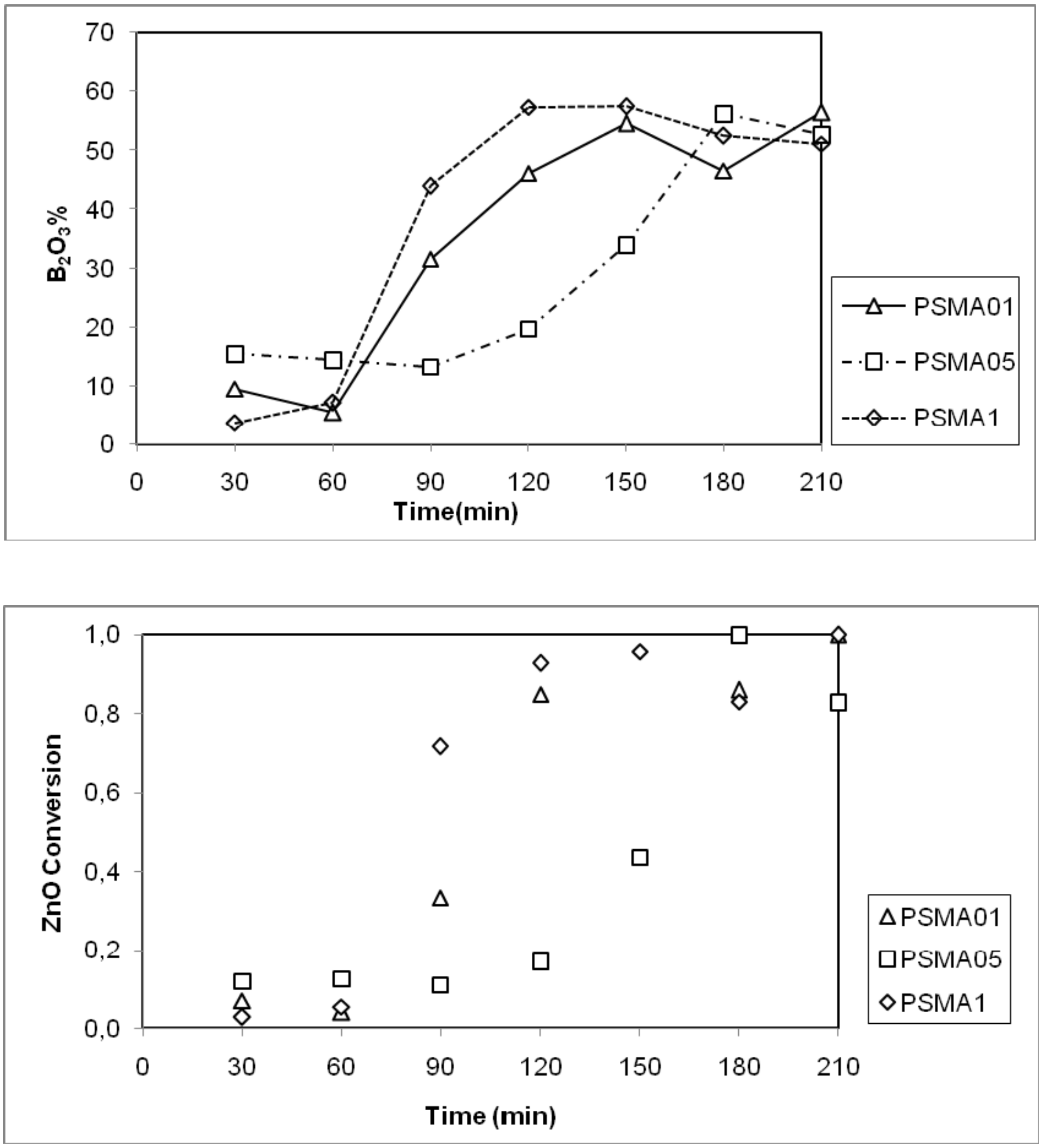
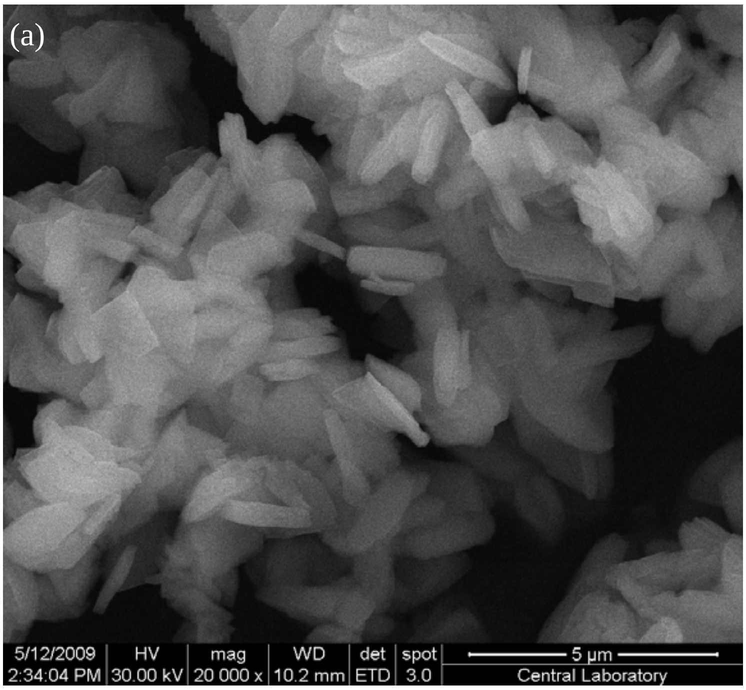
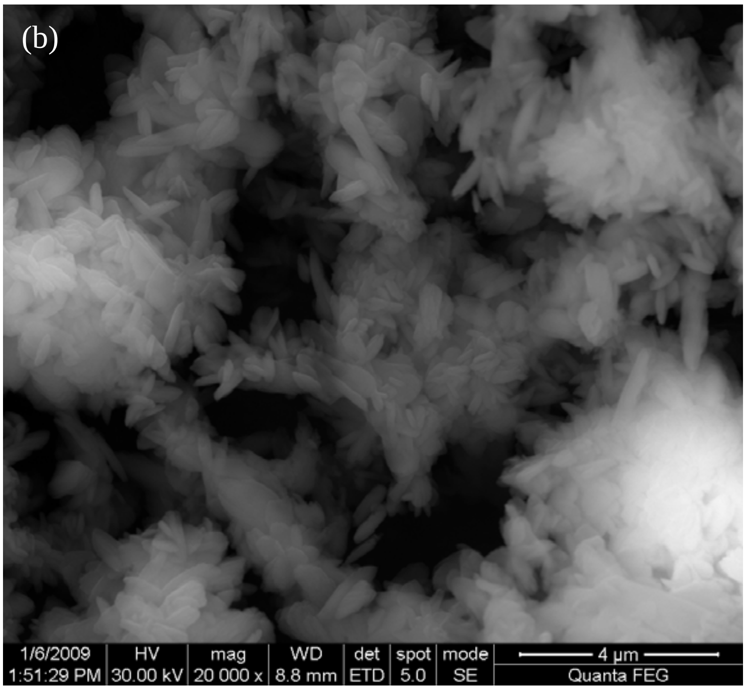
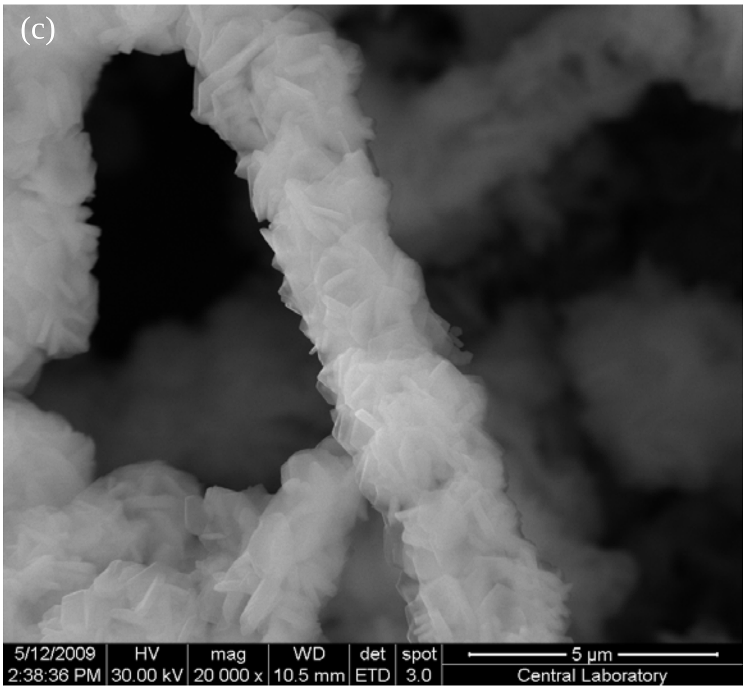


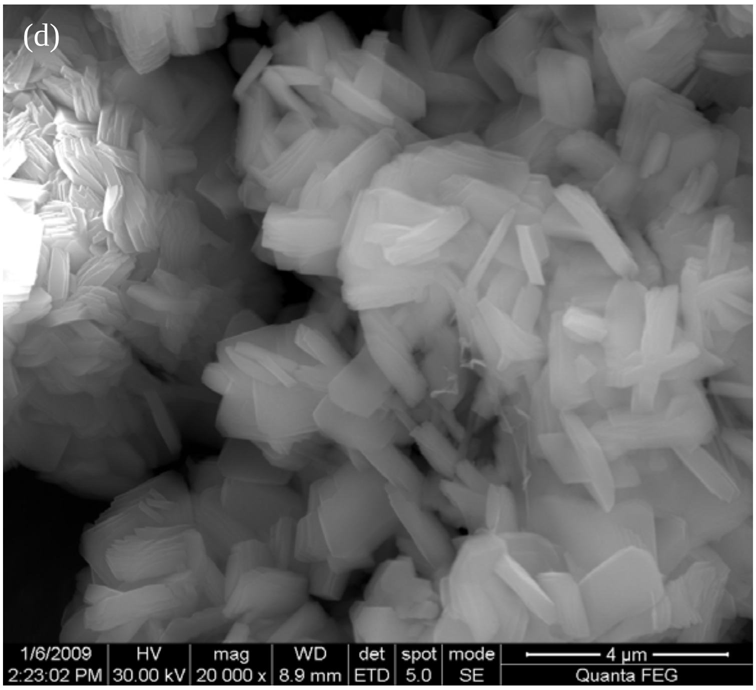
Figure 4.10 Effect of surfactant concentration (PSMA01, PSMA05 and PSMA1) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1 and average particle size of zinc oxide (<1µm) were constant)

SEM micrographs of zinc borates, which were synthesized separately in the presence of 0.1%, 0.5% and 1% PAA and PSMA are given in Figure 4.11 with 20000 magnification. It is seen from the micrographs that changing surfactant concentration was ineffective to prevent agglomeration since all synthesized zinc borate products have sub-micron particles which stuck together because of high energy on the surface of crystals. All of the samples have agglomerate disc-like structure.






(c)
5/12/2009 2:38:36 PM
HV 30.00 kV
mag 20 000 x
WD 10.5 mm
det ETD
spot 3.0
5 μm
Central Laboratory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WD 8.9 mm
det ETD
spot 5.0
mode SE
4 μm
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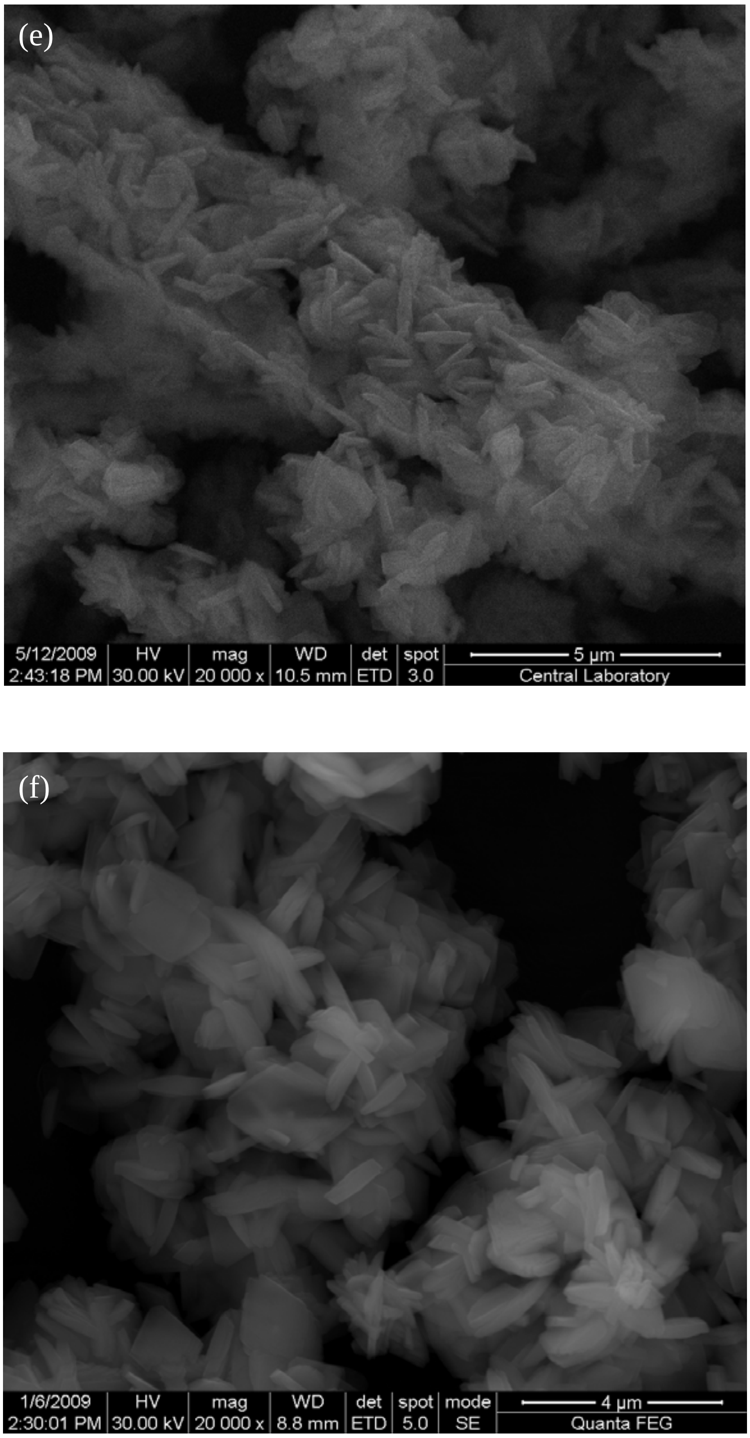


Figure 4.11 SEM micrographs of final zinc borate products a) PAA01 b) PAA05 c) PSMA01 d) PSMA05 e) PSMA1 f) NP with 20000 magnification.

Table 4.4 shows dimensions of zinc borate particles determined by ImageJ programme.

Table 4.4 Dimensions of zinc borate particles synthesized by different concentrations of surfactants

Sample Code	Radius (μm)	Thickness(nm)
PAA01	1±0.2	320±90
PAA05	0.84±0.15	140±45
PSMA01	1±0.2	150±40
PSMA05	1.2±0.2	350±50
PSMA1	0.9±0.15	170±30
NP	1.1±0.2	280±60

According to the Table 4.4, radii of final zinc borate products vary between 0.84 μm to 1.2 μm and thickness changes in the range of 140-350 nm. Smallest particle sizes belong to PAA05. From Table 4.4, it can be said that increasing PAA concentration in reaction medium, decreases particle size of zinc borates. Because surfactant can cover produced zinc borate particles and prevents crystal growth. On the other hand, increasing PSMA concentration from 0.1% to 0.5% first increase both dimensions of zinc borate particles but then decrease both radius and thickness of final zinc borate products for synthesis of 1% PSMA addition.

To sum up, effect of surfactant concentration on the reaction medium was determined from XRD, TGA, ZnO% - B_2O_3% content and SEM analyses. Synthesized zinc borates had similar ZnO% - B_2O_3% contents with commercial zinc borate (FB) except PSMA1. In addition, zinc borates showed consistent XRD patterns with the commercial zinc borate (FB) which means zinc borates were successfully synthesized. Hydration water of synthesized zinc borates was retained in the structure until the process temperature of PET (260°C) based composites. Especially for zinc borates synthesized with PSMA; as PSMA concentration in the zinc borate increased, the radius and thickness of the zinc borate particles first increased and then decreased. Effect of some of these synthesized zinc borates on flame retardant and mechanical properties of PET based flame retardants were investigated in upcoming sections.

4.1.3 Effect of Zinc Oxide Average Particle Size on the Production of Zinc Borate

Mean average particle size of zinc oxide may have a drastic influence on final zinc borate product particle size [2]. It is expected that if ZnO which has smaller particle size is used in the synthesis, zinc borate product will also be obtained in smaller particle size [53]. In this manner ZnO having average particle size <100 nm was used as reactant in addition to ZnO having average particle size <1μm to see the effect of ZnO particle size on final product properties. Selected surfactants from previous characterization results (PAA and PSMA) are added to the reaction medium at 0.5% concentration. XRD, TGA, ZnO% - B_2O_3% content and SEM analyses were performed to characterize the final products.

XRD patterns of zinc borates synthesized by ZnO having average particle size <1μm and <100 nm are shown in Figure 4.12. All products show same characteristic peaks at same 2θ values when compared to the commercial one, supporting the successful synthesis of zinc borates.

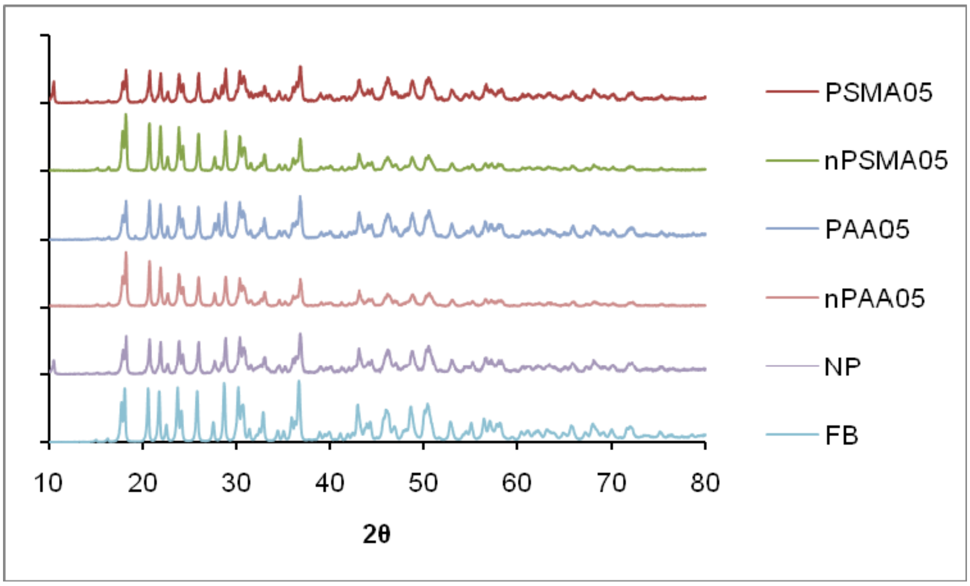


Figure 4.12 XRD peaks of zinc borates zinc borates synthesized by ZnO having average particle size <100 nm

TGA graphs of zinc borates synthesized by using ZnO having average particle size <100 nm are shown in Figure 4.13. All zinc borate samples retain their 3.5 mole hydration water till 325˚C. This information proved that zinc borates synthesized by using ZnO with average particle size <100 nm did not lose their 3.5 mole hydration water during the preparation of PET based composites.

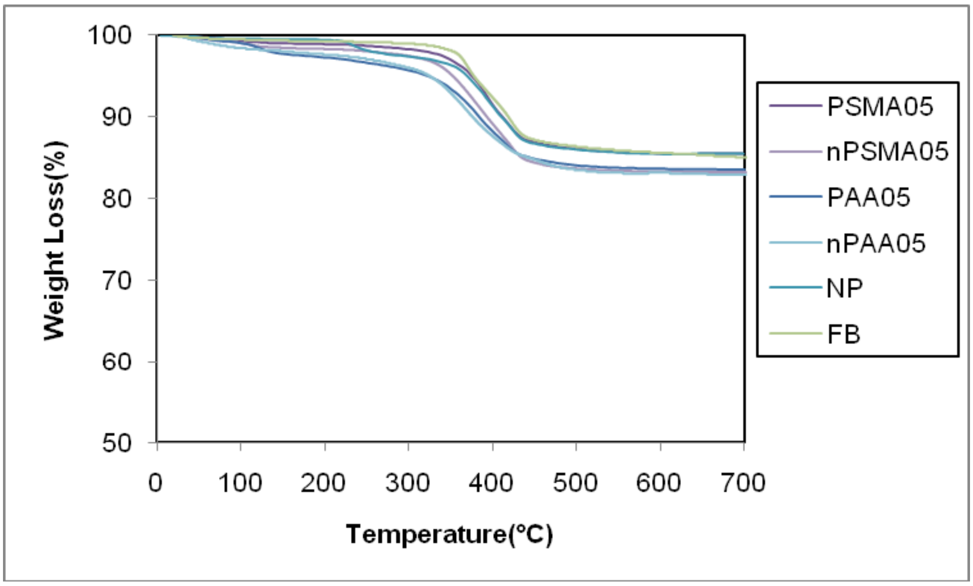


Figure 4.13 TGA curves of zinc borates synthesized by ZnO having average particle size <100 nm

The results of ZnO% - B_2O_3% content analyses of final zinc borate product, synthesized by using ZnO with average particle size <100 nm, are given in Table 4.5. It is observed that, all zinc borates synthesized with <100 nm ZnO had similar B_2O_3 and ZnO content when compared to those of FB. Same contents with the commercial one indicated that 3.5 mole hydrated zinc borate was successfully synthesized.

Table 4.5 Final ZnO and B_2O_3 content of zinc borates synthesized by using ZnO with average particle size <100 nm

Sample Code	ZnO%	B_2O_3%	H_2O% from TGA	B_2O_3% from TGA
FB	37.4	48.0	13.80	48.80
NP	36.4	51.5	11.8	51.8
NP*	39.9	45.7	6.25	53.9
nNP*	39.4	48.2	8.03	52.6
nPAA05	38.0	43.2	15.1	46.9
PAA05	34.3	59.1	13.6	52.1
nPSMA05	34.7	49.2	14.9	50.4
PSMA05	38.4	52.6	13.3	48.3

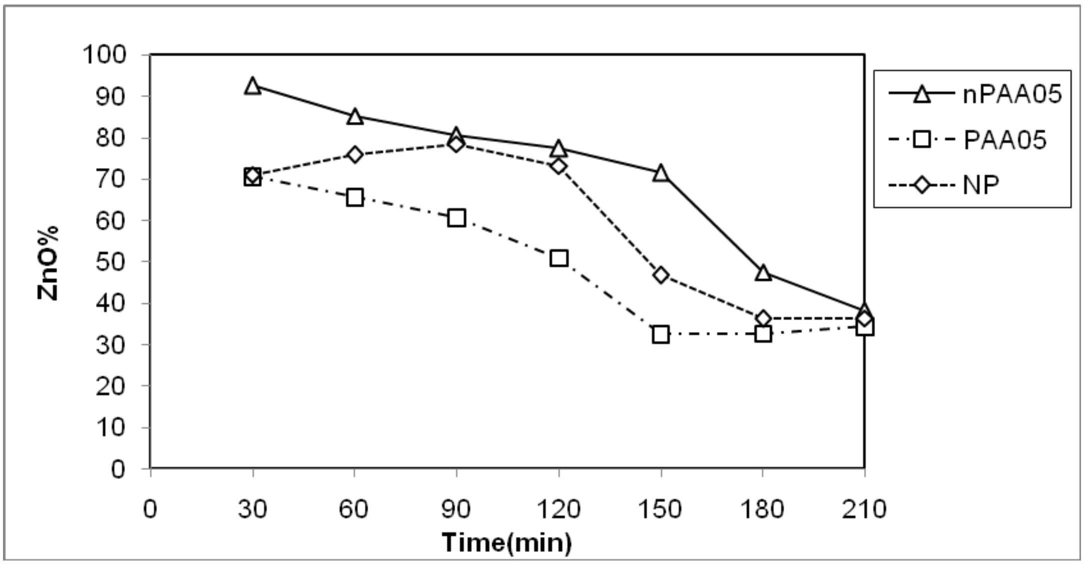
: zinc borate synthesized in our previous study [2] under the same conditions with NP and with the use of nano-sized zinc oxide (nNP).

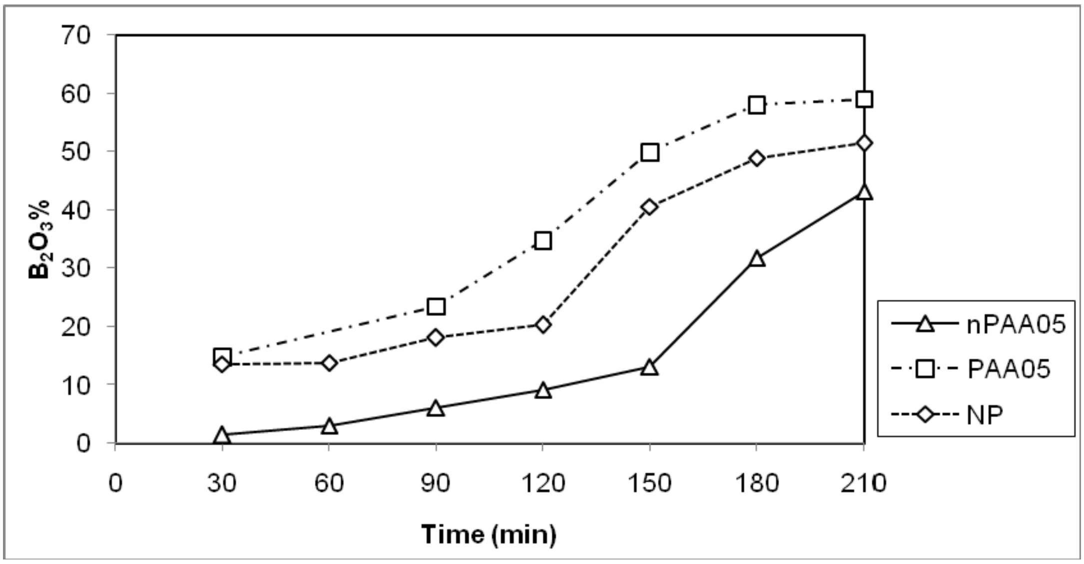
Figures 4.14 and 4.15 show ZnO%, B_2O_3% and ZnO conversion with respect to time in terms of effect of using nano-sized zinc oxide on zinc borate production. For comparison, analytical results for NP are also given. When ZnO% - B_2O_3% content graphs were considered; 210 minutes of reaction time were enough to reach ZnO% - B_2O_3% content of commercial zinc borate (FB) and to make ZnO% - B_2O_3% content stable with respect to time for nPSMA05 and nPAA05.

From Figures 4.14 and 4.15, it can be concluded that decreasing average particle size of zinc oxide increased the reaction rate for nPAA05. Decreasing average particle size of ZnO increased the surface area of ZnO particles hence zinc borate particles could occur in large number of active sites that should increase the reaction rate for PAA05 [2]. Moreover, time needed to complete reaction increased with using nano-sized zinc oxide when compared to the zinc borates synthesized with <1µm zinc oxide.

On the contrary, decreasing particle size for nPSMA did not increase reaction rate. However, time needed to start conversion of ZnO decreased when nano zinc oxide used instead of zinc oxide <1µm.

When NP and NP* were compared with each other; for both cases conversion started at nearly 120 minutes and took 90 minutes to reach complete conversion of ZnO to zinc borate.





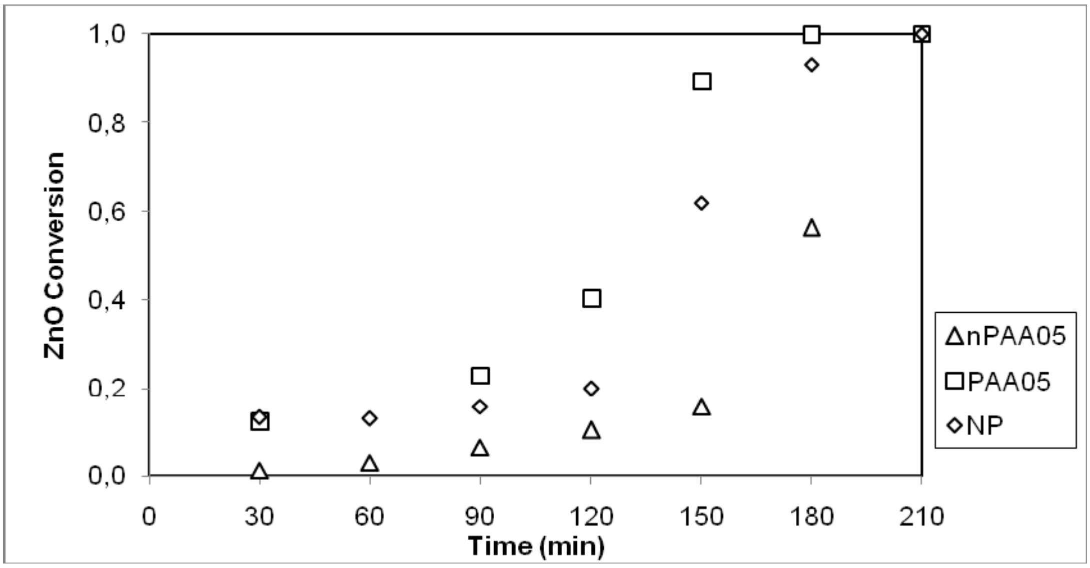
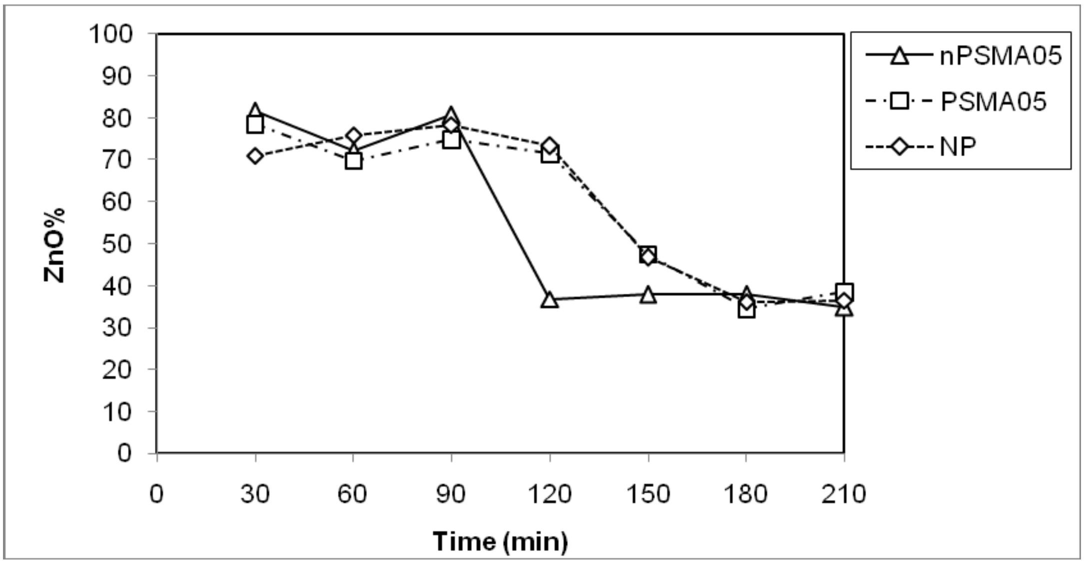
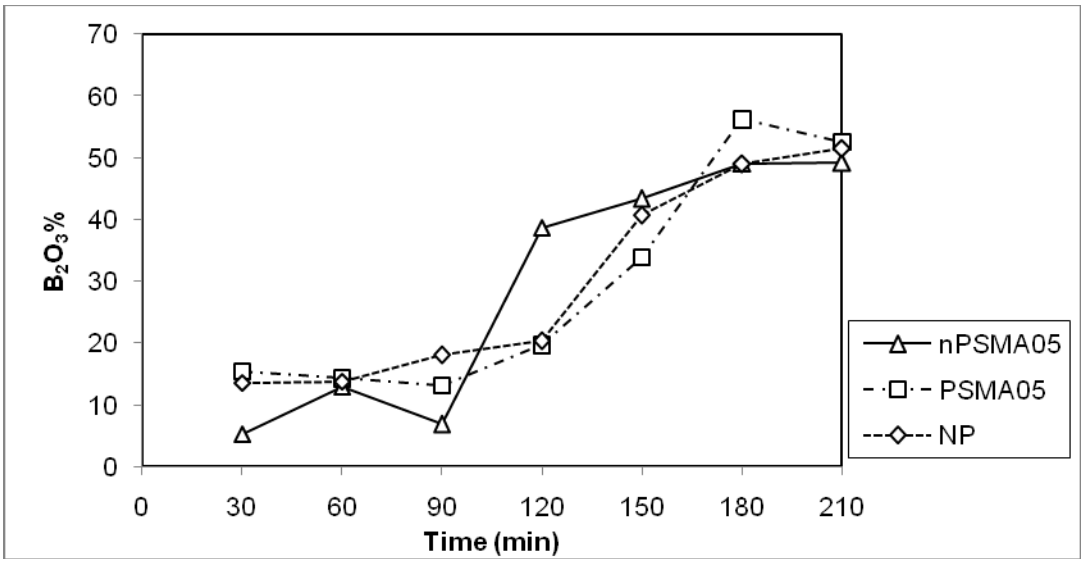


Figure 4.14 Effect of using nano-sized ZnO (nPAA05 and PAA05) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1)





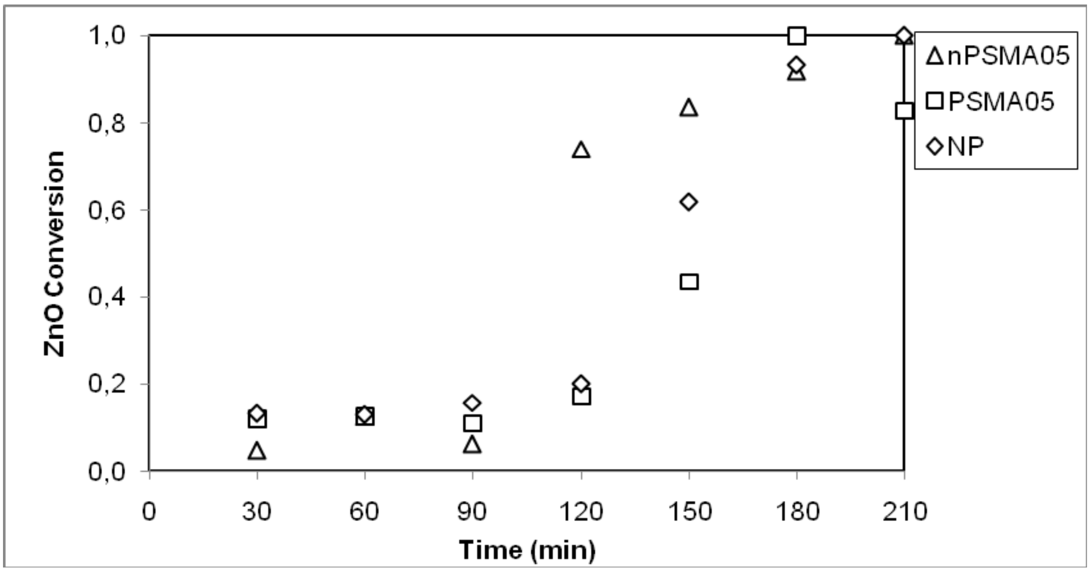


Figure 4.15 Effect of using nano-sized ZnO (nPSMA05 and PSMA05) on zinc borate production reaction (temperature of 85°C, seed amount of 1.5%, initial reactants mole ratio (H_3BO_3:ZnO) of 5:1)

SEM micrographs of zinc borates, which were synthesized by using nanosized zinc oxide, nPAA05 and nPSMA05 are given in Figure 4.16 with 40000 magnification. The micrographs of PAA05 and PSMA05 which were synthesized with <1μm ZnO were given in Figure 4.6.

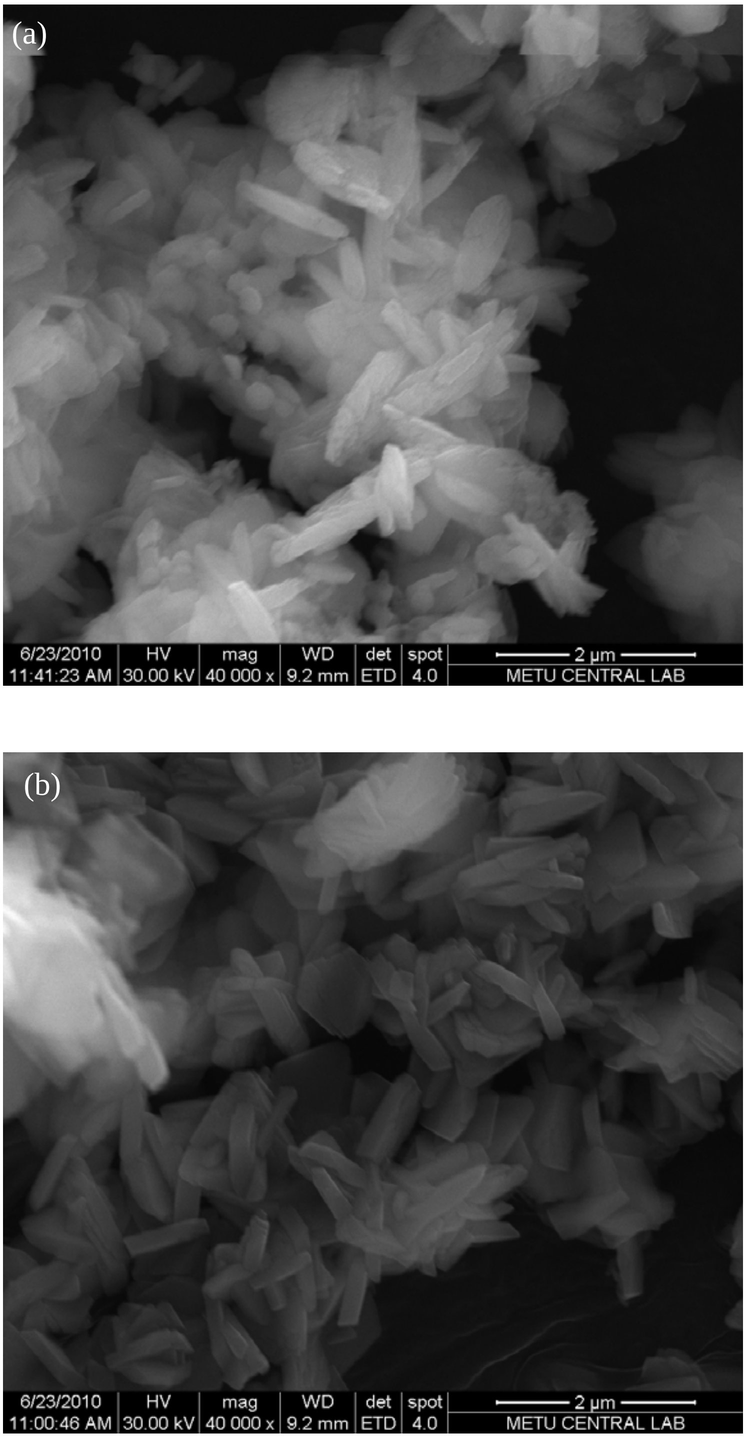


Figure 4.16 SEM micrographs of final zinc borates synthesized by ZnO having average particle size <100 nm with 40000 magnification; (a) nPAA05, (b) nPSMA05.

Figure 4.16 shows that all samples have agglomerate disc-like structure. Dimensions of the zinc borate particles from these syntheses are given in Table 4.6.

Table 4.6 Dimensions of zinc borate particles zinc borates synthesized by using ZnO with average particle size <1µm and <100 nm

Sample Code	Radius (µm)	Thickness(nm)
NP	1.1±0.2	280±60
nPAA05	1±0.2	300±40
PAA05	0.84±0.15	140±45
nPSMA05	0.88±0.3	180±50
PSMA05	1.2±0.2	350±50

It was expected that when smaller particle sized zinc oxide was used as reactant, the final product had also smaller mean particle size. According to Table 4.6, using nano sized ZnO in nPSMA05 production caused a decrease in both dimensions compared to PSMA05 production. On the contrary, using nano sized ZnO slightly increased particle size of PAA05.

To sum up the characterization results of three different cases (effect of surfactant type, effect of surfactant concentration and effect of using nano zinc oxide); it was decided that effect of PAA05, PSMA05 and PSMA1 on the flammability and mechanical properties can be investigated in different compositions of PET based composites. These types of zinc borates were selected due to their chemical composition, particle size and suitability to processing temperature.

PAA05, PSMA05 and PSMA1 have nearly similar ZnO% - B_2O_3% content with the commercial one and have relatively lower radius and thickness values when compared to other synthesized zinc borates. They have also same potential of interacting with functional groups of PET.

4.2 Characterization of Flame Retardant PET Composites

Flame retardant polymer composites were prepared by using amorphous PET, synthesized zinc borates (PAA05, PSMA05, PSMA1 and NP) and some flame retardant materials. Synergist flame retardant additives, which are boron phosphate (BP) and triphenyl phosphate (TPP), were used as in same compositions of the previous work, proved to be effective choices for improving flame retardancy of PET [2].

In the upcoming sections; flammability and mechanical properties of the PET based composites are given and discussed respectively. Flammability was determined by limiting oxygen index (LOI) value and smoke density test. Furthermore, tensile test was performed to determine mechanical properties like tensile strength, tensile modulus, elongation at break and impact strength.

4.2.1 Flammability Analysis of PET Based Flame Retardant Composites

4.2.1.1 Limiting Oxygen Index (LOI) Test of PET Based Flame Retardant Composites

LOI values of prepared composites are given in Table 4.7.

Table 4.7 LOI values of prepared polymer composites

Content	LOI Value (%)
100P	22.5
90 P/5 TPP/5 PAA05	23
90 P/5 TPP/5 NP	22.5
90 P/5 TPP/5 FB	24.5
95 P/5 FB	22.5
95 P/5 BP	24
95 P/5 PSMA05	23
90 P/5 TPP/5 PSMA05	23
95 P/2 PSMA05/3 BP	26
95 P/5 PSMA1	22.5
90 P/5 TPP/5 PSMA1	23.5
95 P/2 PSMA1/3 BP	25.5

It was seen from Table 4.7 that LOI value of pure PET was 22.5%. Adding synthesized zinc borate alone did not have a distinct effect on LOI value of neat PET as can be seen from 95 P/5 PSMA1. However, adding 5% of TPP to neat PET increased the LOI value to 23.5% for 90 P/5 TPP/5 PSMA1 composite. In addition, it can be observed from 90 P/5 TPP/5 NP, 90 P/5 TPP/5 PSMA05 and 90 P/5 TPP/5 PSMA1 that increasing surfactant concentration with TPP caused a slight increase in LOI values. The increase in LOI value with the addition of TPP can be attributed to the fact that triphenyl phosphate has three phenyl groups and high carbon content moreover it first decomposes to phosphoric acid which inhibits H・ radicals and accelerates char formation [2].

Highest LOI values were obtained for 95 P/2 PSMA05/3 BP at 26% and for 95 P/2 PSMA1/3 BP at 25.5%, respectively. The reason of this high LOI value can be due to the glassy layer created on polymer surface at high temperatures by the formation of released B_2O_3. Boron phosphate is an effective flame retardant additive in the polymers since it has oxygen in the main backbone by forming phosphorous oxides to interrupt radical formation [54]. Besides, zinc borate can lose its hydration water during the flammability test and decrease composite temperature and therefore should increase LOI value. Highest LOI values (26 and

25.5) of the composites (95 P/2 PSMA05/3 BP and 95 P/2 PSMA1/3 BP) having zinc borate and boron phosphate together showed that these two additives acted as synergistic agents in polymer matrix since using only 5% BP caused a slight increase in LOI value of 24.

4.2.1.2 Smoke Density Measurement of PET Based Flame Retardant Composites

There are several toxic compounds occurred during and after the smoke formation. The most hazardous smoke product is carbon monoxide (CO) which causes carbon monoxide poisoning. Therefore smoke inhalation can quickly lead to lose consciousness [55].

This study also focused on the effect of synthesized zinc borates on formation of smoke occurred during burning of PET based flame retardant composites. In Table 4.8; percent light transmittance values of flame retardant composites are given.

Table 4.8 Percent light transmittance values of flame retardant composites

Content	Light Transmittance (%)
100P	93.5
90 P/5 TPP/5 PAA05	86.3
90 P/5 TPP/5 NP	94.2
90 P/5 TPP/5 FB	95.3
95 P/5 FB	95.9
95 P/5 BP	97.8
95 P/5 PSMA05	86.4
90 P/5 TPP/5 PSMA05	97.4
95 P/2 PSMA05/3 BP	95.2
95 P/5 PSMA1	95.5
90 P/5 TPP/5 PSMA1	96
95 P/2 PSMA1/3 BP	96

As can be seen from Table 4.8, adding zinc borate only (95 P/5 PSMA05) did not have a significant effect on decreasing smoke density. However, using boron phosphate (95 P/5 BP, 95 P/2 PSMA05/3 BP and 95 P/2 PSMA1/3 BP) increased light transmittance value and decreased smoke density of PET based composites. Because CO turns into CO_2 and formation of CO_2 causes a decrease in smoke density [2].

4.2.2 Mechanical Properties of Flame Retardant PET Composites

It is extremely important to predict how chemistry and morphology of the polymer matrix act in a synergism with the size, shape and surface of filler material [26]. Hence; in this study the main idea is to increase flame retardancy and provide better mechanical properties of PET based composites with using synthesized zinc borates and flame retardant synergists.

In this manner, mechanical properties of PET based composites were analyzed in terms of tensile strength, tensile modulus, elongation at break behaviour and impact strength. The average values of mechanical properties and their standard deviations are also given in APPENDIX G.

4.2.2.1 Tensile Properties of Flame Retardant PET Composites

Tensile strength of PET based composites are shown in Figure 4.17. Tensile strength value of neat PET was obtained as 52.9 MPa. When compared to the neat PET, tensile strength values did not increase in any of prepared PET based composites. This may be attributed to the agglomeration of the fillers which created stress concentrated areas in the composites.

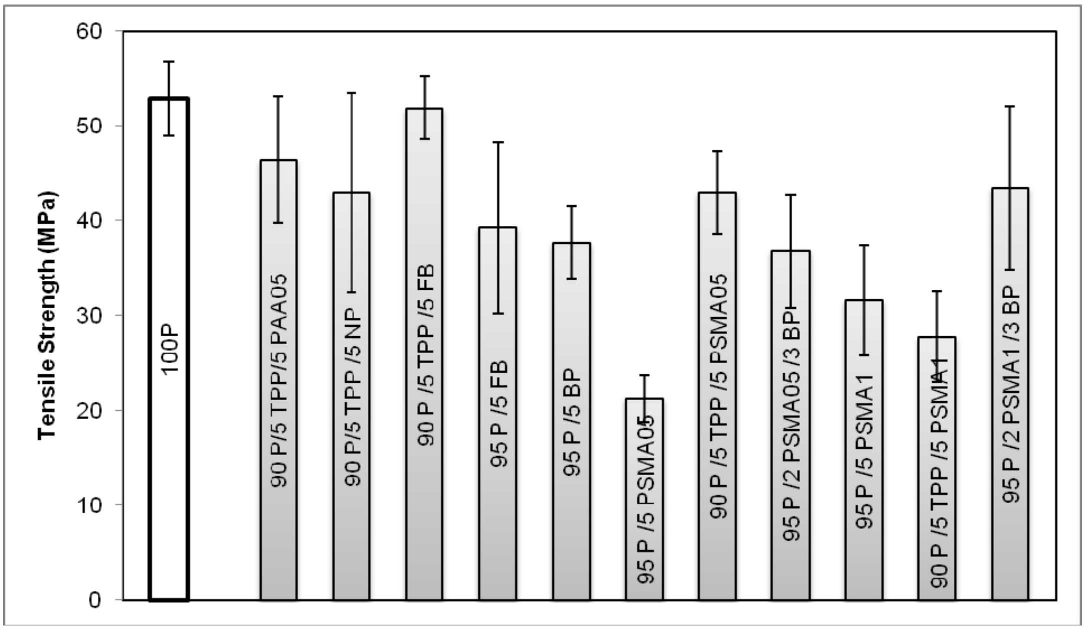


Figure 4.17 Tensile strength values of PET based flame retardant composites

Tensile modulus values of PET based composites are given in Figure 4.18. Neat PET has a tensile modulus around 1687 MPa. It can be observed from Figure 4.18 that tensile modulus value of 95 P/5 PSMA1, 90 P/5 TPP/5 PSMA1 and 95 P/2 PSMA1/3 BP did not change with the addition of zinc borate, TPP and BP when compared to neat PET. Other composites mostly exhibited lower tensile modulii than neat PET. This may be resulted from the agglomeration of filler particles as mentioned before.

Drying of PET composites is one of the most critical factors during processing. Prepared composites must be moisture-free to prevent voids in the final products and also to have better physical/mechanical properties. Moisture absorption directly depends on several factors like processing time, temperature, atmospheric humidity (dew point) and degree of crystallinity. When type of PET is considered; amorphous type of PET absorbs moisture more rapidly (nearly twice) than crystalline form PET. During plasticizing in the extruder, presence of moisture breaks down polymer chains cause a decrease in molecular weight and intrinsic viscosity. This would affect the properties of final product [56].

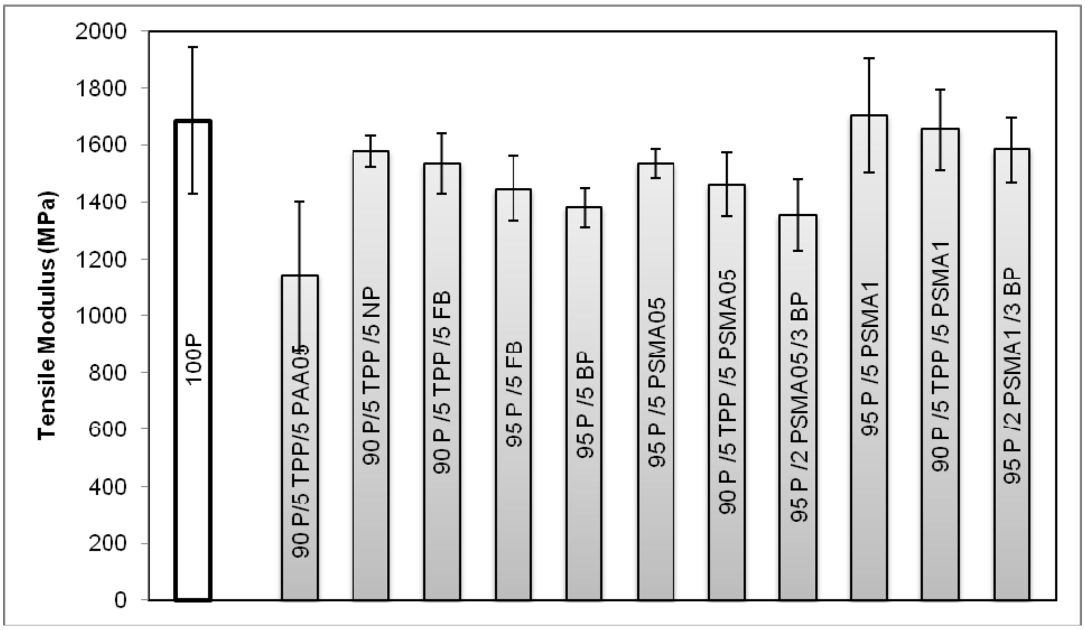


Figure 4.18 Tensile modulus values of prepared flame retardant composites

Elongation at break data for prepared flame retardant PET based composites is given in Figure 4.19. As seen from the figure; elongation at break value of neat PET is 3.9% and there are not any significant differences between elongation at break values of the composites prepared. Only the composites having TPP in their formulation showed slight improvement in percent elongation because of the plasticizing effect of TPP.

When 95 P/5 PSMA05 and 95 P/5 PSMA1 were compared with each other to see the effect of surfactant concentration on elongation at break values; it was concluded that increasing PSMA percent slightly increased the elongation at break values. Similarly, when 95 P/2 PSMA05/3 BP and 95 P/2 PSMA1/3 BP were compared to see the effect of surfactant concentration with boron phosphate addition; 1% PSMA containing composite caused higher elongation at break value resulting from better compatibilization between the additives and polymer matrix.

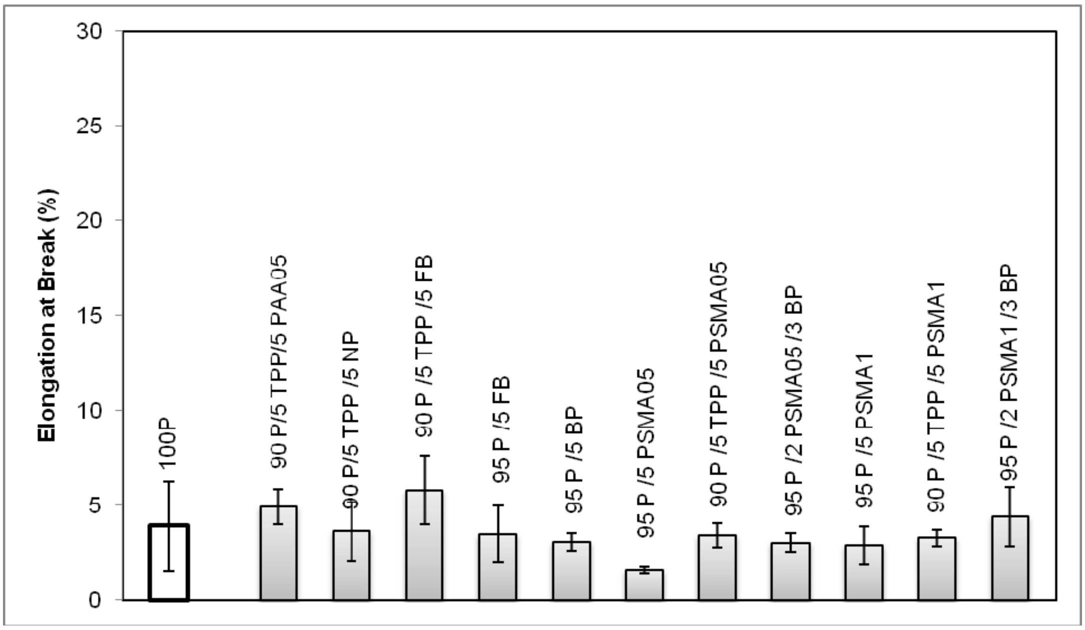


Figure 4.19 Elongation at break values for prepared flame retardant PET based composites

4.2.2.2 Impact Properties of Flame Retardant PET Composites

Impact testing gives idea about material ability to resist high loadings. Impact strength value is a critical measurement of service life, product safety and liability [57].

Impact strength values of prepared PET based composites are given in Figure 4.20. Neat PET has impact strength of 9.63 kJ/m^2. In Figure 4.20; highest impact strength value belongs to 95P/5BP where the lowest value belongs to 90P/5TPP /5PSMA05. Non-homogeneous distribution during polymer processing causes stress concentrated regions in polymer matrix that reduce resistance to deformation and decrease impact strength values (90P/5TPP/5PAA05).

In some composites such as 95P/2PSMA05/3BP and 95P/2PSMA1/3BP; higher impact strength values were obtained due to the homogeneous distribution and better adhesion between the flame retardant fillers and the polymer matrix when compared to neat PET. LOI values of these composites were also the highest among the studied ones. It can be said that use of PSMA05, PSMA1 and BP at these contents in the PET matrix provided the best composition for the flammability and impact properties. This can be due to the synergy between the fillers.

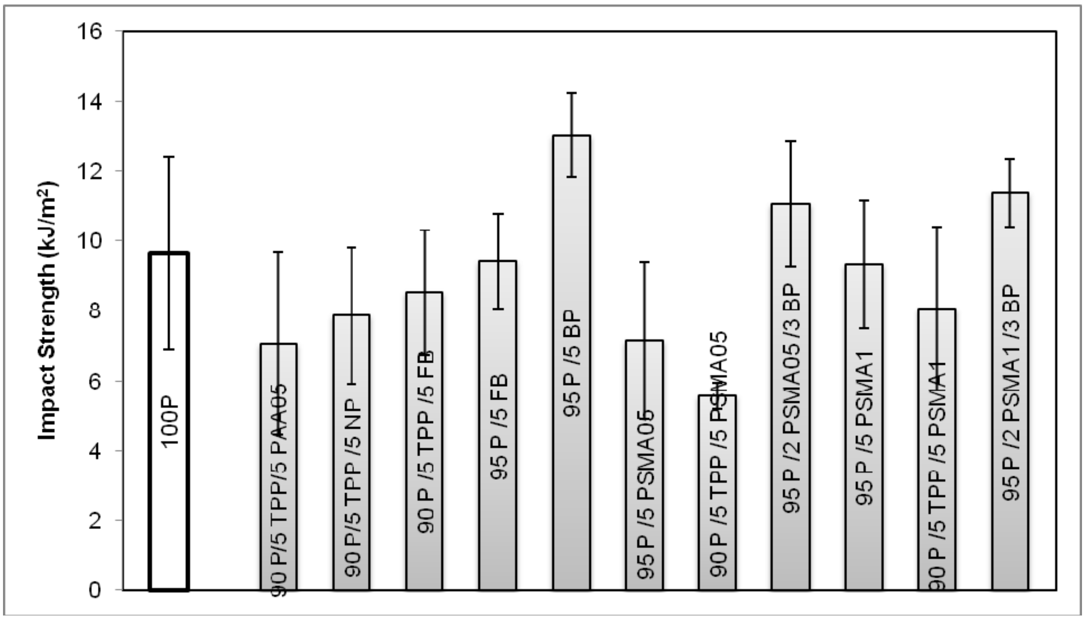


Figure 4.20 Impact strength values of prepared PET based composites

SEM micrographs of the composite containing 2% PSMA1 and 3% BP are given in Figure 4.21. Homogeneous distribution of fillers in the polymeric matrix was observed in the micrographs that should be responsible for enhancing the impact strength of neat PET.

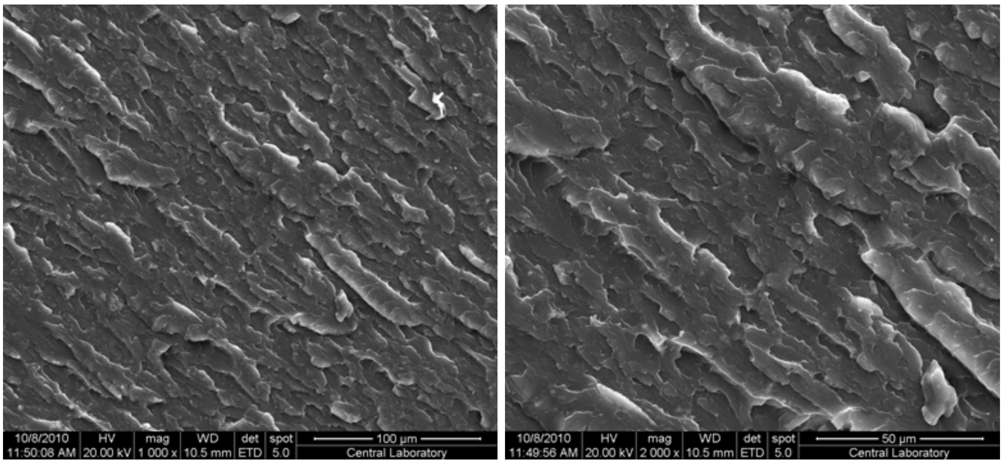


Figure 4.21 SEM micrographs of 95 P/2 PSMA1/3BP (x1000 and x2000)

CHAPTER 5

CONCLUSIONS

This study can be divided into two main parts: i) production and characterization of 3.5 mole hydrated zinc borate; ii) processing and characterization of flame retardant PET based polymer composites.

In the first part, the main idea was to synthesize 3.5 mole hydrated zinc borate having a consistent chemical content with the commercial one and to produce zinc borates having sub-micron particle size. So in this manner; different surfactants were used in the syntheses to prevent crystal growth without influencing chemical formulation and thermal stability of final product. Effect of surfactant type, effect of surfactant concentration and effect of using nano-sized zinc oxide as reactant were investigated on the production of 3.5 mole hydrated zinc borate. Conclusions of the first part of this study were listed below:

- Zinc borates synthesized in the presence of PAA05, SA05, PVP05 and PSMA05 had same crystalline structure when compared to commercial 3.5 mole hydrated zinc borate (FB).
- Synthesized zinc borates retained their hydration water till at least 325°C which means zinc borate did not decompose during processing of PET based flame retardant composites.
- Among the surfactants used in the synthesis of 3.5 mole hydrated zinc borate; Poly(acrylic acid) (PAA) and Poly(styrene-co-maleic anhydride) (PSMA) seemed to be the most effective surfactants in terms of their chemical structure, thermal stability and mean average particle size.
- Using nano-sized ZnO as reactant; did not affect considerably the average particle size of zinc borate.

- Synthesized zinc borates had disc-like structure and sub-micron sizes were observed at least in one dimension.

Second part of this study included preparation; processing and characterization of PET based flame retardants with synthesized zinc borates (PAA05, PSMA05, PSMA1 and NP) and other flame retardant additives like boron phosphate (BP), triphenyl phosphate (TPP) and commercial zinc borate (FB). Both synthesized zinc borates and other flame retardant additives were added at maximum 5 wt. % in the polymer composites. Prepared flame retardant composites were characterized in terms of flammability and mechanical properties. Limiting oxygen index (LOI) and smoke density were measured to determine flammability whereas tensile strength, tensile modulus, elongation at break and impact strength were measured to comment on mechanical properties. Conclusions of this second part were listed below:

- Adding zinc borate only to flame retardant composite was not sufficient to increase LOI value of neat PET.
- Using zinc borate together with boron phosphate resulted in highest increase in LOI values and decreased smoke density of pure PET because of synergistic effect.
- There were not significant improvement in tensile strength and tensile modulus values of PET composites with the addition of fillers. Elongation at break values of composites did not change significantly with the fillers.
- Highest LOI value was obtained when 2% PSMA05 and 3% BP were added to pure PET whereas highest impact strength was observed when 2% PSMA1 was used together with 3% BP in PET matrix.

CHAPTER 6

RECOMMENDATIONS

Following recommendations can be given to the researchers focusing on synthesis of zinc borate:

- Optimizing the washing parameters of the final product for removing both excess boric acid and surfactant can be performed.
- FTIR analysis can be used to understand the interactions between the surface of the zinc borate and the surfactant.
- In addition to using surfactant in the reaction; a dispersant can also be added to prevent agglomeration. Other than this, using a dispersant in the reaction may help to perform dry method particle size analysis accurately.

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APPENDIX A

INVESTIGATION OF SYNTHESIS PRODUCTS HAVING DIFFERENT CRYSTALLINE STRUCTURES

Properties of synthesis products having different structures are given below in Table A.1:

Table A.1. Final product specifications of synthesis products having different crystalline structures

Zinc Borate Code	Final Product Specifications						
	ZnO(%)	B_2O_3(%)	B_2O_3(%) from TGA	H_2O(%) from TGA	Dehydration temp.(°C)	Avg. Part. Size (μm)	
						Radius (μm)	Thickness (nm)
SDS05	33.30	56.9	54.12	12.58	340	1.95±0.15	500±150
OA05[1]	-	-	-	13.15	323	1.6±0.2	400±100
UREA05	34.70	56.8	52.05	13.3	323	2±0.3	350±70
PSSA05	50.40	34.0	18.78	30.8	97	-	-
PSMA10[2]	19.3	37.4	50.96	29.7	326	0.8±0.2	95±20
PEG01[3]	26.6	34.0	63.03	10.4	328	1.25±0.4	170±50
nPEG05	39	50.9	47.67	13.8	300	1.9±0.1	350±45
PEG05	25.6	37.1	64.66	9.7	330	0.9±0.2	170±30
PEG1	28.8	42.3	60.27	10.9	335	0.95±0.1	200±50

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[1] : titration method could not have performed on OA05. For OA05, homogeneous solution could not have prepared for titration since oleic acid is insoluble in water

[2] : one extra set of experiment was performed with 10% PSMA to see the effect of higher surfactant concentration than 0.1%, 0.5% and 1%.

[3] : Poly(ethylene glycol) (PEG) was selected since it is inexpensive, non-toxic and has a wide distribution of the molecular weight (200-20000) [6]

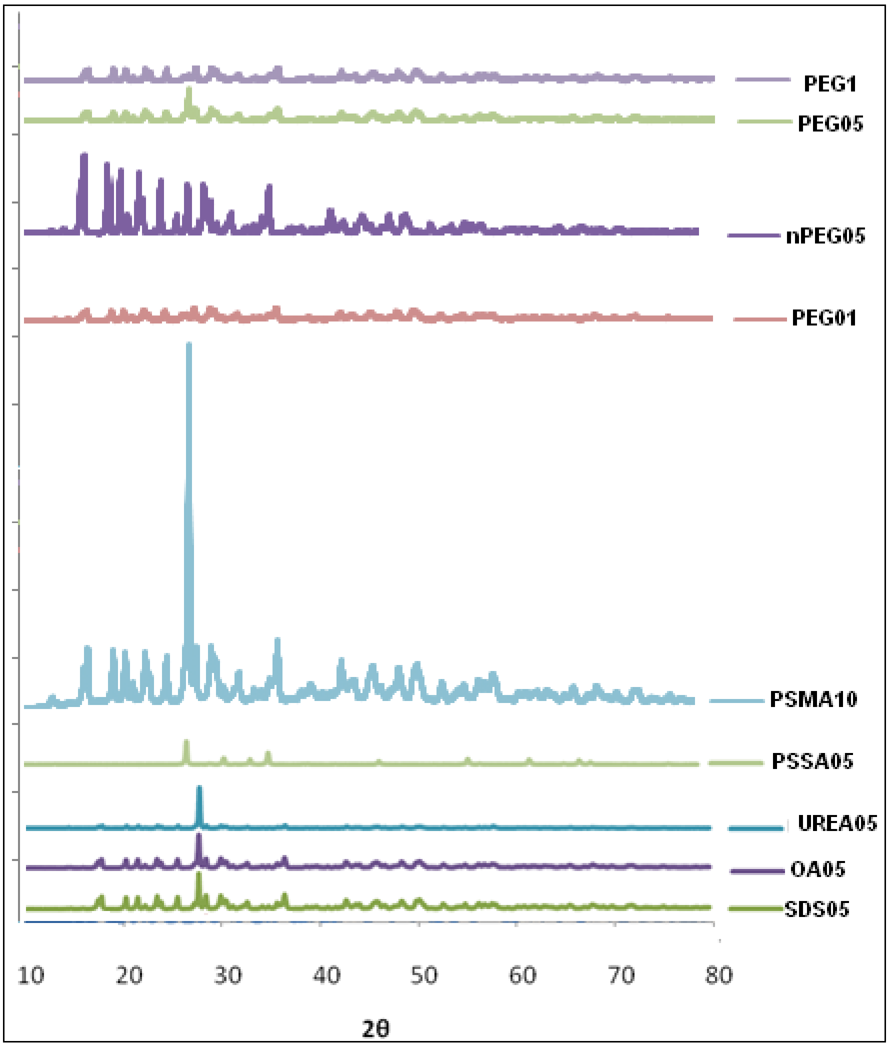


Figure A.1 XRD Patterns of synthesis products having different crystalline structures

Comments about Figure A.1 are given below:

- For UREA05 there is a sharp peak at nearly 27°. This value is one of the characteristic peaks of pure boric acid [APPENDIX C, Figure C.2]. So this sharp peak supports the high B_2O_3% value of UREA05 (56.8%) result from insufficient washing of excess boric acid of final product.

- For PSMA10, there is a sharp peak at 27° and it belongs to characteristic peak of boric acid. Unreacted excess boric acid in the reaction medium can cause this sharp peak. As seen in Table A.1.; lower B_2O_3% value of PSMA10 (%37.4) support the presence of unreacted excess boric acid in the system.

APPENDIX B

CHEMICAL ANALYSIS OF 3.5 MOLE HYDRATED ZINC BORATES

Table B.1 Chemical analysis results for PAA01

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2080	39.04	76.37	0.159	0.2030	0.79	13.55	0.028
60	0.2090	45.32	88.23	0.184	0.2050	0.36	6.11	0.013
90	0.2083	45.41	88.71	0.185	0.2025	0.44	7.56	0.015
120	0.2085	39.46	77.01	0.161	0.2043	1.20	20.45	0.042
150	0.2059	25.89	51.16	0.105	0.2082	1.80	30.10	0.063
180	0.2092	20.61	40.09	0.084	0.2020	2.83	48.77	0.099
210	0.2033	18.81	37.65	0.077	0.2078	2.80	46.90	0.097

Table B.2 Chemical analysis results for nPAA05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2018	45.86	92.47	0.187	0.2037	0.08	1.37	0.003
60	0.2055	43.03	85.20	0.175	0.2036	0.18	3.08	0.006
90	0.2034	40.22	80.47	0.164	0.2037	0.36	6.15	0.013
120	0.2022	38.46	77.40	0.157	0.2069	0.55	9.25	0.019
150	0.2055	36.12	71.52	0.147	0.2071	0.78	13.11	0.027
180	0.2048	23.87	47.43	0.097	0.2022	1.85	31.85	0.064
210	0.2012	18.81	38.04	0.077	0.2087	2.59	43.20	0.090

Table B.3 Chemical analysis results for PAA05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2028	35.18	70.59	0.143	0.204	0.87	14.85	0.030
60	0.2073	33.38	65.52	0.136	-	-	-	-
90	0.2055	30.64	60.67	0.125	0.209	1.41	23.48	0.049
120	0.2026	25.35	50.91	0.103	0.206	2.06	34.81	0.072
150	0.2023	16.18	32.54	0.066	0.203	2.91	49.90	0.101
180	0.2010	16.16	32.71	0.066	0.204	3.40	58.02	0.118
210	0.2050	17.30	34.34	0.070	0.205	3.48	59.09	0.121

Table B.4 Chemical analysis results for SA05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2034	46.09	92.20	0.188	0.207	0.39	6.56	0.014
60	0.2096	40.66	78.93	0.165	0.203	0.78	13.38	0.027
90	0.2054	39.91	79.06	0.162	0.204	0.65	11.09	0.023
120	0.2038	30.03	59.96	0.122	0.207	1.88	31.61	0.065
150	0.2070	18.18	35.74	0.074	0.206	3.19	53.90	0.111
180	0.2053	17.28	34.25	0.070	0.208	3.33	55.73	0.116
210	0.2060	18.43	36.40	0.075	0.202	3.29	56.70	0.115

Table B.5 Chemical analysis results for PVP05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2000	44.07	89.66	0.179	0.206	0.73	12.34	0.025
60	0.2066	48.51	95.54	0.197	0.206	0.21	3.55	0.007
90	0.2039	47.89	95.57	0.195	0.200	0.22	3.83	0.008
120	0.2013	45.07	91.10	0.183	0.206	0.47	7.94	0.016
150	0.2016	31.23	63.03	0.127	0.202	1.85	31.88	0.064
180	0.2035	18.00	35.99	0.073	0.207	2.70	45.40	0.094
210	0.2030	19.57	39.23	0.080	0.205	3.21	54.51	0.112

Table B.6 Chemical analysis results for PSMA01

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2018	45.96	92.67	0.187	0.2044	0.56	9.54	0.019
60	0.2030	45.99	92.18	0.187	0.2017	0.32	5.52	0.011
90	0.2083	32.06	62.63	0.130	0.2064	1.87	31.54	0.065
120	0.2020	18.58	37.43	0.076	0.2077	2.75	46.09	0.096
150	0.2040	17.83	35.56	0.073	0.2042	3.20	54.55	0.111
180	0.2005	18.36	37.26	0.075	0.2059	2.75	46.49	0.096
210	0.2082	19.10	37.33	0.078	0.2055	3.33	56.41	0.116

Table B.7 Chemical analysis results for nPSMA05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2015	40.36	81.50	0.164	0.2024	0.31	5.33	0.011
60	0.2075	36.75	72.07	0.150	0.2032	0.76	13.02	0.026
90	0.2030	40.24	80.66	0.164	0.2062	0.41	6.92	0.014
120	0.2025	18.29	36.75	0.074	0.2023	2.25	38.72	0.078
150	0.2020	18.75	37.77	0.076	0.2085	2.60	43.41	0.091
180	0.2014	18.75	37.88	0.076	0.2028	2.86	49.09	0.100
210	0.2017	17.21	34.72	0.070	0.2025	2.86	49.16	0.100

Table B.8 Chemical analysis results for PSMA05

Sample time (min)	Weight of sample (g)	EDTA used (ml)	ZnO in the sample (%)	Amount of ZnO in the sample (g)	Weight of sample (g)	NaOH used (ml)	B_2O_3 in the sample (%)	Amount of B_2O_3 in the sample (g)
30	0.2039	39.32	78.47	0.160	0.200	0.89	15.49	0.031
60	0.2082	35.73	69.83	0.145	0.206	0.85	14.36	0.030
90	0.2030	37.30	74.77	0.152	0.205	0.78	13.24	0.027
120	0.2023	35.52	71.44	0.145	0.203	1.15	19.72	0.040
150	0.2034	23.74	47.49	0.097	0.201	1.96	33.94	0.068
180	0.2044	17.30	34.44	0.070	0.203	3.28	56.24	0.114
210	0.2070	19.55	38.43	0.080	0.203	3.07	52.64	0.107

Table B.9 Chemical analysis results for PSMA1

Sample time (min)	**Weight of sample (g)**	**EDTA used (ml)**	**ZnO in the sample (%)**	**Amount of ZnO in the sample (g)**	**Weight of sample (g)**	**NaOH used (ml)**	**B_2O_3 in the sample (%)**	**Amount of B_2O_3 in the sample (g)**
30	0.2008	37.86	76.72	0.154	0.2036	0.21	3.59	0.007
60	0.2067	37.78	74.37	0.154	0.2044	0.42	7.15	0.015
90	0.2070	17.67	34.73	0.072	0.2026	2.56	43.98	0.089
120	0.2035	18.24	36.47	0.074	0.2074	3.42	57.40	0.119
150	0.2034	17.45	34.91	0.071	0.2047	3.38	57.48	0.118
180	0.2070	18.59	36.54	0.076	0.2071	3.12	52.44	0.109
210	0.2045	14.74	29.33	0.060	0.2030	2.98	51.10	0.104

Table B.10 Chemical analysis results for NP

Sample time (min)	**Weight of sample (g)**	**EDTA used (ml)**	**ZnO in the sample (%)**	**Amount of ZnO in the sample (g)**	**Weight of sample (g)**	**NaOH used (ml)**	**B_2O_3 in the sample (%)**	**Amount of B_2O_3 in the sample (g)**
30	0.2060	35.93	70.97	0.146	0.202	0.79	13.61	0.027
60	0.2057	38.34	75.84	0.156	0.207	0.82	13.79	0.029
90	0.2070	39.88	78.39	0.162	0.200	1.04	18.10	0.036
120	0.2053	36.95	73.23	0.150	0.209	1.22	20.32	0.042
150	0.2071	23.77	46.70	0.097	0.209	2.44	40.64	0.085
180	0.2068	18.38	36.16	0.075	0.202	2.84	48.94	0.099
210	0.2080	18.62	36.43	0.076	0.209	3.09	51.47	0.108

APPENDIX C

ORfor REACTANTS (ZINC OXIDE AND BORIC ACID) AND SURFACTANT (POLYSTYRENE AND MALEIC ANHYDRIDE)

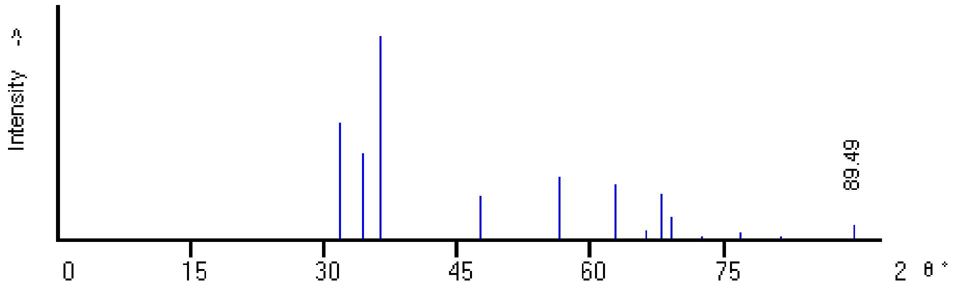


Figure C.1 Characteristic XRD peaks of zinc oxide

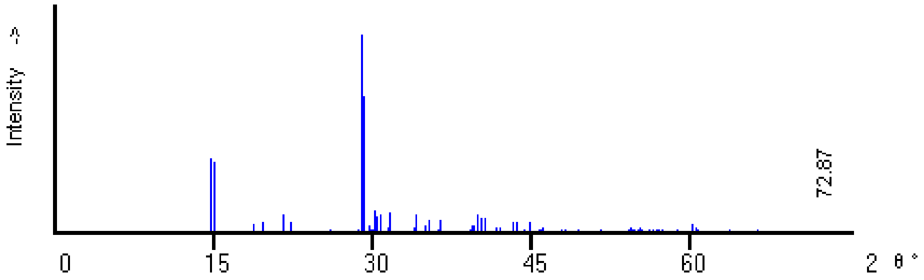


Figure C.2 Characteristic XRD peaks of boric acid

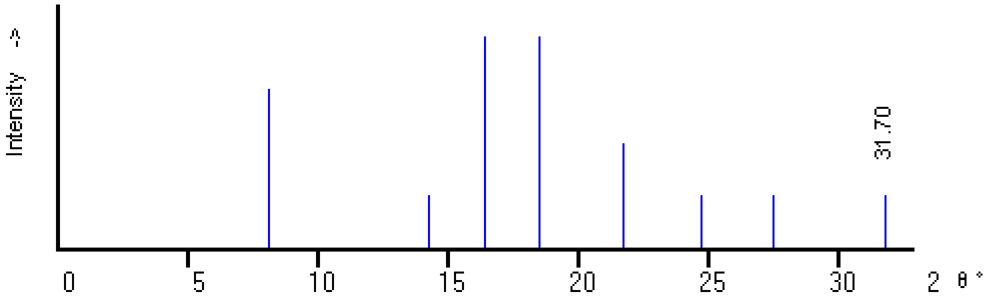


Figure C.3 Characteristic XRD peaks of polystyrene

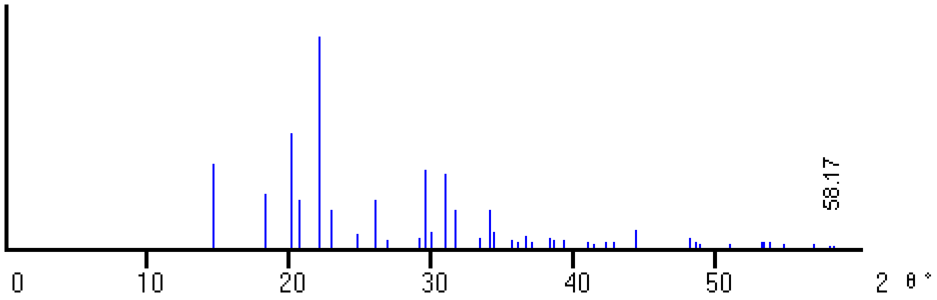


Figure C.4 Characteristic XRD peaks of maleic anhydride

APPENDIX D

TGA RESULTS of 3.5 HYDRATED ZINC BORATES

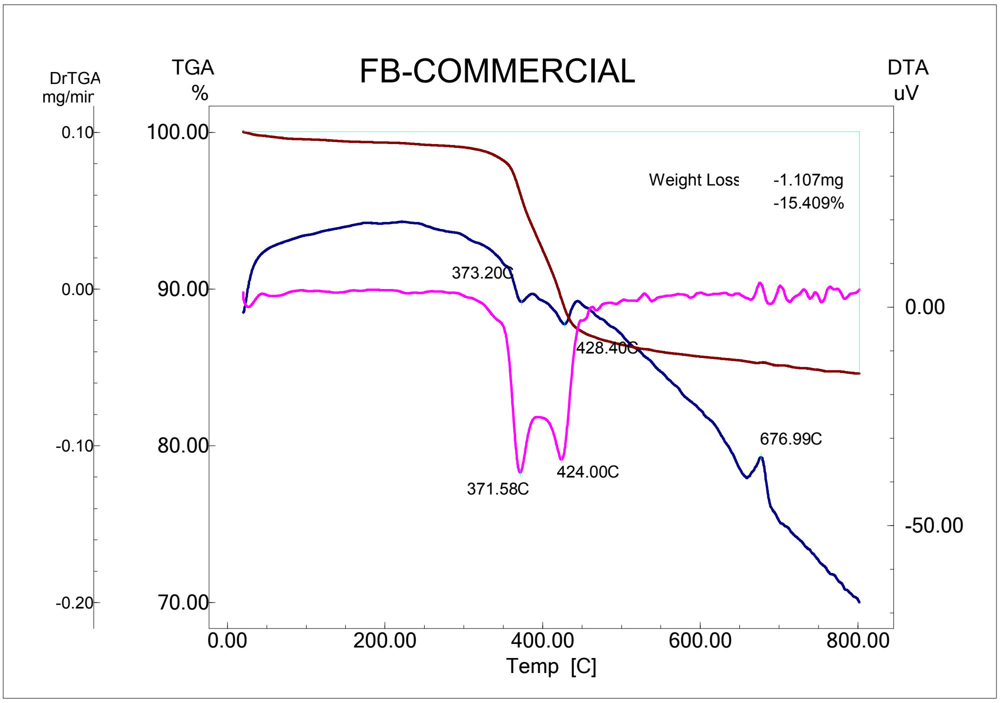


Figure D.1 TG/DTA thermogram of Firebrake ZB 3.5 hydrated zinc borate

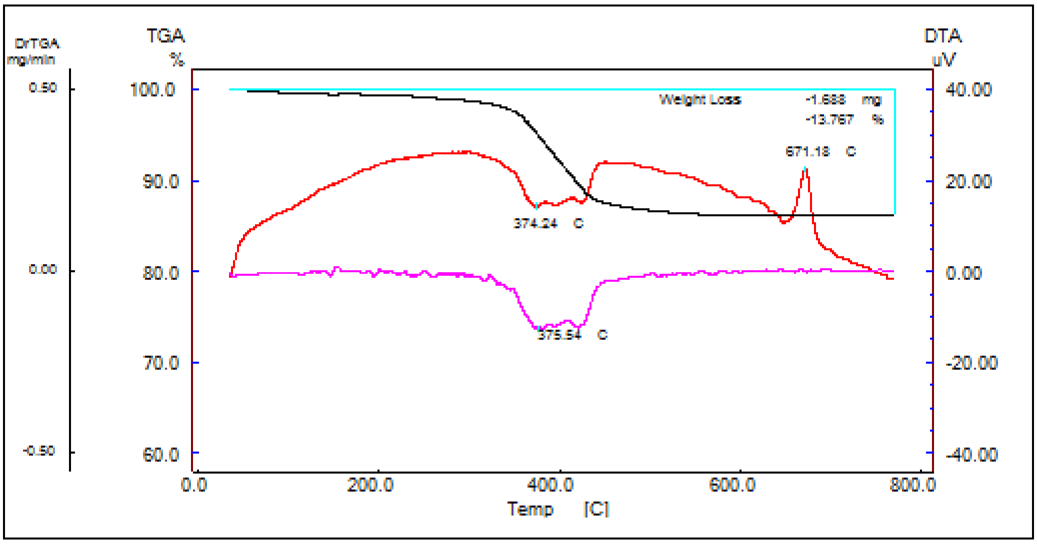


Figure D.2 TG/DTA thermogram of PAA01

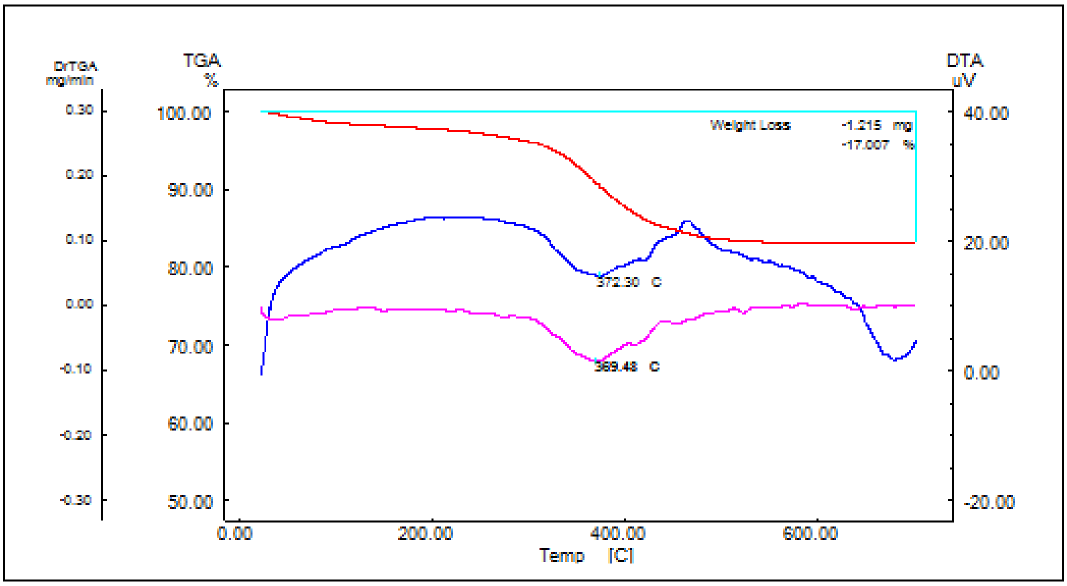


Figure D.3 TG/DTA thermogram of nPAA05

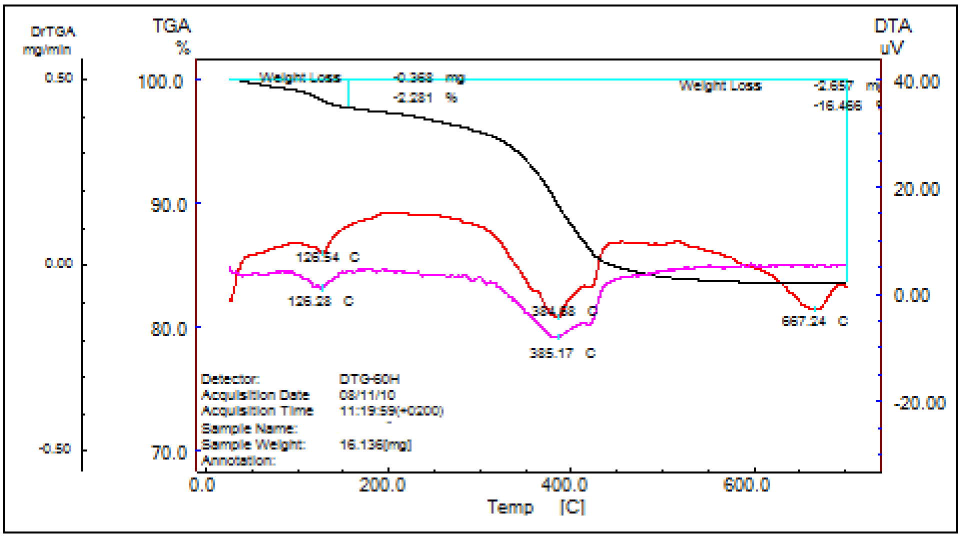


Figure D.4 TG/DTA thermogram of PAA05

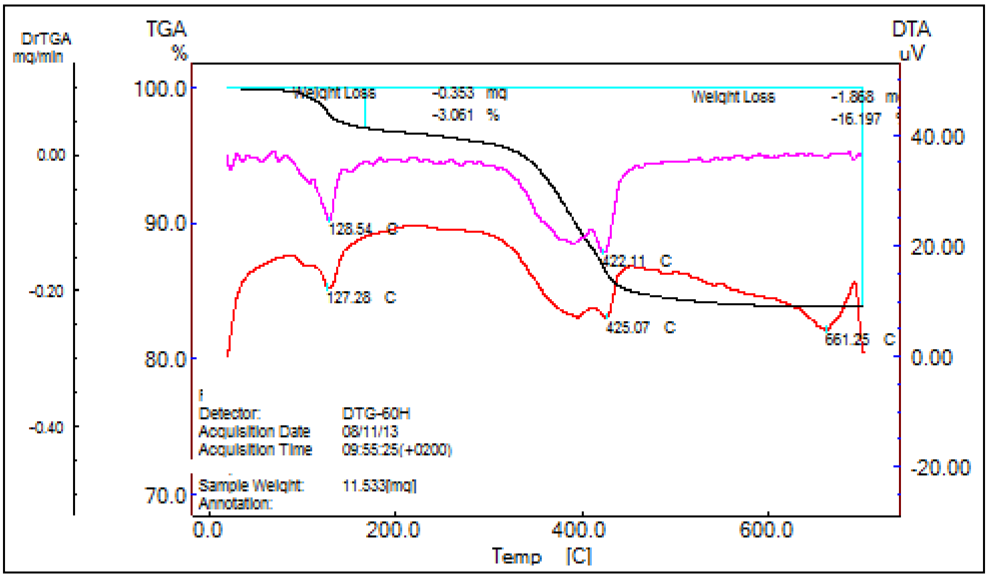


Figure D.5 TG/DTA thermogram of SA05

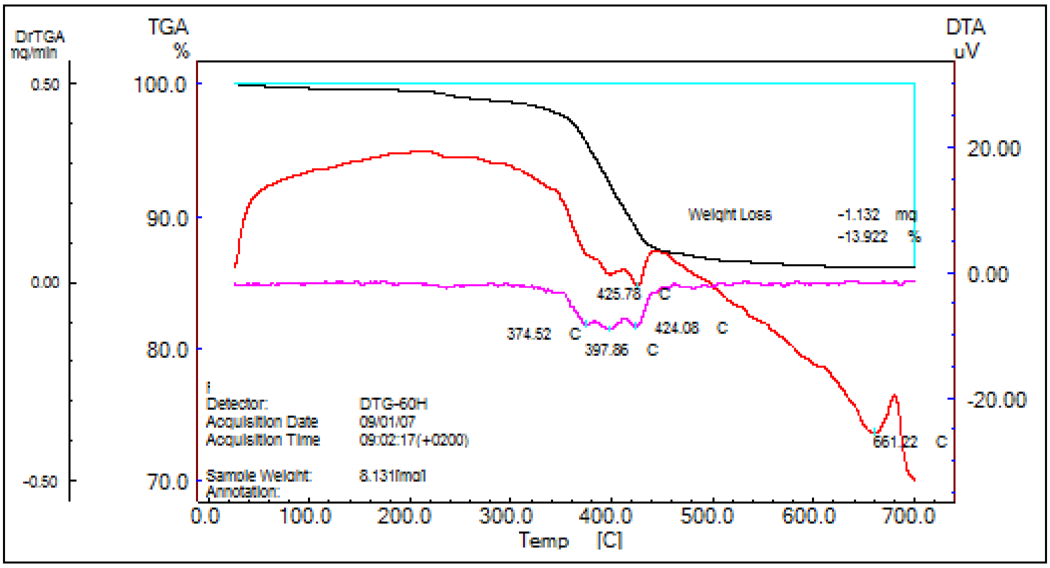


Figure D.6 TG/DTA thermogram of PVP05

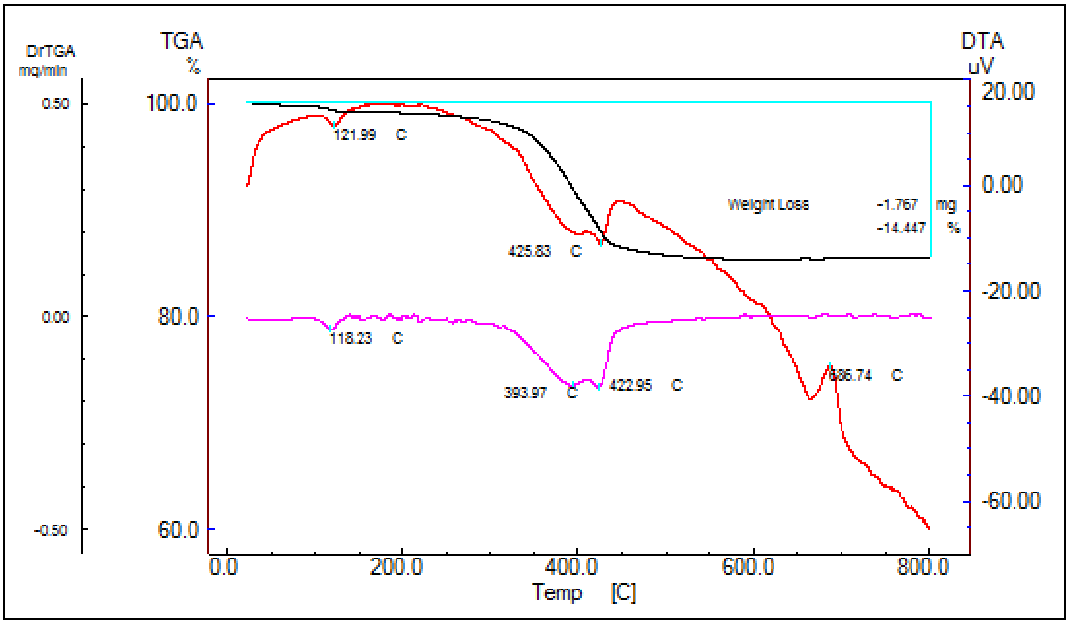


Figure D.7 TG/DTA thermogram of PSMA01

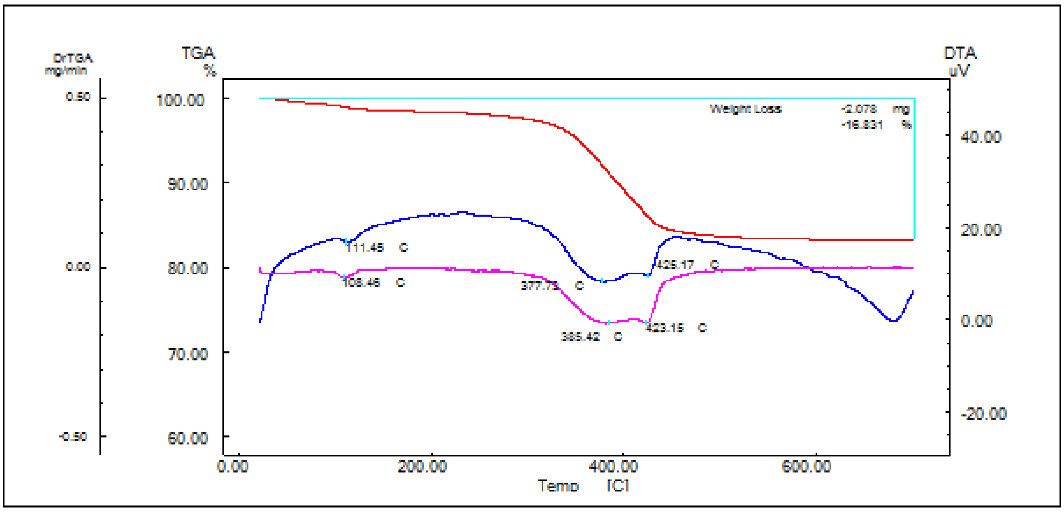


Figure D.8 TG/DTA thermogram of nPSMA05

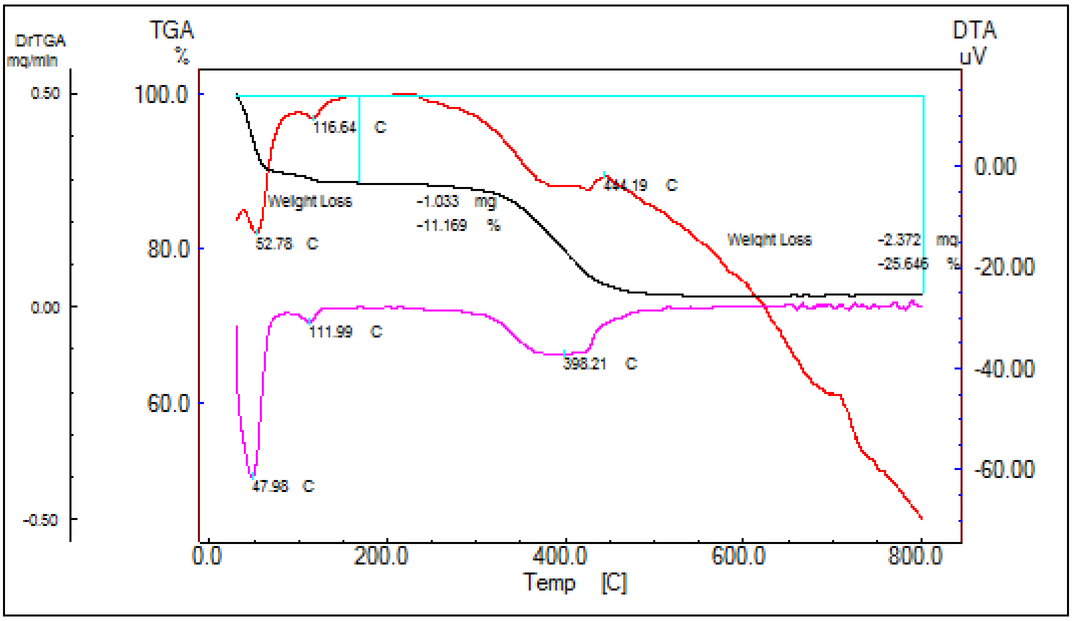


Figure D.9 TG/DTA thermogram of PSMA1

APPENDIX E

SEM MICROGRAPHS OF PURE ZINC OXIDE, BORIC ACID AND POLY(STYRENE-CO-MALEIC ANHYDRIDE)

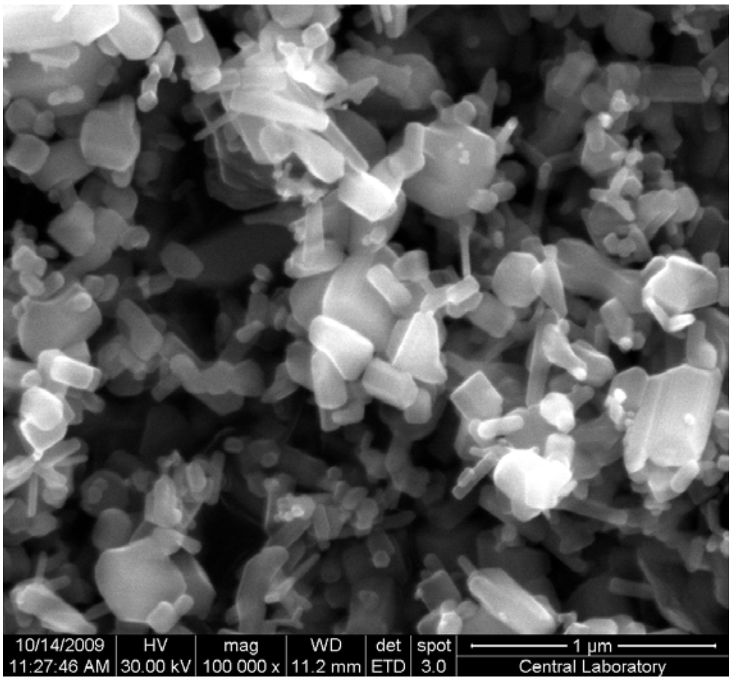


Figure E.1 SEM micrograph of pure zinc oxide (x 100000 mag)

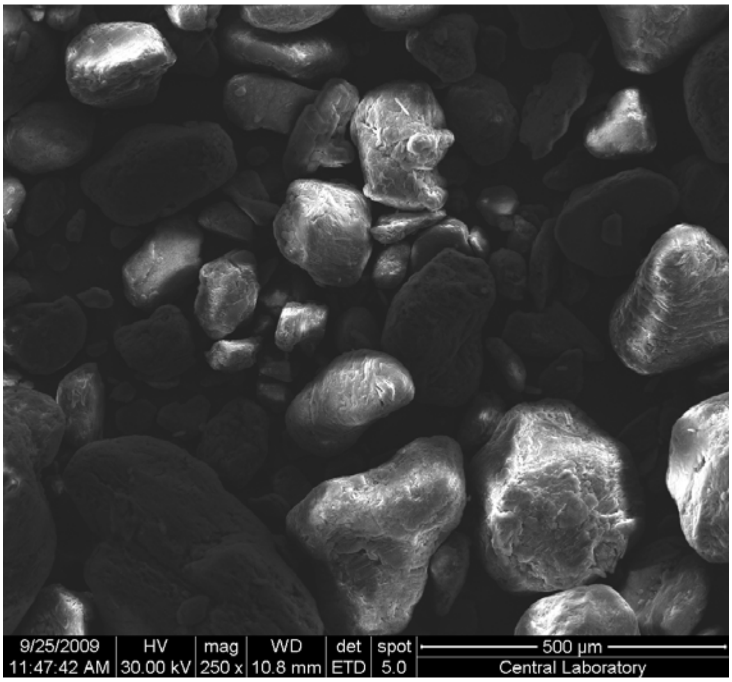


Figure E.2 SEM micrograph of pure boric acid (x 250 mag)

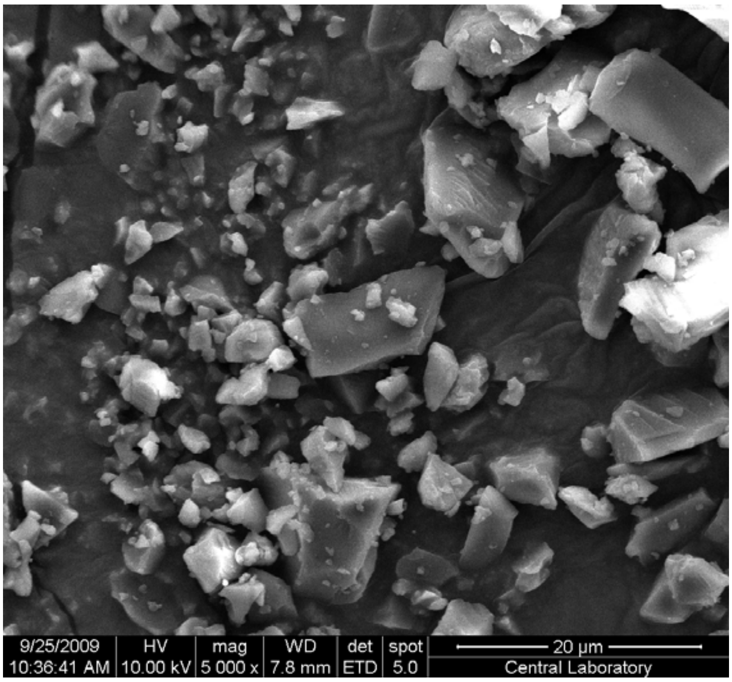
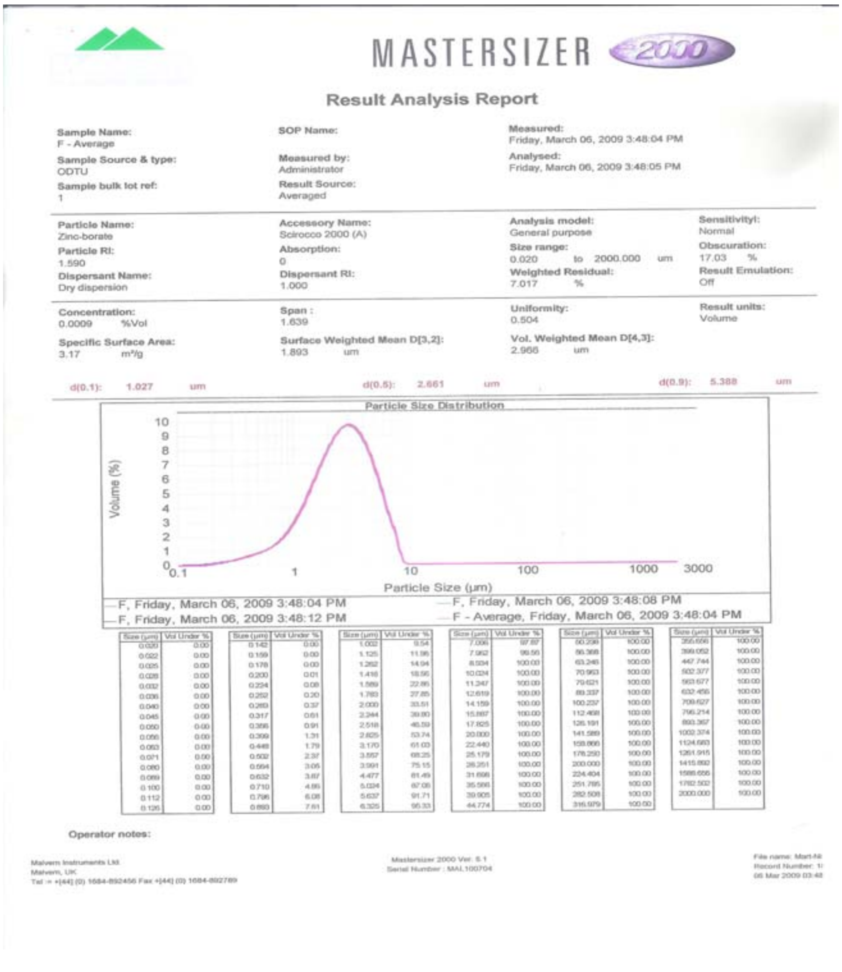


Figure E.3 SEM micrograph of pure poly(styrene-co-maleic anhydride) (x 5000 mag)

APPENDIX F

PARTICLE SIZE ANALYSIS RESULTS PERFORMED ON ZINC BORATES WITH DRY METHOD



MASTERSIZER 2000

Result Analysis Report

Sample Name:
F - Average

Sample Source & type:
ODTU

Sample bulk lot ref:
1

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
Friday, March 06, 2009 3:48:04 PM

Analysed:
Friday, March 06, 2009 3:48:05 PM

Particle Name:
Zinc-borate

Particle RI:
1.590

Dispersant Name:
Dry dispersion

Accessory Name:
Scirocco 2000 (A)

Absorption:
0

Dispersant RI:
1.000

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
7.017 %

Sensitivityl:
Normal

Obscuration:
17.03 %

Result Emulation:
Off

Concentration:
0.0009 %Vol

Specific Surface Area:
3.17 m²/g

Span :
1.639

Surface Weighted Mean D[3,2]:
1.893 um

Uniformity:
0.504

Vol. Weighted Mean D[4,3]:
2.966 um

Result units:
Volume

d(0.1): 1.027 um   d(0.5): 2.661 um   d(0.9): 5.388 um

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.020	0.00	0.142	0.00	1.002	9.54	7.096	97.87	50.238	100.00	355.656	100.00
0.022	0.00	0.159	0.00	1.125	11.96	7.962	99.56	56.368	100.00	399.052	100.00
0.025	0.00	0.178	0.00	1.262	14.94	8.934	100.00	63.246	100.00	447.744	100.00
0.028	0.00	0.200	0.01	1.416	18.56	10.024	100.00	70.963	100.00	502.377	100.00
0.032	0.00	0.224	0.08	1.589	22.86	11.247	100.00	79.621	100.00	563.677	100.00
0.036	0.00	0.252	0.20	1.783	27.85	12.619	100.00	89.337	100.00	632.456	100.00
0.040	0.00	0.283	0.37	2.000	33.51	14.159	100.00	100.237	100.00	709.627	100.00
0.045	0.00	0.317	0.61	2.244	39.80	15.887	100.00	112.468	100.00	796.214	100.00
0.050	0.00	0.356	0.91	2.518	46.59	17.825	100.00	126.191	100.00	893.367	100.00
0.056	0.00	0.399	1.31	2.825	53.74	20.000	100.00	141.589	100.00	1002.374	100.00
0.063	0.00	0.448	1.79	3.170	61.03	22.440	100.00	158.866	100.00	1124.683	100.00
0.071	0.00	0.502	2.37	3.557	68.25	25.179	100.00	178.250	100.00	1261.915	100.00
0.080	0.00	0.564	3.05	3.991	75.15	28.251	100.00	200.000	100.00	1415.892	100.00
0.089	0.00	0.632	3.87	4.477	81.49	31.698	100.00	224.404	100.00	1588.656	100.00
0.100	0.00	0.710	4.85	5.024	87.06	35.566	100.00	251.785	100.00	1782.502	100.00
0.112	0.00	0.796	6.08	5.637	91.71	39.905	100.00	282.508	100.00	2000.000	100.00
0.126	0.00	0.893	7.61	6.325	95.33	44.774	100.00	316.979	100.00		

Operator notes:

Malvern Instruments Ltd.
Malvern, UK
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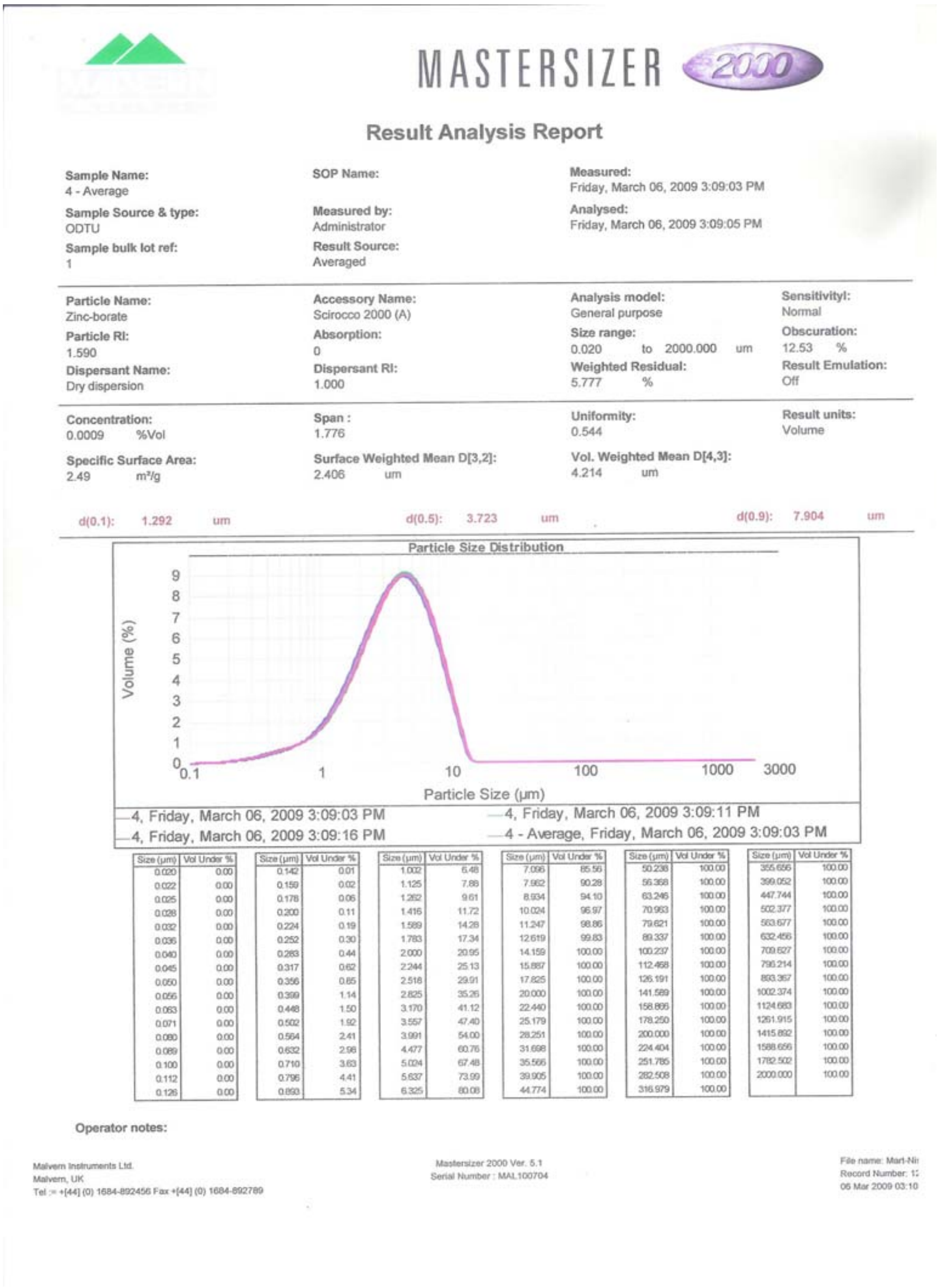
Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-N
Record Number: 1
06 Mar 2009 03:48

Figure F.1 Particle size data for commercial zinc borate (FB)



MASTERSIZER 2000

Result Analysis Report

Sample Name:
4 - Average

Sample Source & type:
ODTU

Sample bulk lot ref:
1

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
Friday, March 06, 2009 3:09:03 PM

Analysed:
Friday, March 06, 2009 3:09:05 PM

Particle Name:
Zinc-borate

Particle RI:
1.590

Dispersant Name:
Dry dispersion

Accessory Name:
Scirocco 2000 (A)

Absorption:
0

Dispersant RI:
1.000

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
5.777 %

Sensitivityl:
Normal

Obscuration:
12.53 %

Result Emulation:
Off

Concentration:
0.0009 %Vol

Specific Surface Area:
2.49 m²/g

Span :
1.776

Surface Weighted Mean D[3,2]:
2.406 um

Uniformity:
0.544

Vol. Weighted Mean D[4,3]:
4.214 um

Result units:
Volume

d(0.1): 1.292 um

d(0.5): 3.723 um

d(0.9): 7.904 um

Particle Size Distribution

Size (µm)	Vol Under %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	0.01
0.159	0.02
0.178	0.06
0.200	0.11
0.224	0.19
0.252	0.30
0.283	0.44
0.317	0.62
0.356	0.85
0.399	1.14
0.448	1.50
0.502	1.92
0.564	2.41
0.632	2.98
0.710	3.63
0.796	4.41
0.893	5.34
1.002	6.48
1.125	7.88
1.262	9.61
1.416	11.72
1.589	14.28
1.783	17.34
2.000	20.95
2.244	25.13
2.518	29.91
2.825	35.26
3.170	41.12
3.557	47.40
3.991	54.00
4.477	60.76
5.024	67.48
5.637	73.99
6.325	80.08
7.096	85.56
7.962	90.28
8.934	94.10
10.024	96.97
11.247	98.86
12.619	99.83
14.159	100.00
15.887	100.00
17.825	100.00
20.000	100.00
22.440	100.00
25.179	100.00
28.251	100.00
31.698	100.00
35.566	100.00
39.905	100.00
44.774	100.00
50.238	100.00
56.368	100.00
63.246	100.00
70.963	100.00
79.621	100.00
89.337	100.00
100.237	100.00
112.468	100.00
126.191	100.00
141.589	100.00
158.866	100.00
178.250	100.00
200.000	100.00
224.404	100.00
251.785	100.00
282.508	100.00
316.979	100.00
355.656	100.00
399.052	100.00
447.744	100.00
502.377	100.00
563.677	100.00
632.456	100.00
709.627	100.00
796.214	100.00
893.367	100.00
1002.374	100.00
1124.683	100.00
1261.915	100.00
1415.892	100.00
1588.656	100.00
1782.502	100.00
2000.000	100.00

Operator notes:

Malvern Instruments Ltd.
Malvern, UK
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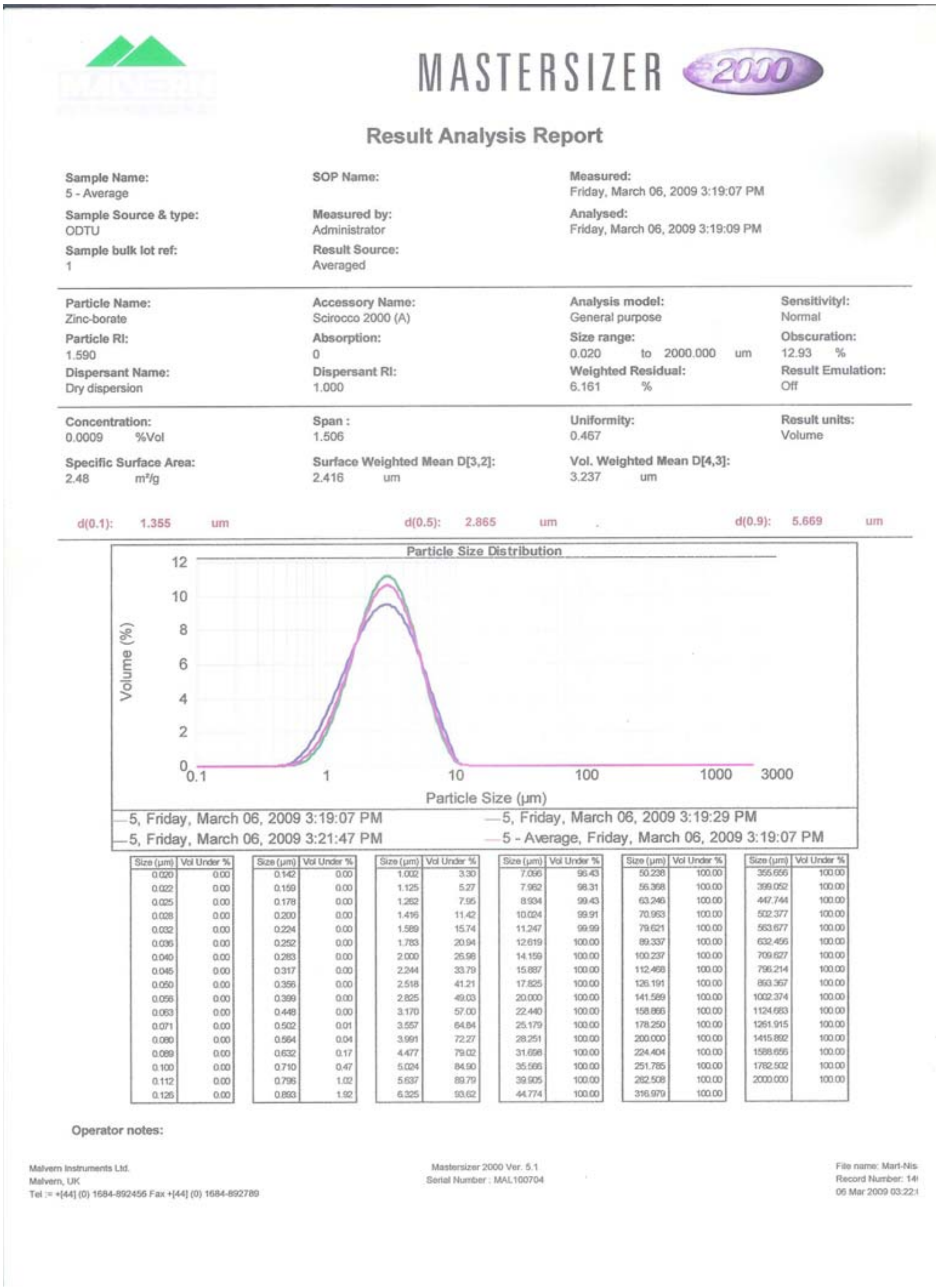
Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-Ni
Record Number: 1
06 Mar 2009 03:10

Figure F.2 Particle size data for PAA05



MASTERSIZER 2000

Result Analysis Report

Sample Name: 5 - Average
SOP Name:
Measured: Friday, March 06, 2009 3:19:07 PM
Sample Source & type: ODTU
Measured by: Administrator
Analysed: Friday, March 06, 2009 3:19:09 PM
Sample bulk lot ref: 1
Result Source: Averaged

Particle Name: Zinc-borate
Accessory Name: Scirocco 2000 (A)
Analysis model: General purpose
Sensitivityl: Normal
Particle RI: 1.590
Absorption: 0
Size range: 0.020 to 2000.000 um
Obscuration: 12.93 %
Dispersant Name: Dry dispersion
Dispersant RI: 1.000
Weighted Residual: 6.161 %
Result Emulation: Off

Concentration: 0.0009 %Vol
Span : 1.506
Uniformity: 0.467
Result units: Volume
Specific Surface Area: 2.48 m²/g
Surface Weighted Mean D[3,2]: 2.416 um
Vol. Weighted Mean D[4,3]: 3.237 um

d(0.1): 1.355 um
d(0.5): 2.865 um
d(0.9): 5.669 um

Size (µm)	Vol Under %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.01
0.564	0.04
0.632	0.17
0.710	0.47
0.796	1.02
0.893	1.92
1.002	3.30
1.125	5.27
1.262	7.95
1.416	11.42
1.589	15.74
1.783	20.94
2.000	26.98
2.244	33.79
2.518	41.21
2.825	49.03
3.170	57.00
3.557	64.84
3.991	72.27
4.477	79.02
5.024	84.90
5.637	89.79
6.325	93.62
7.096	96.43
7.962	98.31
8.934	99.43
10.024	99.91
11.247	99.99
12.619	100.00
14.159	100.00
15.887	100.00
17.825	100.00
20.000	100.00
22.440	100.00
25.179	100.00
28.251	100.00
31.698	100.00
35.566	100.00
39.905	100.00
44.774	100.00
50.238	100.00
56.368	100.00
63.246	100.00
70.963	100.00
79.621	100.00
89.337	100.00
100.237	100.00
112.468	100.00
126.191	100.00
141.589	100.00
158.866	100.00
178.250	100.00
200.000	100.00
224.404	100.00
251.785	100.00
282.508	100.00
316.979	100.00
355.656	100.00
399.052	100.00
447.744	100.00
502.377	100.00
563.677	100.00
632.456	100.00
709.627	100.00
796.214	100.00
893.367	100.00
1002.374	100.00
1124.683	100.00
1261.915	100.00
1415.892	100.00
1588.656	100.00
1782.502	100.00
2000.000	100.00

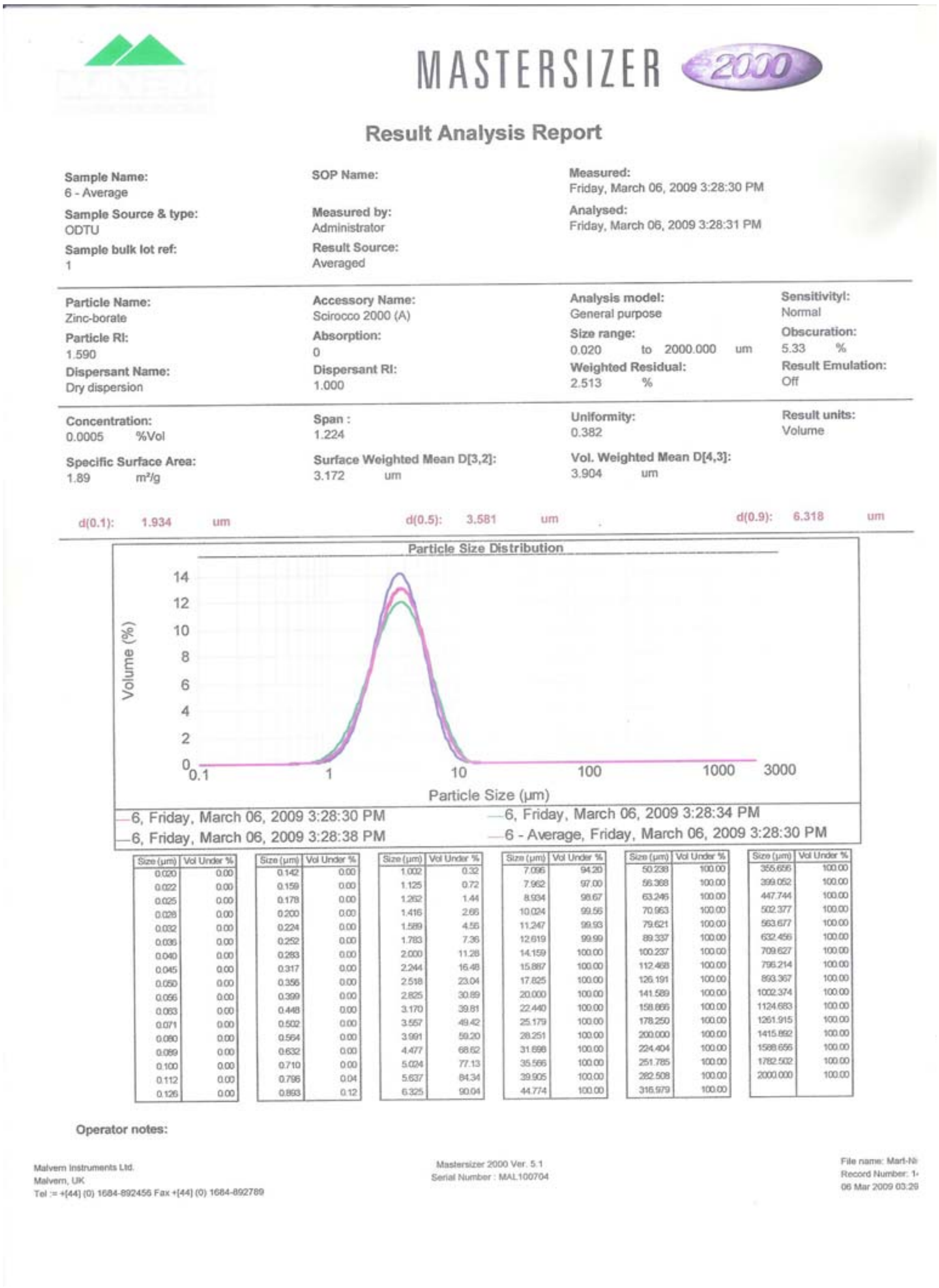
Operator notes:

Malvern Instruments Ltd.
Malvern, UK
Tel := +[44] (0) 1684-892456 Fax +[44] (0) 1684-892789

Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-Nis
Record Number: 14
06 Mar 2009 03:22:

Figure F.3 Particle size data for SA05



Result Analysis Report

Sample Name:
6 - Average

Sample Source & type:
ODTU

Sample bulk lot ref:
1

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
Friday, March 06, 2009 3:28:30 PM

Analysed:
Friday, March 06, 2009 3:28:31 PM

Particle Name:
Zinc-borate

Particle RI:
1.590

Dispersant Name:
Dry dispersion

Accessory Name:
Scirocco 2000 (A)

Absorption:
0

Dispersant RI:
1.000

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
2.513 %

Sensitivityl:
Normal

Obscuration:
5.33 %

Result Emulation:
Off

Concentration:
0.0005 %Vol

Specific Surface Area:
1.89 m²/g

Span :
1.224

Surface Weighted Mean D[3,2]:
3.172 um

Uniformity:
0.382

Vol. Weighted Mean D[4,3]:
3.904 um

Result units:
Volume

d(0.1): 1.934 um d(0.5): 3.581 um d(0.9): 6.318 um

Size (µm)	Vol Under %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.00
0.796	0.04
0.893	0.12
1.002	0.32
1.125	0.72
1.262	1.44
1.416	2.66
1.589	4.56
1.783	7.36
2.000	11.28
2.244	16.48
2.518	23.04
2.825	30.89
3.170	39.81
3.557	49.42
3.991	59.20
4.477	68.62
5.024	77.13
5.637	84.34
6.325	90.04
7.096	94.20
7.962	97.00
8.934	98.67
10.024	99.56
11.247	99.93
12.619	99.99
14.159	100.00
15.887	100.00
17.825	100.00
20.000	100.00
22.440	100.00
25.179	100.00
28.251	100.00
31.698	100.00
35.566	100.00
39.905	100.00
44.774	100.00
50.238	100.00
56.368	100.00
63.246	100.00
70.963	100.00
79.621	100.00
89.337	100.00
100.237	100.00
112.468	100.00
126.191	100.00
141.589	100.00
158.866	100.00
178.250	100.00
200.000	100.00
224.404	100.00
251.785	100.00
282.508	100.00
316.979	100.00
355.656	100.00
399.052	100.00
447.744	100.00
502.377	100.00
563.677	100.00
632.456	100.00
709.627	100.00
796.214	100.00
893.367	100.00
1002.374	100.00
1124.683	100.00
1261.915	100.00
1415.892	100.00
1588.656	100.00
1782.502	100.00
2000.000	100.00

Operator notes:

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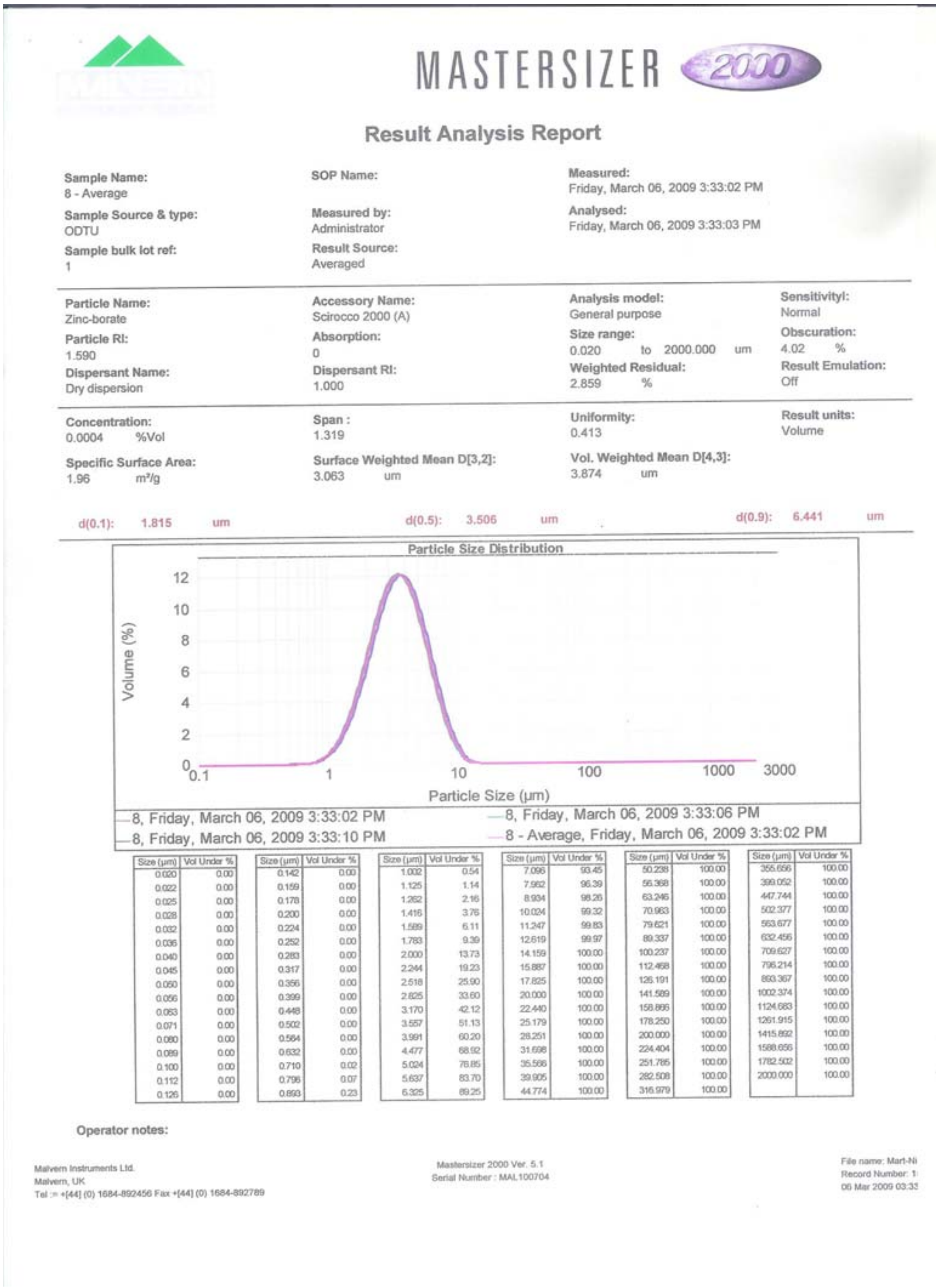
Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-N
Record Number: 1
06 Mar 2009 03:29

Figure F.4 Particle size data for PVP05



Result Analysis Report

Sample Name:
8 - Average

Sample Source & type:
ODTU

Sample bulk lot ref:
1

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
Friday, March 06, 2009 3:33:02 PM

Analysed:
Friday, March 06, 2009 3:33:03 PM

Particle Name:
Zinc-borate

Particle RI:
1.590

Dispersant Name:
Dry dispersion

Accessory Name:
Scirocco 2000 (A)

Absorption:
0

Dispersant RI:
1.000

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
2.859 %

Sensitivityl:
Normal

Obscuration:
4.02 %

Result Emulation:
Off

Concentration:
0.0004 %Vol

Specific Surface Area:
1.96 m²/g

Span :
1.319

Surface Weighted Mean D[3,2]:
3.063 um

Uniformity:
0.413

Vol. Weighted Mean D[4,3]:
3.874 um

Result units:
Volume

d(0.1): 1.815 um   d(0.5): 3.506 um   d(0.9): 6.441 um

Size (μm)	Vol Under %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.00
0.564	0.00
0.632	0.00
0.710	0.02
0.796	0.07
0.893	0.23
1.002	0.54
1.125	1.14
1.262	2.16
1.416	3.76
1.589	6.11
1.783	9.39
2.000	13.73
2.244	19.23
2.518	25.90
2.825	33.60
3.170	42.12
3.557	51.13
3.991	60.20
4.477	68.92
5.024	76.85
5.637	83.70
6.325	89.25
7.096	93.45
7.962	96.39
8.934	98.26
10.024	99.32
11.247	99.83
12.619	99.97
14.159	100.00
15.887	100.00
17.825	100.00
20.000	100.00
22.440	100.00
25.179	100.00
28.251	100.00
31.698	100.00
35.566	100.00
39.905	100.00
44.774	100.00
50.238	100.00
56.368	100.00
63.246	100.00
70.963	100.00
79.621	100.00
89.337	100.00
100.237	100.00
112.468	100.00
126.191	100.00
141.589	100.00
158.866	100.00
178.250	100.00
200.000	100.00
224.404	100.00
251.785	100.00
282.508	100.00
316.979	100.00
355.656	100.00
399.052	100.00
447.744	100.00
502.377	100.00
563.677	100.00
632.456	100.00
709.627	100.00
796.214	100.00
893.367	100.00
1002.374	100.00
1124.683	100.00
1261.915	100.00
1415.892	100.00
1588.656	100.00
1782.502	100.00
2000.000	100.00

Operator notes:

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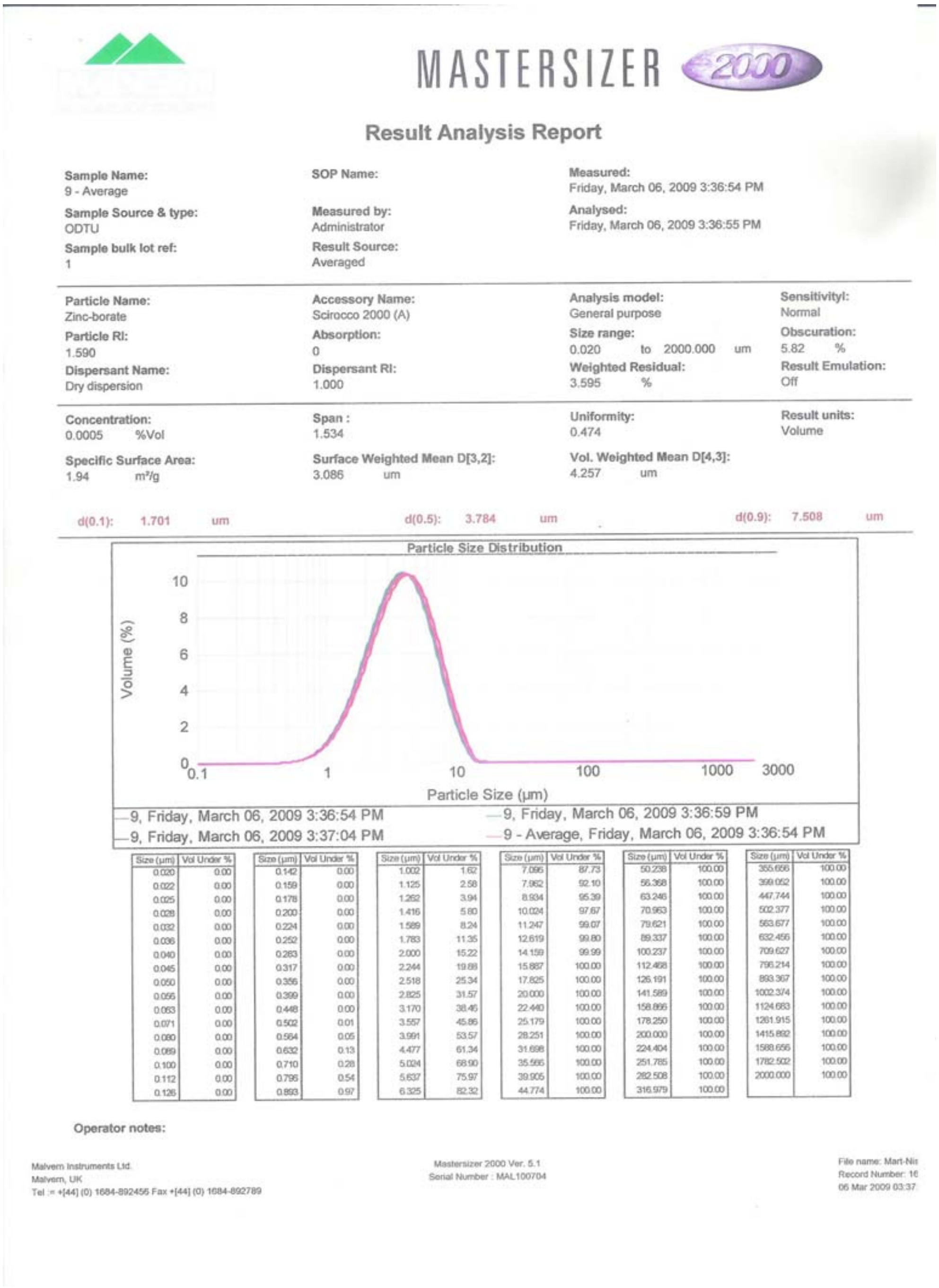
Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-Ni
Record Number: 1
06 Mar 2009 03:33

Figure F.5 Particle size data for PSMA05



MASTERSIZER 2000

Result Analysis Report

Sample Name:
9 - Average

Sample Source & type:
ODTU

Sample bulk lot ref:
1

SOP Name:

Measured by:
Administrator

Result Source:
Averaged

Measured:
Friday, March 06, 2009 3:36:54 PM

Analysed:
Friday, March 06, 2009 3:36:55 PM

Particle Name:
Zinc-borate

Particle RI:
1.590

Dispersant Name:
Dry dispersion

Accessory Name:
Scirocco 2000 (A)

Absorption:
0

Dispersant RI:
1.000

Analysis model:
General purpose

Size range:
0.020 to 2000.000 um

Weighted Residual:
3.595 %

Sensitivityl:
Normal

Obscuration:
5.82 %

Result Emulation:
Off

Concentration:
0.0005 %Vol

Specific Surface Area:
1.94 m²/g

Span :
1.534

Surface Weighted Mean D[3,2]:
3.086 um

Uniformity:
0.474

Vol. Weighted Mean D[4,3]:
4.257 um

Result units:
Volume

d(0.1): 1.701 um d(0.5): 3.784 um d(0.9): 7.508 um

Particle Size Distribution

Size (μm)	Vol Under %
0.020	0.00
0.022	0.00
0.025	0.00
0.028	0.00
0.032	0.00
0.036	0.00
0.040	0.00
0.045	0.00
0.050	0.00
0.056	0.00
0.063	0.00
0.071	0.00
0.080	0.00
0.089	0.00
0.100	0.00
0.112	0.00
0.126	0.00
0.142	0.00
0.159	0.00
0.178	0.00
0.200	0.00
0.224	0.00
0.252	0.00
0.283	0.00
0.317	0.00
0.356	0.00
0.399	0.00
0.448	0.00
0.502	0.01
0.564	0.05
0.632	0.13
0.710	0.28
0.796	0.54
0.893	0.97
1.002	1.62
1.125	2.58
1.262	3.94
1.416	5.80
1.589	8.24
1.783	11.35
2.000	15.22
2.244	19.88
2.518	25.34
2.825	31.57
3.170	38.45
3.557	45.86
3.991	53.57
4.477	61.34
5.024	68.90
5.637	75.97
6.325	82.32
7.096	87.73
7.962	92.10
8.934	95.39
10.024	97.67
11.247	99.07
12.619	99.80
14.159	99.99
15.887	100.00
17.825	100.00
20.000	100.00
22.440	100.00
25.179	100.00
28.251	100.00
31.698	100.00
35.566	100.00
39.905	100.00
44.774	100.00
50.238	100.00
56.368	100.00
63.246	100.00
70.963	100.00
79.621	100.00
89.337	100.00
100.237	100.00
112.468	100.00
126.191	100.00
141.589	100.00
158.866	100.00
178.250	100.00
200.000	100.00
224.404	100.00
251.785	100.00
282.508	100.00
316.979	100.00
355.656	100.00
399.052	100.00
447.744	100.00
502.377	100.00
563.677	100.00
632.456	100.00
709.627	100.00
796.214	100.00
893.367	100.00
1002.374	100.00
1124.683	100.00
1261.915	100.00
1415.892	100.00
1588.656	100.00
1782.502	100.00
2000.000	100.00

Operator notes:

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Mastersizer 2000 Ver. 5.1
Serial Number : MAL100704

File name: Mart-Ni
Record Number: 16
06 Mar 2009 03:37

Figure F.6 Particle size data for NP

APPENDIX G

MECHANICAL TEST RESULTS OF FLAME RETARDANT COMPOSITES

Table G.1 Tensile strength data for flame retardant composites

Sample Code	Tensile Strength (MPa)	Standard Deviations(±)
100P	52.87	3.91
90 P/5 TPP/5 PAA05	46.42	6.70
90 P/5 TPP/5 NP	42.95	10.56
90 P/5 TPP/5 FB	51.88	3.30
95 P/5 FB	39.25	9.02
95 P/5 BP	37.68	3.82
95 P/5 PSMA05	21.27	2.41
90 P/5 TPP/5 PSMA05	42.96	4.38
95 P/2 PSMA05/3 BP	36.79	6.01
95 P/5 PSMA1	31.58	5.83
90 P/5 TPP/5 PSMA1	27.73	4.75
95 P/2 PSMA1/3 BP	43.47	8.60
95 P/5 PSMA10	15.89	5.72
95 P/2 PSMA10/3 BP	26.82	10.31

Table G.2 Tensile modulus data for flame retardant composites

Sample Code	Tensile Modulus (MPa)	Standard Deviations(±)
100P	1686.95	257.33
90 P/5 TPP/5 PAA05	1141.69	262.19
90 P/5 TPP/5 NP	1577.40	52.85
90 P/5 TPP/5 FB	1535.26	103.82
95 P/5 FB	1445.72	114.72
95 P/5 BP	1379.58	69.78
95 P/5 PSMA05	1533.87	51.77
90 P/5 TPP/5 PSMA05	1460.24	112.19
95 P/2 PSMA05/3 BP	1352.60	125.58
95 P/5 PSMA1	1703.20	200.42
90 P/5 TPP/5 PSMA1	1652.93	141.69
95 P/2 PSMA1/3 BP	1582.82	114.91
95 P/5 PSMA10	1518.80	94.52
95 P/2 PSMA10/3 BP	1490.87	76.16

Table G.3 Elongation at break values for flame retardant composites

Sample Code	Elongation at break (%)	Standard Deviations(±)
100P	3.92	2.35
90 P/5 TPP/5 PAA05	4.93	0.93
90 P/5 TPP/5 NP	3.63	1.55
90 P/5 TPP/5 FB	5.79	1.79
95 P/5 FB	3.50	1.46
95 P/5 BP	3.08	0.46
95 P/5 PSMA05	1.61	0.18
90 P/5 TPP/5 PSMA05	3.40	0.63
95 P/2 PSMA05/3 BP	3.02	0.48
95 P/5 PSMA1	2.88	1.01
90 P/5 TPP/5 PSMA1	3.28	0.43
95 P/2 PSMA1/3 BP	4.39	1.58
95 P/5 PSMA10	2.59	0.46
95 P/2 PSMA10/3 BP	3.27	0.70

Table G.4 Impact strength data for flame retardant composites

Sample Code	**Impact Strength (kJ/m^2)**	**Standard Deviations(±)**
100P	9.63	2.75
90 P/5 TPP/5 PAA05	7.06	2.61
90 P/5 TPP/5 NP	7.86	1.95
90 P/5 TPP/5 FB	8.53	1.78
95 P/5 FB	9.42	1.36
95 P/5 BP	13.03	1.20
95 P/5 PSMA05	7.15	2.24
90 P/5 TPP/5 PSMA05	5.56	0.37
95 P/2 PSMA05/3 BP	11.07	1.79
95 P/5 PSMA1	9.32	1.84
90 P/5 TPP/5 PSMA1	8.05	2.34
95 P/2 PSMA1/3 BP	11.38	0.97
95 P/5 PSMA10	3.84	1.22
95 P/2 PSMA10/3 BP	6.16	0.43

APPENDIX H

SAMPLE CONVERSION CALCULATION OF SYNTHESIZED ZINC BORATES

A sample calculation for the zinc borate produced at reaction conditions of 580 rpm stirring rate, 85°C reaction temperature, seed amount of 1.5%, H_3BO_3:ZnO mole ratio of 5:1 and in the presence of 0.1% PAA (PAA01) is given below.

For the sample conversion calculation, firstly, determination of amount of ZnO and B_2O_3 in the sample was needed. Analytical ZnO and B_2O_3 analysis results for PAA01 are tabulated in Table H.1.

Table H.1. Analytical ZnO and B_2O_3 analysis results for PAA01

Sample time (min)	Amount of ZnO in the sample (g)	Amount of B_2O_3 in the sample (g)	Consumed ZnO amount (g)	Conversion
30	0.159	0.028	0.022	0.136
60	0.184	0.013	0.010	0.053
90	0.185	0.015	0.012	0.065
120	0.161	0.042	0.033	0.204
150	0.105	0.063	0.049	0.467
180	0.084	0.099	0.077	0.923
210	0.077	0.097	0.077	1.000

For the determination of consumed ZnO amount during the reaction, a constant was needed to be calculated which defines the ratio of the B_2O_3 content to ZnO content at the final product at 210 minutes of reaction time. This coefficient is 1.2733 for PAA01. Thereby, the consumed ZnO amounts were calculated dividing the final ZnO amounts at the samples by this constant. Consequently, ZnO conversion was calculated by dividing consumed ZnO amounts to the ZnO amounts in the samples for each 30 minute time intervals.