T.C.
MARMARA UNIVERSITY
INSTITUTE FOR GRADUATE STUDIES IN
PURE AND APPLIED SCIENCES

PRODUCTION AND CHARACTERIZATION OF ZINC BORATE-POLYMER NANO COMPOSITES

HÜLYA BÖLEK

THESIS

FOR THE DEGREE OF MASTER OF SCIENCE
IN
METALLURGICAL AND MATERIALS ENGINEERING

SUPERVISOR
Prof. Dr. Ayhan MERGEN

İSTANBUL 2011

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ÇİNKO BORAT-POLİMER NANO KOMPOZİTLERİN ÜRETİLMESİ VE KARAKTERİZASYONU

Yapılan bu çalışmada, çinko borat takviyeli polimer nano kompozitler çinko boratın kompozit malzemeler üzerindeki etkisinin özellikle alev geciktirme özelliğinin incelenmesi amacıyla üretilmiştir. $2ZnO.3B_2O_3.3\text{-}3.5H_2O$ formülasyonuna sahip nano boyutlu çinko borat tozu $Zn(NO_3)_2.6H_2O$ ve $Na_2B_4O_7.5H_2O$ ve yüzey modifiye edici olarak oleik asit kullanılarak sulu çözelti içerisinde yaş kimyasal yöntem ile üretilmiştir. Üretilen tozlar x-ışını toz kırınımı (XRD), diferansiyel ısıl ve termogravimetrik analiz (DTA-TG), geçirmeli elektron mikroskobu (TEM) ve fourier dönüşümlü kızılötesi spektroskopisi (FT-IR) teknikleri kullanılarak karakterize edilmiştir. Üretilen çinko borat tozları farklı oranlarda (% 1, 3 ve 5) etilen vinil asetat (EVA) ve yüksek yoğunluğa sahip poli etilen (HDPE) ile çift vidalı ekstrüder kullanılarak karıştırılmıştır. Son olarak enjeksiyon şekillendirme tekniği ile nano kompozitler başarılı bir şekilde üretilmiştir. Nano kompozitlerin iç yapıları taramalı elektron mikroskobu (SEM) ile incelenmiştir. Nano kompozitlerin alev geciktirici özellikleri kısıtlayıcı oksijen imleci deneyi (LOI) ve diferansiyel taramalı kalorimetri (DSC) teknikleri kullanılarak incelenmiştir ve sonuçlar mikron boyutlu çinko borat takviyeli kompozitler ile karşılaştırılmıştır. Farklı oranlarda çinko borat ilavesinin mekanik özellikler üzerindeki etkisi ayrıca incelenmiş olup nano çinko borat ilavesinin mekanik özellikleri çok olumsuz etkilemediği saptanmıştır. Elde edilen kısıtlayıcı oksijen imleci deneyi test sonuçlarına göre nano boyutlu çinko borat takviyeli EVA ve HDPE kompozitlerin alev geciktirici özelliğinin gelişmiş olduğu görülmektedir.

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ABSTRACT

PRODUCTION AND CHARACTERIZATION OF ZINC BORATE-POLYMER NANO COMPOSITES

In this study, zinc borate added polymer nano composites were produced in order to investigate the effect of zinc borate on various properties of composite, mainly flame retardancy. Nano-sized zinc borate powders with the formula of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$ were prepared by a wet chemical method using $Zn(NO_3)_2.6H_2O$ and $Na_2B_4O_7.5H_2O$ as a raw material in aqueous solution, and oleic acid as a modifying agent. The produced powders were characterized by X-ray powder diffraction (XRD), differential thermal and thermogravimetric analysis (DTA-TG), and transmission electron microscopy (TEM), fourier transform infrared (FT-IR) spectroscopy. Different ratio of (1, 3, and 5 wt.%) of zic borate powder were blended with ethylene vinyl acetate (EVA) and high density poly ethylene (HDPE) by twin screw extruder and finaly processed by enjection machine and nano composites were successfully produced. The microstructures of nano composite samples were studied by scanning electron microscopy (SEM). The flame retardancy properties of the nano composites were investigated by limiting oxygen index (LOI) and differential scanning calorimetry (DSC) and the results were compared with the micron-sized zinc borate filled composites. The effect of different amounts of zinc borate on mechanical properties of nano composites was examined and it was observed that nano zinc borate addition did not affect the mechanical properties significantly also discussed. It is observed that flame retardancy property of nano-sized zinc borate filled EVA and HDPE composites were improved according to the limiting oxygen index results.

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SYMBOLS

T : Temperature (°C)
t : Time (s)
µm : Micrometer
nm : Nanometer
mm : Milimeter
mL : Milliliter
kJ : Kilojoule
g : Gram
rpm : Revolution per minute
kN : Kilonewton
Ak : Impact energy (J)
X : Thickness (mm)
Yk : Difference of width and notch depth (mm)
L/D : Length/Diameter

ABBREVIATIONS

XRD : X-ray Powder Diffractometer
TGA : Thermogravimetric Analysis
TEM : Transmission Electron Microscopy
FT-IR : Fourier Transform Infrared
EVA : Ethylene Vinyl Acetate
HDPE : High Density Poly Ethylene
SEM : Scanning Electron Microscopy
LOI : Limiting Oxygen Index
DSC : Differential Scanning Calorimetry
FR : Fire Retardant
PVC : Poly Vinyl Chloride
EC : European Community
US : United States
WHO : World Health Organisation
EPA : Environmental Protection Agency
UL : Underwriters Laboratories
ASTM : American Society for Testing and Materials
NFPA : National Fire Protection Association
ISO : International Organization for Standardization
OIT : Oxidative Induction Time
EDS : Energy Dispersive Spectrometer
OA : Oleic Acid
h : Hour

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CHAPTER I

INTRODUCTION AND AIM

Various commercial flame retardants are used to improve the flame retardancy and safety of polymeric materials. Although halogen-based materials are the most effective fire retardant (FR) additives in polymers, they are known to be a source of corrosive, obscuring and toxic smoke during combustion. Therefore, the limitation of using halogen-based FR systems is the major present tendency [1] and investigations turn towards halogen-free FR formulations.

Previous studies have demonstrated that in halogen-free systems combining zinc borates with other FRs in several kinds of polymers (ethylene vinyl acetate (EVA), polyvinyl chloride (PVC), and polyamides) have major advantages such as smoke suppressant, afterglow suppressant, corrosion inhibition, anti-tracking agent and synergistic agent. [2] Many researchers have found that more than 60 wt% loading of metal hydroxides as FR is required to obtain an adequate FR property. However, high loading levels lead to a great decrease in the mechanical properties of filled polymeric material. [3]

Zinc borate is a boron-based inorganic material with a chemical composition of $xZnO.yB_2O_3.zH_2O$ and widely used as FR in polymeric materials, antibacterial and additive to protect wood products from insect and fungal attacks. [4] The most widely used zinc borate types are $2ZnO.3B_2O_3.3.0\text{-}3.5H_2O$ and $ZnO.B_2O_3.2H_2O$ due to their excellent flame retardant property. [5] Zinc borate has no demonstrated adverse public health effects. Zinc borate is used in polymeric materials, dyes, cables, fabrics, carpets, internal parts of automobiles and planes, textile and paper industry to increase the FR. Zinc borate slows down the degradation of the polymer creating a vitreous protective residual layer, which could act as a physical barrier and a glassy cage for polymer chains. [6]

Nano-composites have been the subject of research interest since 1961 due to their enhanced mechanical, thermal and barrier properties over the conventional micro composite materials. [5] Recent studies have showed that nano-sized flame retardants as nano-composite systems with polymers have superior FR and other properties (like mechanical properties, surface quality etc.) than micron sized flame retardants. This is mainly resulted from more homogenous dispersion of nano-sized flame retardants. In addition, lower quantities of nano-sized flame retardants are sufficient to provide high flame resistance. [5-7]

In this study, nano-sized zinc borate powders synthesized by a wet chemical method were added into ethylene vinyl acetate (EVA) and high density polyethylene (HDPE) plastic materials in order to investigate the effect of zinc borate on various properties of nano-composites, like flame retardancy and mechanical properties. The results were compared with micron sized commercial zinc borate filled composites.

CHAPTER II

GENERAL BACKGROUND

In this chapter, general literature information about zinc, boron, zinc borate and flame retardancy are given.

II.1. ZINC

Zinc is a metallic chemical element which has the symbol Zn and atomic number of 30. It is the first element in group 12 of the periodic table. Zinc is chemically similar to magnesium in some respects that they have similar ion size and same oxidation state of +2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. The most exploited zinc ore is sphalerite, a zinc sulphide and the largest exploitable deposits are found in Australia, Asia, and the United States. Zinc production includes froth flotation of the ore, roasting, and final extraction using electricity (electrowinning). Physical properties of zinc are given in Table II.1. [8]

Table II.1 Physical properties of zinc.

Phase:	Solid
Density:	7.14 $g{\cdot}cm^{-3}$
Melting Point:	419.53 °C
Boiling Point:	907 °C
Heat of Fusion:	7.32 $kJ{\cdot}mol^{-1}$
Heat of Vaporization:	123.6 $kJ{\cdot}mol^{-1}$
Specific Heat Capacity:	(25 °C) 25.470 $J{\cdot}mol^{-1}{\cdot}K$

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 10 million tonnes. There are zinc mines throughout the world, with the main mining areas being China, Australia and Peru. China produced over one-fourth of the global zinc output in 2006. [9]

Nyrstar is the world's largest zinc producer, a merger of the Australian OZ Minerals and the Belgian Umicore. About 70% of the world's zinc originates from mining, while the remaining 30% comes from recycling secondary zinc. Commercially pure zinc is known as Special High Grade and is 99.995% pure. Top zinc output countries are given in Table II.2. [8]

Table II.2 Top zinc output countries in 2009.

Rank	**Country**	**Tonnes**
1	China	2.875.000
2	Peru	1.439.000
3	Australia	1.279.000
4	United States	735
5	Canada	695

Applications of zinc include [8]:

- Galvanizing (59%)
- Die casting (16%)
- Brass and bronze (10%)
- Rolled zinc (6.5%)
- Chemicals (6.0%)
- Miscellaneous (2.5%)

II.1.1. Zinc Nitrate

Zinc nitrate is usually prepared by dissolving zinc in nitric acid. Chemical formula and structure are shown in Figure II.1, and some properties of zinc nitrate are listed below. [10]

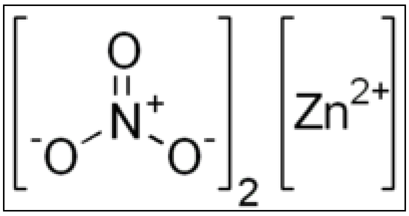


Figure II.1 The chemical formula and structure of zinc nitrate.

Molecular Formula: $Zn(NO_3)_2$
Molar Mass: 297.49 g/mol (hexahydrate)
Appearance: colourless, deliquescent crystals
Melting Point: 36.4 °C (hexahydrate)
Boiling Point: ~125 °C, decomposition (hexahydrate)
Density: 2.065 g/cm^3 (hexahydrate)
Solubility in water: 184.3 g/100 ml, 20 °C (hexahydrate)

Zinc nitrate can be used as a mordant in dyeing. Zinc nitrate is soluble in both water and alcohol.

II.2. BORON

Boron is the chemical element with atomic number of 5 and the chemical symbol B. Elemental boron (B) is a light element with several forms, none occurring in nature, that differ in the way the atoms are packed. The element is generally used to make fibreglass, heat-resistant borosilicate glass, and cleaning products, but it’s most important role on Earth is as an essential micronutrient for plants.

Boron is a rare portion of Earth‘s crust, although it is about 57,000 times more common in rocks than gold, representing only about seventeen atoms out of every million. More than 200 minerals include boron, but only twelve are commercially significant, and only four satisfy nearly 90 percent of the demand.

Besides semiconductors, boron and its compounds have been used in glassware and cleaning products, fire retardants, cancer treatment, high-energy fuel, cosmetics, adhesives, pesticides, wood preservatives, and the leather tanning industry. Boron is also an essential part of Silly Putty. Other boron compounds are used as abrasives, in pyrotechnic flares, fiber optics, and advanced aerospace structures.

Joseph Gay-Lussac and Louis Thénard, French chemists, and independently by English chemist Sir Humphry Davy discovered the elemental, in 1808. Davy, thinking the new substance had metallic properties, proposed the name boracium, which combined “boracic” (the older form of “boric”) with the Latin “ium” ending that indicates a metallic substance. However, after chemists determined it was not a metal, the new element was called boron in 1812. The name partly combines “borax” and “carbon” (C), element 6 in the periodic table. [11]

Boron is a Group 3 element; its closest relative is aluminium which is a hard, brittle semi-metallic element. Physical properties of boron are given in Table II.3. Boron has several allotropes: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on Mohs' scale), and a poor conductor at room temperature. Elemental boron is used as a dopant in the semiconductor industry. [12]

Table II.3 Physical properties of boron.

Phase:	Solid
Liquid Density at m.p.:	2.08 g·cm^{-3}
Melting Point:	2076 °C
Boiling Point:	3927 °C
Heat of Fusion:	50.2 kJ·mol^{-1}
Heat of Vaporization:	480 kJ·mol^{-1}
Specific Heat Capacity:	(25 °C) 11.087 J·mol^{-1}·K

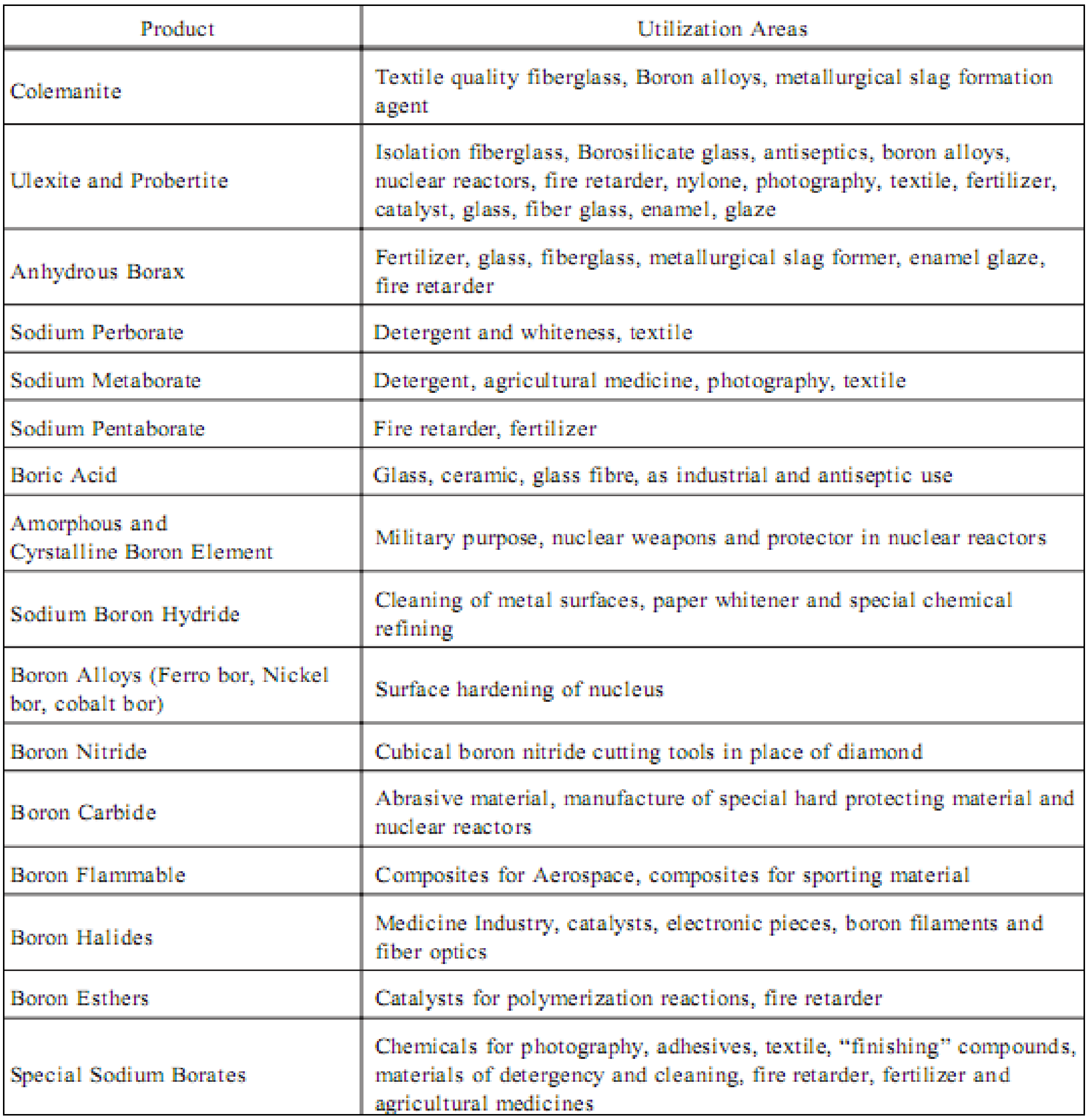
Crystalline boron is a very hard, black material which has high melting point of above 2000 °C. It exists in four major polymorphs: α, β, γ and T. The γ-phase can be described as a rock salt-type arrangement of the icosahedra and B_2 atomic pairs, whereas α, β and T phases are based on B_{12} icosahedra. γ-phase can be produced by compressing other boron phases under 12–20 GPa and heating to 1500–1800 °C; it remains stable after releasing the temperature and pressure. The T phase is produced at higher temperatures of 1800–2200 °C, but at similar pressures. α and β phases might both coexist at ambient conditions with the β phase being more stable. [13, 14] Compressing boron above 160 GPa produces a boron phase with an as yet unknown structure, and this phase is a superconductor at temperatures 6–12 K. Boron allotropes are given in Table II.4.

Table II.4 Boron allotropes.

Boron Phase	**α**	**β**	**γ**	**T**
Symmetry	Rhombohedral	Rhombohedral	Orthorhombic	Tetragonal
Atoms / unit cell	12	~105	28	
Density (g/cm^3)	2.46	2.35	2.52	2.36
Vickers hardness (GPa)	42	45	50-58	
Bulk modulus (GPa)	185	224	227	
Band gap (eV)	2	1.6	2.1	

Boron is used in more than 200 fields of application. Principal utilized boron compounds and related application areas are given in Table II.5, the share of application areas is given in Figure II.2. [15]

Table II.5 Applications of boron compounds.



Product	Utilization Areas
Colemanite	Textile quality fiberglass, Boron alloys, metallurgical slag formation agent
Ulexite and Probertite	Isolation fiberglass, Borosilicate glass, antiseptics, boron alloys, nuclear reactors, fire retarder, nylone, photography, textile, fertilizer, catalyst, glass, fiber glass, enamel, glaze
Anhydrous Borax	Fertilizer, glass, fiberglass, metallurgical slag former, enamel glaze, fire retarder
Sodium Perborate	Detergent and whiteness, textile
Sodium Metaborate	Detergent, agricultural medicine, photography, textile
Sodium Pentaborate	Fire retarder, fertilizer
Boric Acid	Glass, ceramic, glass fibre, as industrial and antiseptic use
Amorphous and Cyrstalline Boron Element	Military purpose, nuclear weapons and protector in nuclear reactors
Sodium Boron Hydride	Cleaning of metal surfaces, paper whitener and special chemical refining
Boron Alloys (Ferro bor, Nickel bor, cobalt bor)	Surface hardening of nucleus
Boron Nitride	Cubical boron nitride cutting tools in place of diamond
Boron Carbide	Abrasive material, manufacture of special hard protecting material and nuclear reactors
Boron Flammable	Composites for Aerospace, composites for sporting material
Boron Halides	Medicine Industry, catalysts, electronic pieces, boron filaments and fiber optics
Boron Esthers	Catalysts for polymerization reactions, fire retarder
Special Sodium Borates	Chemicals for photography, adhesives, textile, "finishing" compounds, materials of detergency and cleaning, fire retarder, fertilizer and agricultural medicines

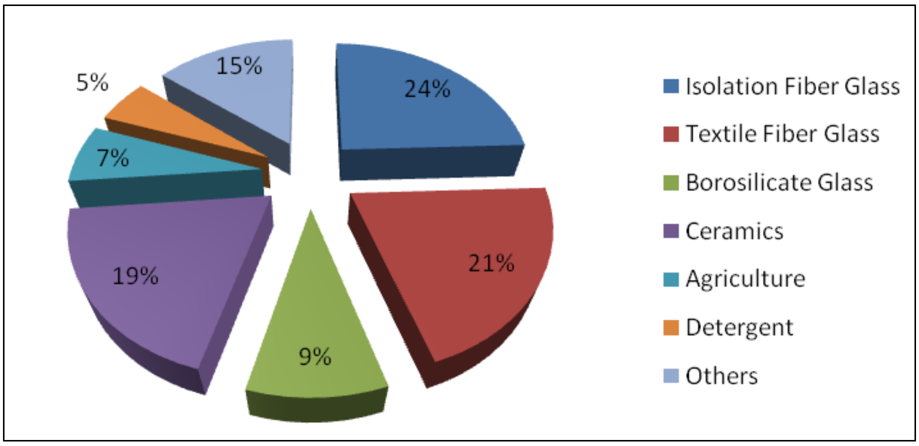


Figure II.2 Applications of boron compounds.

Borate compounds show an ionic character as they contain a boron oxoanion, such as the metaborate anion $[B(OH)_4]^-$ in combination with cationic species, such as Na^+. For instance, sodium metaborate is $Na^+[B(OH)_4]^-$, also represented as $Na_2B_2O_4 \cdot 4H_2O$ or resolved oxide, $NaO \cdot B_2O_3 \cdot 4H_2O$. Table II.6 lists known borate anions include the structural formula and resolved oxide formula for the corresponding compounds formed in combination with monovalent cations (represented by M^+). [16]

Table II.6 Borate anions.

Boron Oxoanion	**Common Name**	**Structural Formula Bearing Metal Cation, M^+**	**Resolved Oxide Formula**
$[B(OH)_4]^-$	metaborate	$M[B(OH)_4]$	$M_2O \cdot B_2O_3 \cdot 4H_2O$
$[B_4O_5(OH)_4]^{2-}$	tetraborate	$M_2[B_4O_5(OH)_4]$	$M_2O \cdot 2B_2O_3 \cdot 4H_2O$
$[B_5O_6(OH)_4]^-$	pentaborate	$M[B_5O_6(OH)_4]$	$M_2O \cdot 5B_2O_3 \cdot 4H_2O$
$[B_3O_3(OH)_4]^-$	triborate	$M[B_3O_3(OH)_4]$	$M_2O \cdot 3B_2O_3 \cdot 4H_2O$
$[B_3O_3(OH)_5]^{2-}$	triborate	$M_2[B_3O_3(OH)_5]$	$2M_2O \cdot 3B_2O_3 \cdot 5H_2O$
$[B_6O_7(OH)_6]^{2-}$	hexaborate	$M_2[B_6O_7(OH)_6]$	$M_2O \cdot 3B_2O_3 \cdot 3H_2O$

Chemical structures of these oxoanions are different from each other. Schematic representations of these structures are given in Figure II.3. [17]

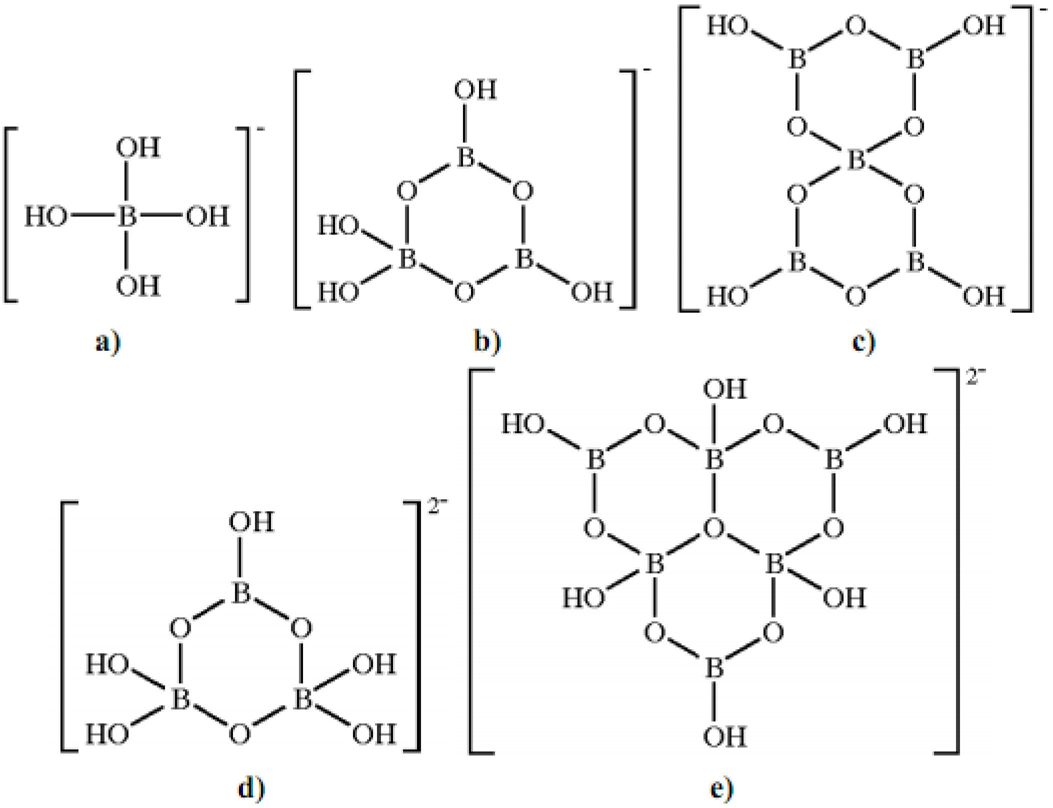


Figure II.3 Schematic representations of borate oxoanions a) $[B(OH)_4]^-$, b) $[B_2O_3(OH)_4]^-$, c) $[B_5O_6(OH)_4]^-$, d) $[B_2O_3(OH)_5]^{2-}$, e) $[B_6O_7(OH)_6]^{2-}$ compounds structures.

II.2.1. Boron Minerals

Generally, boron minerals exist and composed of alkali and earth alkali metals such as Na, Ca and Mg. Boron minerals take their names according to proportion of metals in its compounds, the water content and the crystal structure. [15] Boric acid (sassolite), borax (tincal), kernite, colemanite, ulexite, probertite, hydroboracite, datolite, and szaibelyite (ascharite) are the boron minerals which have commercial importance are given in Table II.7 with their B2O3 wt% and chemical formula. [17]

Table II.7 Some commercially important boron minerals.

Type	**Mineral**	**Composition**	**B_2O_3 weight percentage**
Hydrogen borates	Sassolite (natural boric acid)	H_3BO_3	56.3
Sodium borates	Tincal	$Na_2B_40_7.10H_2O$	36.5
	Tincalconite	$Na_2B_40_7.5H_2O$	47.8
	Kernite	$Na_2B_40_7.4H_2O$	51.0
Calcium borates	Colemanite	$Ca_2B_6O_{11}.5H_2O$	50.8
	Pandermite	$CaB_{10}O_{19}.7H_2O$	49.8
Sodium-calcium borates	Probertite	$NaCaB_30_9.5H_2O$	49.6
	Ulexite	$NaCaB_50_9.8H_2O$	43.0
Calcium borosilicates	Datolite	$CaBSiO_4OH$	24.9
Magnesium borates	Hydroboracite	$CaMgB_6O_{11}.6H_2O$	50.5
	Szaibelyite	$MgBO_2OH$	41.4
	Boracite	$Mg_3B_7O_{13}Cl$	62.2

Borax is the most important boron substance found in nature. In ancient times, borax was a rare and precious material. The merchants traded in kept their borax sources as a secret. However, most of it seems to have come from remote salt lakes hidden in the mountains of Tibet. Deposits of boron compounds were discovered in Death Valley, California, from the mid-1800s onward and elsewhere in the western United States. Pictures of the wagons were used to advertise boron-containing products, such as soaps and laundry powders. [18] The other significantly important boron minerals are colemanite and ulexite.

II.2.2. Boron Reserves

Global demand for borates rised strongly in the three years to 2008, at up to 8%py, which is largely driven by growth in the Chinese market where consumption rose by 15%py from 2000 to 2008. 2009 saw a sharp drop in demand for borates following the years of strong growth, but, in the second half of the year, markets for both textile grade fibreglass and borosilicate glass recovered and demand for borosilicate glass in LCd screens was expected more to grow by 15% in 2010. Construction activity should provide a recovering market for insulation-grade fibreglass in the medium term (Figure II.4). Natural and refined borates remains world production highly concentrated in Turkey and the USA; the two countries accounting for around 75% of supply. [19]

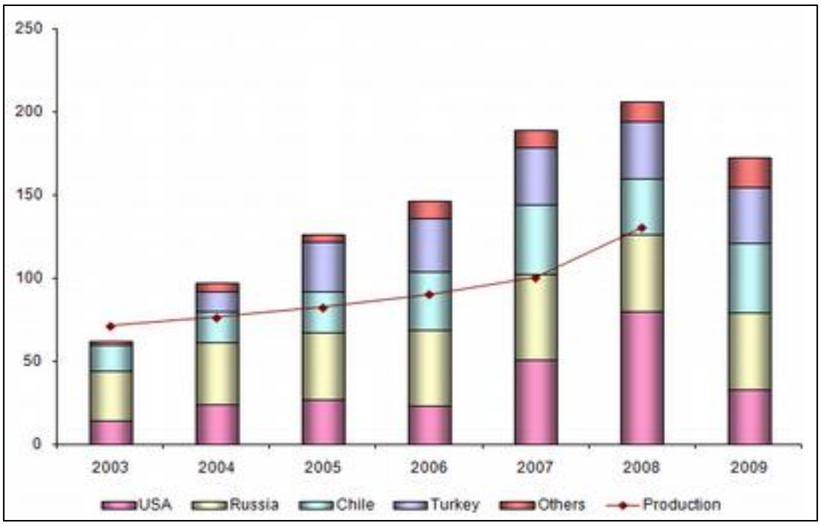


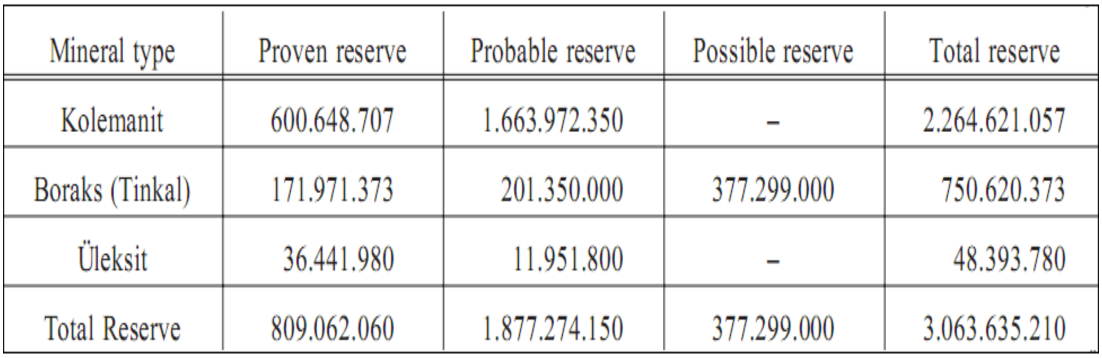
Figure II.4 Demand for borates.

Boron mining started in Turkey in 1861 by foreign companies. Then, mining exploitation rights were transferred to state sector, namely, Etibank. Turkey has 72% of the world reserves, but 35% in the production and trade. On the basic of equivalent B_2O_3 content, boron reserves are known as 1.176 billon tons. 72.2% of the reserves as 851 million tons are known to exist in Turkey. The regional distribution of borates reserves of Turkey in Table II.8 and the distribution in accordance with mineral kinds are given, respectively in Table II.8. [20]

Table II.8 The regional distribution of Turkish boron reserves**.**

Location	Proven reserve	Probable reserve	Possible reserve	Total reserve
Bigadiç	363.534.560	259.924.150	–	623.458.710
Emet	266.561.602	1.416.000.000	–	1.682.561.602
Kestelek	6.994.525	–	–	6.994.525
Kırka	171.971.373	201.350.000	377.299.000	750.620.373
Total Reserve	809.062.060	1.877.274.150	377.299.000	3.063.635.210

Table II.9 Distribution of Turkish boron reserves according to mineral types.



Mineral type	Proven reserve	Probable reserve	Possible reserve	Total reserve
Kolemanit	600.648.707	1.663.972.350	–	2.264.621.057
Boraks (Tinkal)	171.971.373	201.350.000	377.299.000	750.620.373
Üleksit	36.441.980	11.951.800	–	48.393.780
Total Reserve	809.062.060	1.877.274.150	377.299.000	3.063.635.210

Turkey, USA and Russia have the important boron mines in the world. In terms of total reserve basis, while Turkey has a share of 72,2%, the other important country USA has a share of 6,8% (Table II.10). [15] Boron production companies are given in Figure II.5 with their shares in total. [20] Total world boron reserves on the basis of B_2O_3 content are 369 million tons proven, 807 million tonnes probable and possible, as a total of 1.176 million tons. Turkey has a total boron reserve of 851 million tons on the basis of B_2O_3 content with a share of 72.2%.

Table II.10 World boron reserves (Million tons).

Country	**Proven Reserve**	**Probable Possible Reserve**	**Total Reserve**	**Percent in Total (%)**
Turkey	227.000	624.000	851.000	72,2
U.S.A.	40.000	40.000	80.000	6,8
Russia	40.000	60.000	100.000	8,5
China	27.000	9.000	36.000	3,1
Argentina	2.000	7.000	9.000	0,8
Bolivia	4.000	15.000	19.000	1,6
Chile	8.000	33.000	41.000	3,5
Peru	4.000	18.000	22.000	1,9
Kazakhstan	14.000	1.000	15.000	1,3
Serbia	3.000	0	3.000	0,3
Total	369.000	807.000	1.176.000	100

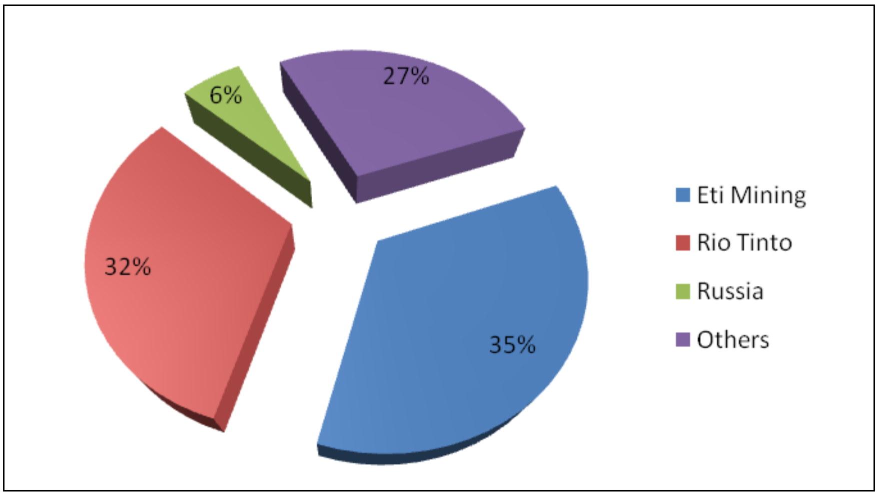


Figure II.5 Boron production companies in the world.

II.3. ZINC BORATE

Zinc borate is a synthetic hydrated metal borate. There are various kinds of crystalline hydrated zinc borates which have compositions $ZnO \cdot B_2O_3 \cdot H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 5H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 7H_2O$, $3ZnO \cdot 5B_2O_3 \cdot 14H_2O$, $ZnO \cdot B_2O_3 \cdot 2H_2O$, $ZnO \cdot 5B_2O_3 \cdot 4.5H_2O$, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, and $6ZnO \cdot 5B_2O_3 \cdot 3H_2O$. In these products, B_2O_3/ZnO molar ratio changes from 0.25 to 5 and it designate the characteristics of the product. [21]

Zinc borate, $3ZnO \cdot 2B_2O_3$, forms a white amorphous powder or triclinic crystals depending on the method of preparation which has specific gravity 3.64 (amorphous), 4.22 (crystalline); and melting point of 980ºC. The amorphous form is slightly soluble in water and hydrochloric acid, the crystalline is insoluble in water and hydrochloric acid. [22]

Heat stability of hydration water of zinc borate is between 290 – 300ºC which enables the polymer processability. Zinc borate enables the pigment load to be low due to the similar refractive index of zinc borate with refractive indices of many polymers. The theoretical composition and physical properties of zinc borate having 3.5 hydration water are given in Table II.11. [23]

Table II.11 The theoretical composition and physical properties commercial zinc borate ($2ZnO \cdot 3B_2O_3 \cdot 3{,}5H_2O$).

B_2O_3, %	48.05
ZnO, %	37.45
Crystal water, %	14.50
Refractive index	1.58
Average particle size, µm	7 – 12
Solubility (At room temperature), %	0.28
Specific gravity, g/cc	2.77

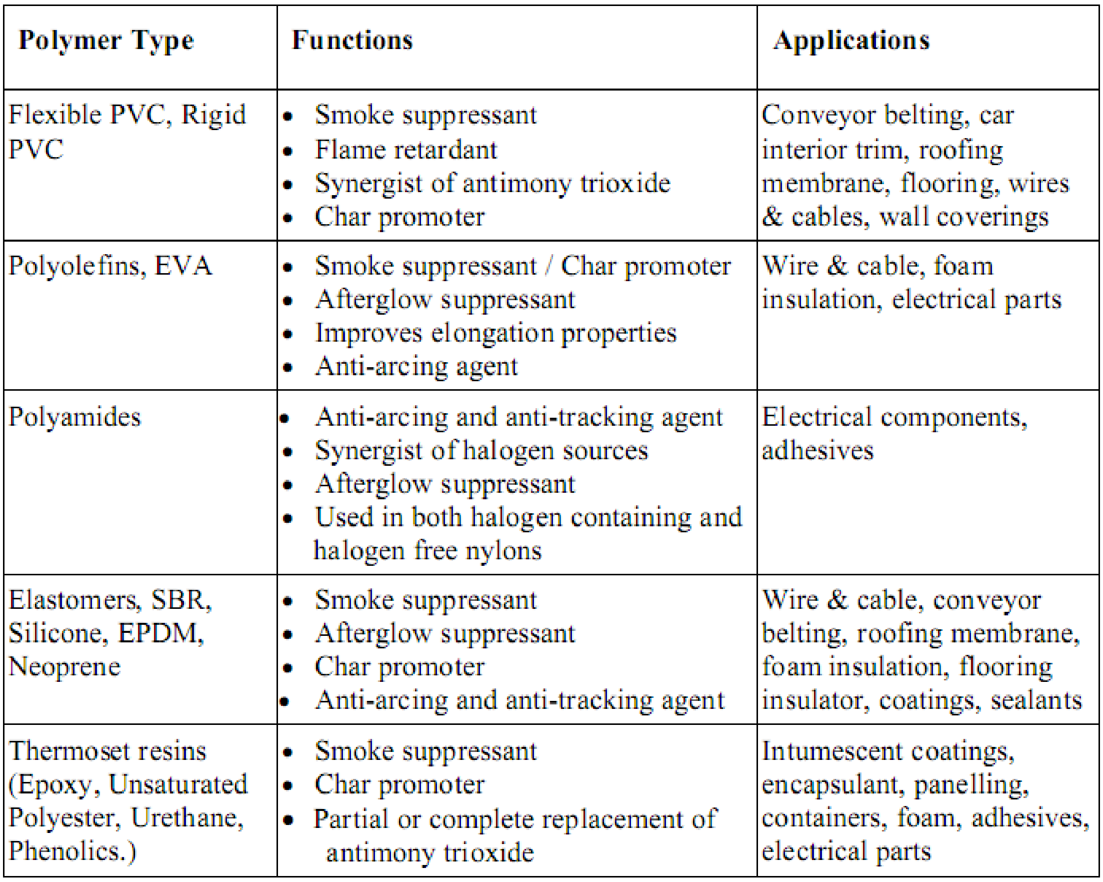
II.3.1. Application of the Zinc Borate

Flammability is important problem for polymers. There are many studies in the literature which are related with preventing or retarding flame at least for a certain time. Many commercial flame retardants are used to improve flame retardancy and supply safety of polymeric materials. Halogenated products, like antimony trioxide and phosphorous compounds are the most commonly used materials as flame retardants. In the near future the use of halogenated flame retardants may be restricted because of their hazardous effects. For example, antimony trioxides are hazardous material because of their toxic content. Aluminiumtrihydrate ($Al(OH_3)$) is another flame retardant which is cheap and non-toxic, but it is not as effective as the others. At this point, zinc borate becomes important as an environmentally friendly flame retardant and also smoke suppressant. It is used as an anti-bacterial material as well [24].

Many different hydrated zinc borates are known and several find commercial application as fire retardants and smoke suppressants for various polymers. Hydrated zinc borates are also used as anti-corrosive pigments for coatings and have demonstrated fungi static and bacteria static properties which find many applications. Several of zinc borate hydrates have commercial importance that fire retardants and smoke suppressants for polymers, rubbers and coatings are the most important application areas. The relatively high dehydration temperature (about 290°C) of $2ZnO \cdot 3B_2O_3 \cdot 5H_2O$ offers a significant advantage over other commercially available hydrated zinc borate. [21]

Previous studies have demonstrated that in halogen-free systems combining zinc borates with other FR in several kinds of polymers (ethylene vinyl acetate (EVA), polyvinyl acetate (PVC), polyamides.) have major advantages. In Table II.12, functions and applications of zinc borate in various polymers are presented. Smoke suppressant, afterglow suppressant, corrosion inhibition, anti-tracking agent and synergistic agent can be given as an example. [25-26]

Table II.12 Zinc borate functions and applications in polymers.



Polymer Type	**Functions**	**Applications**
Flexible PVC, Rigid PVC	• Smoke suppressant • Flame retardant • Synergist of antimony trioxide • Char promoter	Conveyor belting, car interior trim, roofing membrane, flooring, wires & cables, wall coverings
Polyolefins, EVA	• Smoke suppressant / Char promoter • Afterglow suppressant • Improves elongation properties • Anti-arcing agent	Wire & cable, foam insulation, electrical parts
Polyamides	• Anti-arcing and anti-tracking agent • Synergist of halogen sources • Afterglow suppressant • Used in both halogen containing and halogen free nylons	Electrical components, adhesives
Elastomers, SBR, Silicone, EPDM, Neoprene	• Smoke suppressant • Afterglow suppressant • Char promoter • Anti-arcing and anti-tracking agent	Wire & cable, conveyor belting, roofing membrane, foam insulation, flooring insulator, coatings, sealants
Thermoset resins (Epoxy, Unsaturated Polyester, Urethane, Phenolics.)	• Smoke suppressant • Char promoter • Partial or complete replacement of antimony trioxide	Intumescent coatings, encapsulant, panelling, containers, foam, adhesives, electrical parts

II.3.2. Production of the Zinc Borate

Zinc borate ($2ZnO.3B_2O_3.3,5H_2O$) is generally produced by using boric acid or borax and zinc compounds as raw materials. Commercially applied zinc borate production method is briefly defined below with flow diagram given in Figure II.6 [23]: First of all, boric acid is dissolved in water between 95-98^{o}C and solid, pulverized zinc oxide and zinc borate seed crystals ($2ZnO.3B_2O_3.3,5H_2O$) are added into this solution in certain proportions. After mixing for certain period of time, zinc borate start to form and solid zinc borate and boric acid solution is separated with a filter. After separating boric acid solution, zinc borate cake is washed with hot water to remove remained boric acid. The weak zinc borate solution obtained is returned to the beginning of the system again. The wet zinc borate cake is dried in a drier and sent to packing unit.

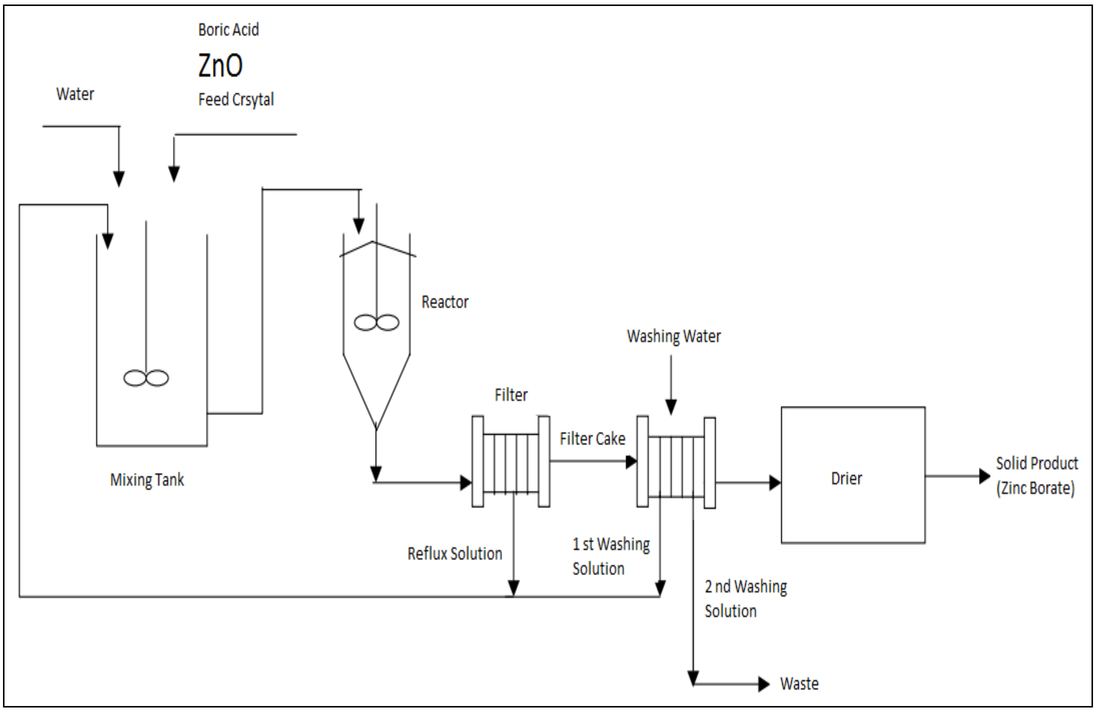


Figure II.6 Commercially applied zinc borate production method.

II.3.2.1. Micron-sized Zinc Borate Production

Various methods have been used for production of micron-sized zinc borate. Some of these methods are explained below:

In a study carried out in 1943, borax and zinc sulphate used as a raw materials. These were mixed in water for 30 minutes and then zinc hydroxide was added to this mixture and mixed again for 18-20 hours and zinc borate with the formula of $2ZnO.3B_2O_3.7H_2O$ was obtained. The speed of mixing of borax solution with zinc sulphate solutions and also the type of mixing affected the particle size of zinc borate crystals. In this process, if borax was added very slowly into the mixture and the zinc sulphate concentration was high, the produced zinc borate crystals were larger and tough. But, if borax addition was fast and zinc sulphate concentration was low this led to fine zinc borate crystals. [27] The reaction between borax decahydrate and zinc sulphate to yield zinc borate can be given as follow:

$Na_2B_4O_7.10H_2O + ZnSO_4 \rightarrow Zn(OH)_2 + Na_2SO_4 + 4H_3BO_3 + 3H_2O$ (II.1)

In another study, a crystalline zinc borate which has the approximate composition of $2ZnO.3B_2O_3.3,5H_2O$ was prepared by reacting boric acid with an inorganic zinc compound in an aqueous medium at temperatures above ~70°C. Solutions of borax pentahydrate and boric acid in water were mixed with the solution of ZnO prepared in H_2SO_4 and seed crystals were added into this mixture. $2ZnO.3B_2O_3.3,5H_2O$ composition was obtained when the solution was mixed at 40°C during the night, however, $2ZnO.3B_2O_3.9H_2O$ zinc borate was obtained when it was mixed at 62°C during the night. Also in this study, zinc chloride was used instead of zinc sulphate. Because of the transportation cost of zinc borate with lower amount of dehydration water is low, it is preferred rather than zinc borate with higher amount of dehydration water. [28]

In another study performed to produce $2ZnO.3B_2O_3.3,3\text{-}3,7H_2O$ zinc borate, borax and a water-soluble zinc salt ($ZnCl_2$, $ZnSO_4$, $ZnBr_2$, $Zn(NO_3)_2$) were used as a raw material. Borax and $ZnCl_2$ were mixed in sodium hydroxide solution and seed crystals were added to this solution. The mixture was mixed at 95°C for 24h and zinc borate crystals were obtained. In case of using $ZnSO_4$ instead of $ZnCl_2$, the mixture was mixed at 97°C after adding seed crystals into the solution. Due to the exothermic heat of the reaction, the temperature of the mixture increased to 103°C about 40 minutes and after mixing for 6 hours, the mixture was cooled to room temperature and then zinc borate was filtered. [29] The reactions between borax and zinc chloride and borax and zinc sulphate are given below:

$2Na_2B_4O_7 + 2ZnCl_2 \rightarrow 2ZnO.3B_2O_3.3,5H_2O + 4NaCl + 2H_3BO_3$ (II.2)

(Zn_2SO_4, $ZnBr_2$ and $Zn(NO_3)_2$ can be used instead of $ZnCl_2$).

$1,75Na_2B_4O_7+2ZnSO_4+0,5NaOH \rightarrow 2ZnO.3B_2O_3.3,5H_2O+2Na_2SO_4+H_3BO_3$ (II.3)

The invention of hydrothermally preparing zinc borate powder with different particle shape and low water content is a new method belonging to the technological process field of preparing inorganic materials. In this method, zinc bloom and boric acid were used as raw material, deionized water as dissolvent and pressure pan as a reactor. The pan had a filling ratio between 65-85%, reacting temperature was 110-160 °C and, reaction time was 6-24 hours. Synthesized zinc borate powder or granular, with a chemical composition of $2ZnO.3B_2O_3.3H_2O$, had an acicular and stick shapes and had a low water content depending on the surface activator or the aging time after reaction. The invention provides simple process and temperate reacting condition and easiness to control the product shape, and possesses a wide usage prospect in combustion inhibitor and anti-smoking agent. [30]

In a study carried out by Mergen et al. in 2003, zinc borate with a formula of $2ZnO.3B_2O_3.3,5H_2O$ was produced by a hydrothermal method. Boric acid and zinc borate were used as starting chemicals. Effects of different parameters (boric acid/zinc oxide ratio, mixing speed, reaction time, and reaction temperature) on zinc borate formation were investigated in this study. The optimum production conditions were calculated as boric acid/zinc oxide ratio: 5.37, reaction time: 8 hours and temperature: 95°C. It was concluded that mixing speed had no effect on zinc borate powder density. Zinc borate powders produced using the optimum conditions had bulk density value of 0.68 g/cm^3 and a mean particle size of 10 µm. Zinc borate crystal particles ranged from very small up to about 4×7 µm which had a regular diamond shapes. [4]

$2ZnO\cdot 3B_2O_3\cdot 3H_2O$ was also synthesized from boric acid and zinc oxide using a rheological phase reaction method. In this method, the main idea is the use of a little amount of water in the reaction. This technique could find use in metal borate production processes is important for environmental legislations which are strictly enforced to minimize the amount of waste streams. Stoichiometric amounts of zinc oxide and boric acid were used in the reaction, in order to complete the use of raw materials. The reactions were carried out at temperatures between 80-95 °C for different reaction periods with various amounts of water. This production method can be preferred for large scale production as there is no need for separations of product from unreacted raw materials and by-products, and no waste water, although longer reaction times (8-10 h) are required to produce zinc borate in this technique. The particle size of $2ZnO\cdot 3B_2O_3\cdot 3H_2O$ has a great importance to its industrial applications. The particle size of zinc borate samples that were synthesized in the presence of 3 mL and 0.04 mL of water at 95 °C for 8 h of reaction time was about 19 µm and 96 µm, respectively. The amount of water used in the reaction was the reason of different particle size of zinc borate samples. If more water was added to the reactants' mixture, the product had a smaller particle size (Figure II.7). The amount of water was the reactants is also responsible for the reaction time. The collision chance of molecules decreases and it induces longer reaction times, if less water is used in the reaction. [31]

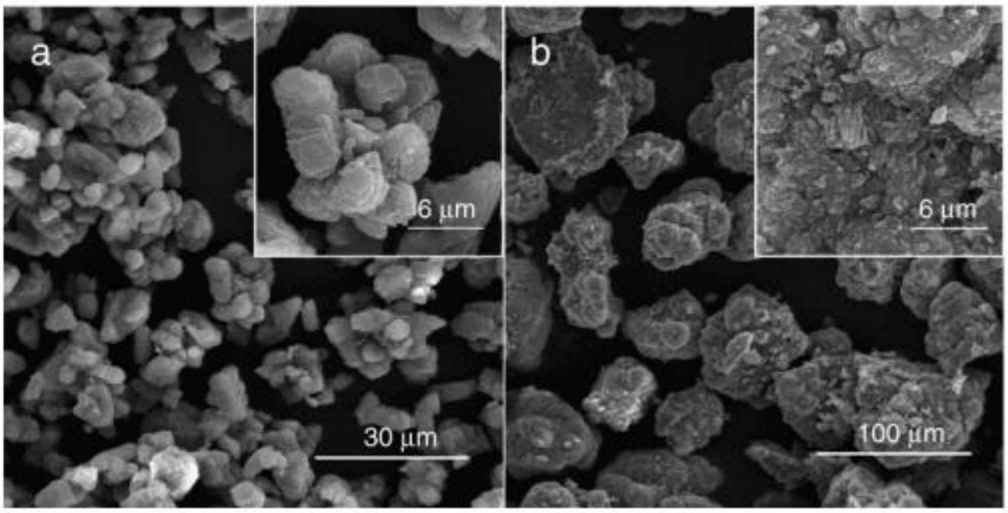


Figure II.7 SEM images of zinc borate particles in the presence of different amounts of water a) 3 mL b) 0.04 mL

Gürhan and co-workers studied, the production of zinc borate in 2009 having the molecular formula of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ and the effects of reaction parameters on the properties of product as well as the reaction kinetics were also investigated. Boric acid and zinc oxide in the presence of seed crystals were mixed in a continuously stirred, temperature-controlled 1.5 L batch reactor to produce zinc borate. The reaction between zinc oxide and boric acid fitted to the logistic model which was mostly used for growth in biological systems. The reaction rate, reaction completion time, composition and particle size distribution of zinc borate samples were examined with following parameters: different reactants ratio (H_3BO_3:ZnO, the initial molar ratio of boric acid to zinc oxide) of 3:1, 3.5:1, 5:1 and 7:1, the particle size of zinc oxide (10 and 25 µm), stirring rate (275, 400, 800 and 1600 rpm), temperature (75, 85 and 95 °C) and the size of seed crystals (10 and 2 µm). It was concluded that the reaction rate increased with the increases in H_3BO_3:ZnO molar ratio, stirring rate and temperature. Therefore, the time needed for the completion of reaction decreased. On the other hand, the size of zinc borate seed crystals had no important effect on reaction rate and completion time. Zinc borate samples obtained were analyzed for particle size distribution. Particle size of zinc borate was affected by stirring rate until a certain limit (800 rpm), but after this limit increasing the mixing rate did not induce any significant change on the particle size of the product. It was concluded that the particle size of zinc oxide did not have a significant effect on the reaction rate and the final size of zinc borate. The average particle sizes of the produced zinc borate were in the range 4.3–16.6 μm according to wet dispersion analysis. Optimum experimental conditions for producing fine zinc borate (3-5 μm) were summarized that: H_3BO_3:ZnO molar ratio of 5:1, zinc oxide particle size of 10-25 μm, stirring rate of 800-1600 rpm, reaction temperature of 85-95 °C and seed particle size of 2-10 μm. [32]

Kılınç and co-workers (2010) studied the synthesis of zinc borate which has $2ZnO\cdot3B_2O_3\cdot3.5H_2O$ molecular formula ans used laboratory and pilot scale batch reactors to see the effect of process variables on the reaction parameters and final product. The results were compared with the small scale reactor experiments in the previous study [32]. Effects of stirring speed, presence of baffles, amount of seed, particle size and purity of zinc oxide, and mole ratio of H_3BO_3:ZnO on the zinc borate formation reaction were studied at constant temperature of 85 °C in a laboratory (4 L) and a pilot scale (85 L) reactor. It was observed that scaling up the reactor either to 4 L or to 85 L did not change the essential results obtained with comparison in the 1.5 L laboratory scale batch reactor. The reaction model adapted to the production of the 3.5 mol hydrated zinc borate in the previous study as mentioned before [26] can also be applied to bigger capacity reactors. The results demonstrated that the specific reaction rate and a model parameter decreases with increase in particle size of zinc oxide and the presence of baffles, but increases with increase in stirring speed and purity of zinc oxide; however, it is unaffected with the changes in the amount of seed and reactants ratio. Also, the reaction completion time remained unaffected by scaling up the reactor. The results demonstrated that the specific reaction rate, a model parameter, decreased with increasing particle size of zinc oxide and with the presence of baffles, but increased with increase in stirring speed and purity of zinc oxide; however, it is unaffected with the changes in the amount of seed and reactants ratio. Dehydration temperature of all the products of zinc borate was above 330 °C. This property of the product is applicable for the usage of zinc borate as a flame retardant additive in plastics. The particle size of zinc borate products obtained varied in a narrow range of 3–5 μm which may provide a good dispersion during the processing of plastics. [33]

II.3.2.2. Nano-sized Zinc Borate Production

Nano-composites have been the subject of research interest since 1961 due to their enhanced mechanical, thermal and barrier properties over the conventional micro composite materials. [5] Recent studies have showed that nano-sized flame retardants as nano-composite systems with polymers have superior FR and other properties (like mechanical properties, surface quality etc.) than micron sized flame retardants. This is mainly resulted from more homogenous dispersion of nano-sized flame retardants. In addition, lower quantities of nano-sized flame retardants are sufficient to provide high flame resistance. [5-34] Literature information related with production of nano-sized zinc borate is summarized below.

In a study carried out in 2001, 3.5 mol water containing zinc borate was produced with very little crystallite. According to this study, zinc borate having a chemical composition $2ZnO \cdot mB_2O_3 \cdot XH_2O$ was produced ($m = 2.8 - 3.2$, and $x<4$). The most important disadvantage of using borax in aqueous methods is that high amounts of sodium may remain as impurity within zinc borate is the most important disadvantage of aqueous methods which causes detrimental effects in the electrical properties of polymers used in especially electric/electronic applications. In this invention, it was stated that finer particles were preferred because of larger particles of zinc borates that led to non-homogenous dispersion and decreased the brightness of polymer and affected its appearance negatively. Therefore, this study aimed of production of zinc borate powder with a finer particle size, a homogenous dispersion and regular particle shape which may improve the dispersion of zinc borate within polymer. Zinc oxide and boric acid were reacted at a low temperature like 45-65°C and then the reaction was completed by increasing the temperature to 70-100°C. Different reaction times with different temperatures were studied and their effects on particle size were examined. Particle size measurements indicated that producing zinc borate particles had an average particle size between 1-6 μm. [35]

In a study carried out in 2006, fire retardant nanometer zinc borate was produced using zinc oxide and boric acid by conventional solid-phase reaction by ball milling. [36]

In another study, nanometer crystal zinc borate with a particle size of 20–50 nm was prepared in order to decrease the friction co-efficient and increase the wear resistance using the ethanol supercritical fluid drying technique. Wear resistance and load-carrying was the main aim of adding zinc borate into base oil. No formula of zinc borate was given in the study. In this study, zinc nitrate and borax were used as starting chemicals and after mixing zinc nitrate with aqueous solution of borax, zinc borate precipitates were formed, and they were washed with distilled water and ethyl alcohol. The washed precipitates were again mixed with ethyl alcohol and then kept in autoclave at 536 K at 8,3 MPa for 30 minutes. Zinc borate powders were in the size range between 20-50 nm. The opportunity to use it practically in industrial application is not strong because this method requires high temperature and pressure which increase the cost. [37]

Crystalline and hydrophobic zinc borate ($Zn_2B_6O_{11}\cdot 3H_2O$) nanodiscs were successfully synthesized by a wet method using $Na_2B_4O_7\cdot 10H_2O$ and $ZnSO_4\cdot 7H_2O$ as raw materials in situ aqueous solution, and oleic acid as the modifying agent. 1% extra oleic acid was determined to be an optimum value. Borax solution was prepared in ethanol, then oleic acid was added into this mixture and it was heated up to 70°C and then zinc sulphate was added into the hot solution and it was mixed for 6.5 hours at constant temperature. Active ratio measurements indicated that $Zn_2B_6O_{11}\cdot 3H_2O$ samples were hydrophobic. It had been found that as-prepared materials have nanodisc morphology with average diameters changing from 100 to 500 nm with a thicknesses of about 30 nm. Nanodisc $Zn_2B_6O_{11}\cdot 3H_2O$ was produced with the aim of adding zinc borate into base oils in order to decrease the friction co-efficient which had a hydrophobic character. [38]

In another study performed with the purpose of producing nano-sized zinc borate nano-tubes zinc borate (ZnB_4O_7) was synthesized by a simple sintering of mixed powders. Raw material powders contained Zn nano-particles and B_2O_3 in the presence of %10 $AgNO_3$ catalysts in argon gas. Then, the mixture was fired at 500°C for 1 h in quartz tube in Ar atmosphere. The produced nano-tubes were 5-15 nm in thickness and a few tens of μm in length. [39]

In the study carried out in 2007, one-dimensional (1D) nanostructure of $4ZnO\cdot B_2O_3\cdot H_2O$ with rectangle rod-like shape with 70 nm thickness, 150-800 nm width and a few μm length has been produced by a hydrothermal route in the presence of surfactant polyethylene glycol-300 (PEG-300). In this study, zinc sulphate and borax were used as starting chemicals and polyethylene glycol (PEG-300) was used as a surfactant. Nano bar zinc borates were produced in stainless steel autoclave by a hydrothermal method which had optimum conditions that temperatures were 100°C and 180°C, reaction time was 24 h and pH was 8. As a result of this study, it was demonstrated that surfactant PEG-300 addition during the production of nano bars had great importance. [40]

Polycrystalline and hydrophobic zinc borate ($Zn_2B_6O_{11}\cdot3H_2O$) nanoplatelets were in situ successfully synthesized via one-step precipitation reaction in aqueous solution. $Na_2B_4O_7\cdot10H_2O$ and $ZnSO_4\cdot7H_2O$ were used as raw materials with oleic acid as the modifying agent. $Zn_2B_6O_{11}\cdot3H_2O$ samples were determined as hydrophobic as a results of measurements of the relative water contact angle and the active ratio. The morphology of the samples was composed nanoplatelet morphology with average diameters between 100–500 nm and thickness 30±5 nm and the morphology and size of the samples were controlled effectively. [41]

Ting and co-workers studied in 2007 a new netlike nano zinc borate which had a molecular formula of $ZnO\cdot yB_2O_3\cdot zH_2O$ (y=0.3–0.4, z=1.0–1.4) with amorphous phase prepared via homogeneous precipitation method and it was introduced into polypropylene (PP) and high-density polyethylene (HDPE) as flame-retardant filler. It had been found that as prepared materials displayed fiber morphology with diameter of about 15 nm and length of about hundreds of nanometers, some of which entangled each other to form dendritic or interconnected networks. The pilot study revealed that the product had better char formation effect than the commercial zinc borate. Carbon residue ratio of PP and HDPE were 75% and 63% respectively when the sample content was about 12 wt.%. [42]

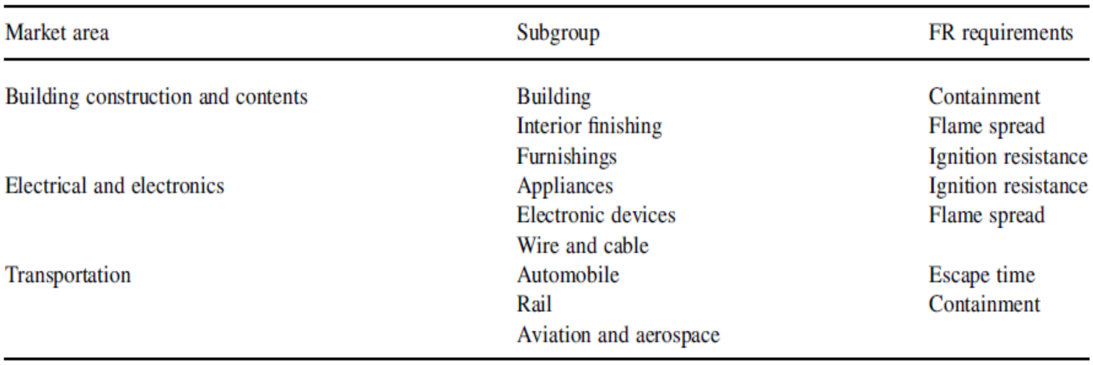
In a study carried out in 2009, zinc borate ($4ZnO\cdot B_2O_3\cdot H_2O$) nanowhiskers were synthesized via one-step precipitation reaction in aqueous solution of sodium borate ($Na_2B_4O_7\cdot10H_2O$) and zinc nitrate ($Zn(NO_3)_2\cdot6H_2O$) as a starting chemicals and phosphate ester as the modifying agent. In a typical procedure, 50 mL of 0.1 mol dm^{-3} $Na_2B_4O_7\cdot10H_2O$ aqueous solution and 1mL of 0.002 mol dm^{-3} phosphate ester were added into a 250-mL three-neck round-bottom flask equipped with a thermometer and a mechanical stirrer. First of all, the mixture was heated to 70 °C, to which 10.0 mL of 2 mol dm^{-3} $Zn(NO_3)_2\cdot6H_2O$ aqueous solution was added over 0.5 h while being stirred. The reaction, which had a pH value of 8.0, was mixed for about 7 h. The precipitate was collected and washed several times with absolute ethanol and distilled water to remove the unreacted products, and then dried at 60 °C for 8 h to obtain the final white zinc borate powders. The zinc borate nanowhiskers morphology had the monoclinic crystal structure with diameters of 50–100 nm, lengths of about 1 μm, and the aspect ratios close to 10–20. The products were dispersed into polyethylene and the results revealed that the presence of phosphate ester and the change of temperature were vital for the preparation of zinc borate nanowhiskers. Moreover, increase upon the addition of the nanowhiskers in polyethylene, increased the thermal stability of composites. [43]

II.4 FLAME RETARDANCY

The massive use of polymer materials in our everyday life is driven by their remarkable combination of properties which are low weight and ease of processing. However, polymers are also known for their relatively high flammability; most often released by the production of corrosive or toxic gases and smoke during combustion. Consequently, improving the fire retardant behaviour of polymers is crucial for extending their use to most applications. While various flame retardant additives, such as halogenated additives, are being phased out for their proven or suspected adverse effects on the environment, safety requirements and environmental restrictions are currently becoming more and more drastic in terms of polymers' reaction to fire and their fire resistance performances. The combined challenge thus consists in developing effective and environmentally friendly green flame retardant systems for polymer materials. The scientific and technical literature contains very different and efficient strategies for improving polymer fire resistance, which depend primarily on the nature and chemical structure of the polymer concerned like its decomposition mode and the required level of fire safety, and also the global performances of the resulting materials. The development of flame retardant materials and understanding the phenomena that take place during combustion often require close collaboration between several fields of scientific expertise such as macromolecular and physical chemistry, physics of mass and heat transfer, rheology, etc. [44]

Now, in the 21st century, natural and synthetic polymer materials are used in many areas and more demanding environmental conditions. However, fire hazards related with the use of polymeric materials, which cause the loss of life and property, are of significant concern among government regulatory bodies, consumers and manufacturers alike. The use of flame retardants to reduce polymers combustibility, and smoke or toxic fume production, therefore becomes essential part of the development and application of new materials. Amongst the major markets which are needed flame retardants, the industries dealing with construction, electrical and electronics components and transportation are the three of greatest importance (Table II.13). For example, advanced composite materials are developed in the aerospace industry to displace metals in response to a strong economic imperative to save weight while at the same time increasing the payload. However, these new materials require properties such as thermo-oxidative stability, low flammability and retention of material strength at elevated temperatures, low corrosion and better fatigue resistance, lower tooling costs and relative ease of fabrication. Of course, the structural materials are cost competitive with metals is very important at the same time. [45]

Table II.13 Flame retardant (FR) market application.



Market area	Subgroup	FR requirements
Building construction and contents	Building	Containment
	Interior finishing	Flame spread
	Furnishings	Ignition resistance
Electrical and electronics	Appliances	Ignition resistance
	Electronic devices	Flame spread
	Wire and cable	
Transportation	Automobile	Escape time
	Rail	Containment
	Aviation and aerospace	

On the other hand, the development of flame retardant materials is mainly driven by the increasing safety awareness of consumers and by environmental issues in household applications. Both the European Community (EC) and the United States (US) government expressed concern about the use of some flame retardants. The major effort is that identify and collate information on the type of flame retardants used in consumer products, principal flame retardants are used to review and assess the toxicity and environmental impact. The EC proposed to restrict the use of brominated diphenyl oxide flame retardants because of high toxicity and potentially carcinogenic brominated furans and dioxins which may form during combustion. In addition, the World Health Organisation (WHO) and the US Environmental Protection Agency (EPA) also recommend exposure limit and risk assessment of dioxins and similar compounds. It is essential that new flame retardant systems are developed to change demand of new regulations, standards and test methods. [45]

II.4.1. Mechanism of Polymer Flame Retardancy

Polymers are highly combustible due to their chemical structure, made up mainly of carbon and hydrogen. The combustion reaction involves two factors: one or more combustibles (reducing agents) and a combustive (oxidizing agent). The combustive is generally the oxygen in the air. The whole process usually starts with an increase in the temperature of the polymeric material due to a heat source, and then polymer bond scissions. The volatile fraction of the resulting polymer fragments diffuses into the air and creates a combustible gaseous mixture which called fuel. This gaseous mixture ignites when the auto-ignition temperature which is defined as the temperature at which the activation energy of the combustion reaction is attained is reached, liberating heat. The fuel can also ignite at a lower temperature is called the flash point upon reaction with an external source of intense energy (spark, flame, etc.) alternatively. Combustion cycle life span of depends on the quantity of heat liberated during the combustion of the fuel. New decomposition reactions are induced in the solid phase when the amount of heat liberated reaches a certain level, and therefore more combustibles are produced. The combustion cycle is thus maintained, and called a fire triangle (Figure II.8). [44]

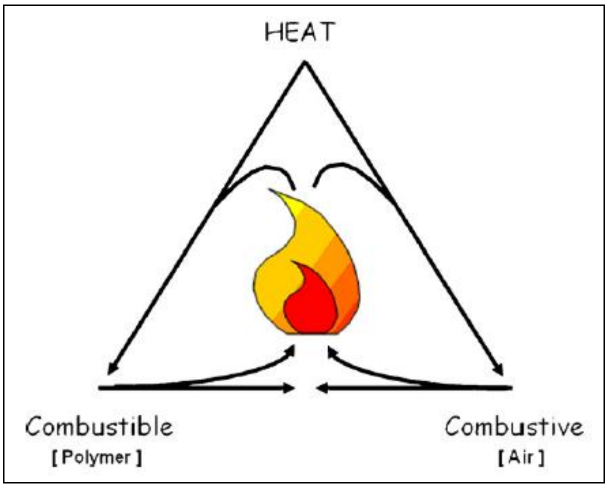


Figure II.8 Principle of the combustion cycle.

The basic combustion cycle of polymer composites is shown schematically in Figure II.9. [46]

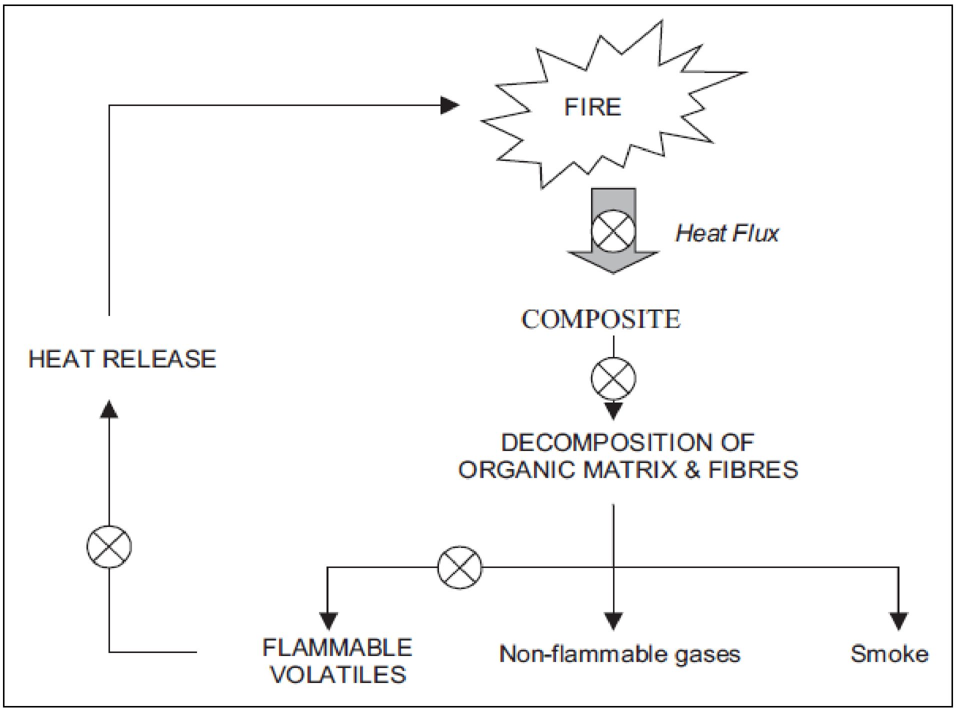


Figure II.9 Combustion cycle for polymer composites in fire.

Global process involves several reactions and transport phenomena in the solid, gaseous and interfacial phases. Heating can be caused by a contribution of thermal energy from external heat sources which are radiation, convection or conduction, by a chemical process induced inside the material (fermentation, oxidation, etc.) or by the exothermicity of the combustion reaction initiated. In polymers, the amount of energy required to initiate combustion varies according to function of the physical characteristics of the material. For instance, the polymer softens melts and drips during the heating of semi-crystalline thermoplastics. The energy stored by the polymer during these processes depends on both its enthalpy of fusion and degree of crystallinity and its heat-storage capacity. Therefore, the temperature increase in the polymer and the related rate depend primarily on the heat flow, due to the exothermicity of the reactions the difference in temperature involved, and the specific heat and thermal conductivity of the semi-crystalline thermoplastic. In contrast, due to the absence of a melting point in the case of amorphous thermoplastics and most thermoset, the heating step leads directly to polymer decomposition. The thermal decomposition of a polymer like covalent bond dissociation is an endothermic reaction, which requires an input of energy. The energy provided to the system must be higher than the binding energy between the covalently linked atoms as 200–400 kJ/mol for most C–C polymers. The decomposition mechanism highly depends on the weakest bonds, and also on the presence or absence of oxygen in the solid and gas phases. Generally, combination of the effects of heat and oxygen causes thermal decomposition. Therefore non-oxidizing thermal degradation and oxidizing thermal degradation must be distinguished. [44]

Non-oxidizing thermal degradation is generally initiated by chain scissions under the simple effect of temperature (pyrolysis) which involves varying degrees of material depolymerization. The initial scission depends on several factors which are the presence of oxygen atoms in the chain and catalyst residues, former residues of oxidation, chemical defects in polymer chains and the existence of weak bonds along the chain, particularly at the end, which can initiate unzipping reactions.

The polymer reacts with oxygen in the air in oxidizing thermal conditions and generates a variety of low molecular weight products: carboxylic acids, alcohols, ketones, aldehydes, etc. This degradation also releases very reactive species, for instance $H^\bullet$ and $OH^\bullet$, particularly in polyolefins. Oxidation can lead to crosslinking through recombination reactions of the macromolecular radicals, but bond scission usually remains the dominant reaction. Wrenching reaction of hydrogen atoms from the polymer chains controls the propagation rate of the degradation. Thus, the oxidation stability of the polymer depends on the C–H bond energy.

Physical factors also affect flame propagation, more specifically thermal transfers. In the initial phase of fire development, conductive and convective transfers are important when the height of the flame remains limited to a few tens of centimeters. Flame propagation on the surface contributes to a rapid increase in radiative transfer in a more advanced phase.

The development of considerable material heterogeneity can be highlighted during these different stages, particularly during combustion. A gradient structure tends to form inside the material, which arising from the interaction with atmospheric oxygen, coupled with the out-diffusion of reactive species and also concomitant polymer chain breakdown within the material. Inside several zones of the material can therefore be identified. An energy balance between the heat transfers occurring during combustion is given in Figure II.10. [44]

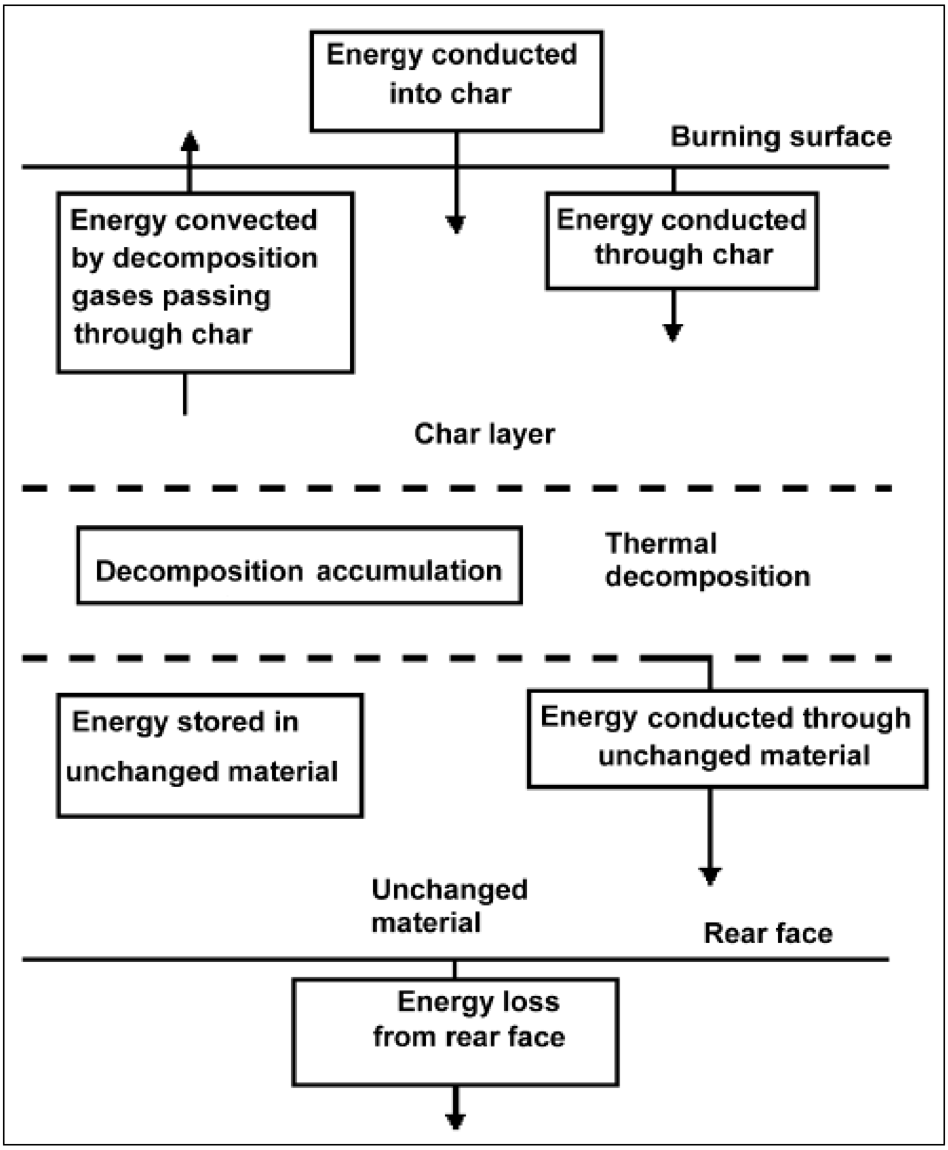


Figure II.10 Identification of thermal transfers during combustion.

II.4.2. Flame Retardant Testing Methods

Many national and international bodies establish polymer materials flammability testing method standards that guidance documents and methods addressing most of the major fire properties. Among them the following are the five main types: [45]

1. Ignitability tests (or UL94);
2. Flame spread tests;
3. Limiting oxygen index (LOI);
4. Heat release tests (Cone calorimeter);
5. Smoke tests.

The LOI measures the minimum oxygen concentration which is in a flowing mixture of oxygen and nitrogen gas required to support candle-like downward flame combustion. The LOI is expressed as following formula (II.5),

$$\mathrm{LOI} = 100\,\frac{[O2]}{[O2] + [N2]} \tag{II.5}$$

Materials with an LOI below 21 are classified as ‘‘combustible’’ whereas those with an LOI above 21 are classified as ‘‘self -extinguishing’’, because their combustion cannot be sustained at ambient temperature without an external energy contribution. The higher of the LOI is mean that the better the flame retardant property. [44] It serves as a measure of the ease of extinction of the materials and the equipment is inexpensive and requirement for sample size is small, so this method is suitable as a semi-qualitative indicator of the effectiveness of flame retardants during research and development stage. Real scale fire performance of a material cannot be based on LOI value because of the low heat input and the simulated high oxygen concentration. [45]

Thermal gravimetric analysis (TGA) is the other useful indicator at the research and development stage is a char yield under either air or nitrogen atmosphere. Thick char undergoes slow oxidative degradation and prevents heat reaching the remaining polymer and becomes a better thermal insulating layer. Lewin demonstrated that the chars obtained in the intumescent systems are different from the chars from TGA. The former are prepared at lower temperatures and are not fully pyrolysed or oxidised. Their rate of formation is high and involves thermo-oxidation though they serve the same purpose which is namely acting as barriers to the passage of molten polymer and decomposition gases.

Some laboratories adopt UL is that Underwriters Laboratories tests, e.g. UL94. These methods are similar to American Society for Testing and Materials (ASTM) or National Fire Protection Association (NFPA) standards. Usually a vertical burn test is carried out and the flammability is rated from V_0 to V_2. To achieve V_0 which is the best flame retardancy rating, the burning must stop within 10 s after two applications of 10 s each of a flame to a test bar and no flaming drips are allowed. [45]

Figure II.11 represents the various techniques available for characterization the polymer degradation which monitors the degradation as well as stabilization. [47]

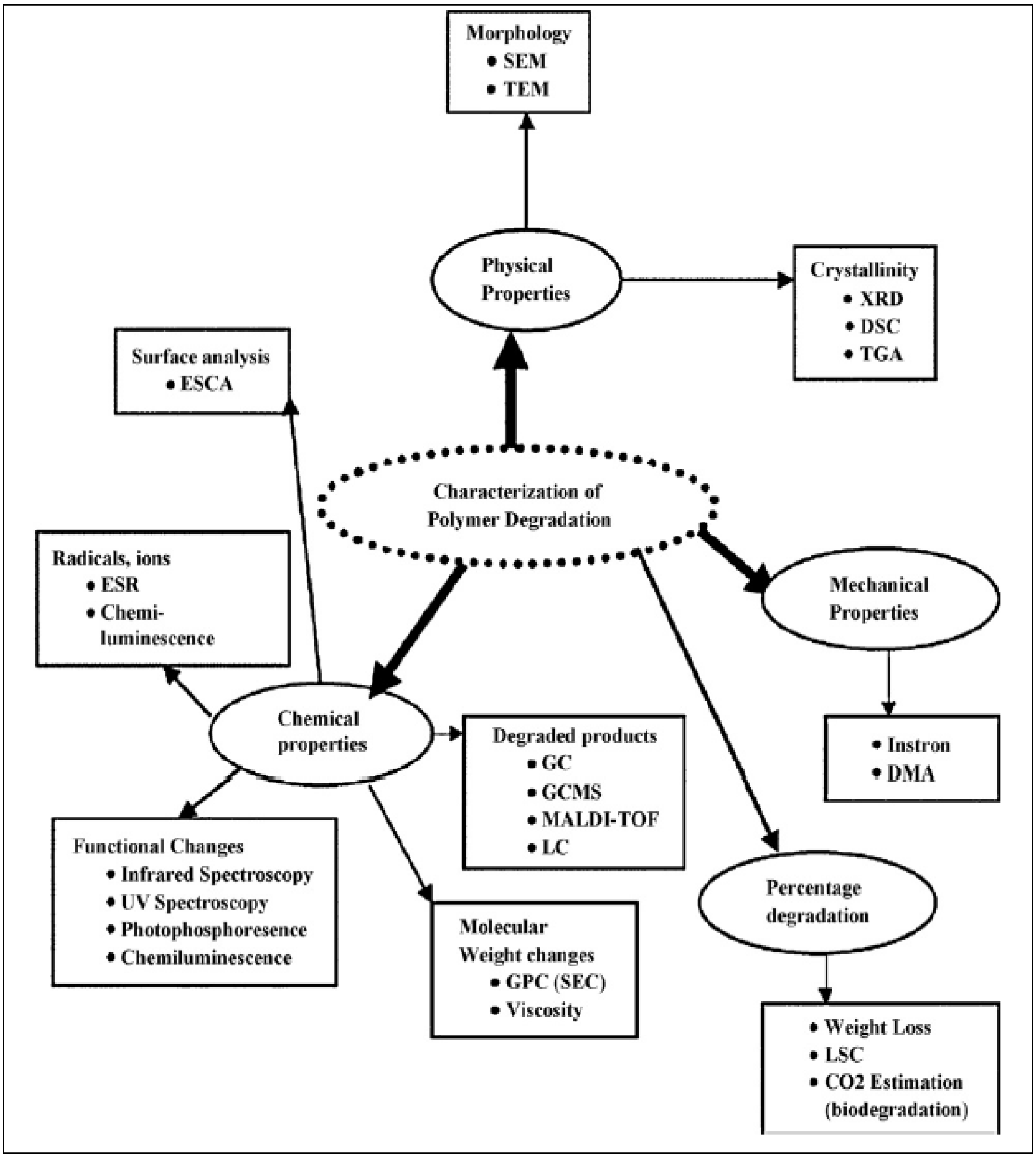


Figure II.11 General techniques for characterizing polymer degradation.

CHAPTER III

THE STUDY

III.1. EXPERIMENTAL

Zinc borate added ethylene vinyl acetate (EVA) and high density polyethylene (HDPE) polymer nano-composites were produced in order to investigate the effect of zinc borate on various properties of composites, mainly flame retardancy and mechanical properties. Nano-sized zinc borate powders with the formula of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$ were prepared by a wet chemical method using oleic acid as modifying agent. Micron-sized commercial zinc borate with the formula of $2ZnO.3B_2O_3.3.5H_2O$ was also added into the EVA and HDPE compare the flame retardancy properties and mechanical properties with nano composites.

Testing and measurements for characterization of samples were listed below;

- Thermal analysis of zinc borate powders and produced zinc borate – EVA and zinc borate – HDPE nano composites,
- Particle size analyses of nano-sized zinc borate powders,
- Scanning electron microscopy studies of zinc borate powders and zinc borate – EVA and zinc borate – HDPE composites,
- Mechanical tests of nano and micron size zinc borate added composite materials,
- Flame retardancy properties of zinc borate – EVA and zinc borate – HDPE composites.

III.2. MATERIALS AND EQUIPMENTS

III.2.1. Starting Materials

The starting chemicals which were used in the production of nano-sized zinc borate powders are given in Table III.1. Distilled water was used in the synthesis. Commercial (micron-sized) zinc borate (MA013-ÇB) powders were supplied from MELOS A.S.

Table III.1 Chemicals for the production of nano-sized zinc borate.

Starting Chemicals	**Chemical Formula**	**Purity**	**Manufacturer**
Zinc Nitrate	$Zn(NO_3)_2.6H_2O$	99,5%	Merck
Borax Pentahydrate	$Na_2B_4O_7.5H_2O$		Eti Maden
Oleic Acid	$C_{17}H_{33}COOH$	99%	Sigma-Aldrich

Ethylene vinyl acetate (EVA) and high density polyethylene (HDPE) polymers were used to produce zinc borate – polymer nano composite materials.

EVA was supplied by REPSOL, as the grade PA-440 (28% vinyl acetate content) with a melt flow index of 7g/10 min (MFI; 190 °C / 2.16 kg), and used as matrix. Chemical formula and structure of EVA are shown in Figure III.1.

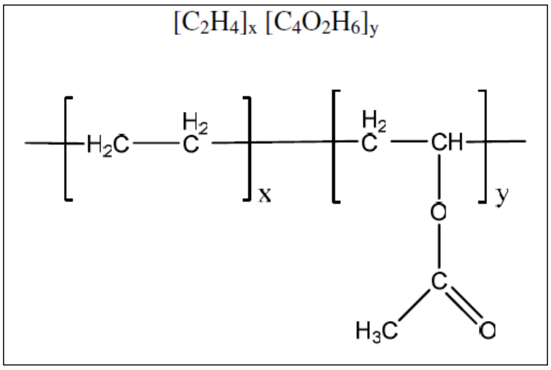


Figure III.1 The chemical formula and structure of EVA.

PE was supplied by PETKIM, as the grade I668 HDPE, and used as matrix. Chemical formula and structure of HDPE are shown in Figure III.2.

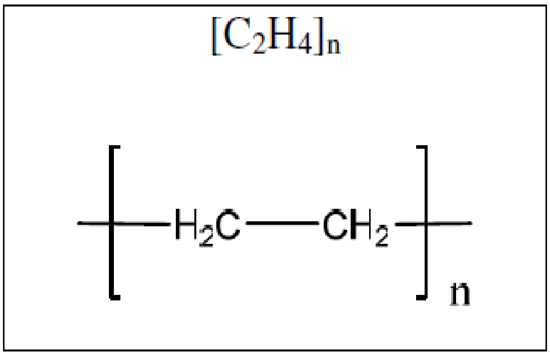


Figure III.2 The chemical formula and structure of PE.

III.2.2. Equipments

Glass reactor was used for the synthesis of the nano-sized zinc borate powders. Synthesized nano zinc borate powders were blended with EVA and HDPE polymers by melt blending the materials using an intermeshing co-rotating twin screw extruder and then by injection machine to produce standard test specimens.

XRD technique was used for structural analyses of synthesized zinc borate powders. DTA-TG and DSC instruments were used for thermal analysis of synthesized powders and composite materials. FT-IR was also employed for structural analysis of zinc borate powders. Particle size measurement was carried out by Zetasizer. Particle shape and degree of agglomeration of synthesized nano zinc borate powders were carried out by TEM. The microstructure of zinc borate added polymer composites were revealed by SEM. Flame retardancy properties of zinc borate – EVA and zinc borate – HDPE composites were investigated by LOI test method. Mechanical properties of composites were determined by mechanical testing methods.

III.2.2.1 Equipment Used For the Synthesis of Nano-Sized Zinc Borate Powders

1000 ml three-neck round-bottomed glass reactor equipped with a thermometer, reflux condenser, and mechanical stirrer was used to produce nano-sized zinc borate powder (Figure III.3).

Figure III.3 Glass reactor.

Glass reactor has a jacket around it and connected to a cryostat (Figure III.4). The solution within glass reactor was mechanically stirred with a mechanical stirrer with a capacity up to 2.000 rpm.

Figure III.4 Cryostat.

After completion of reaction time, the final mixture was then filtered to separate the surplus liquid (Figure III.5). After that zinc borate powders were washed several times with distilled water and alcohol. Finally, filtered zinc borate powders were dried at 70°C for 24 in a dryer.

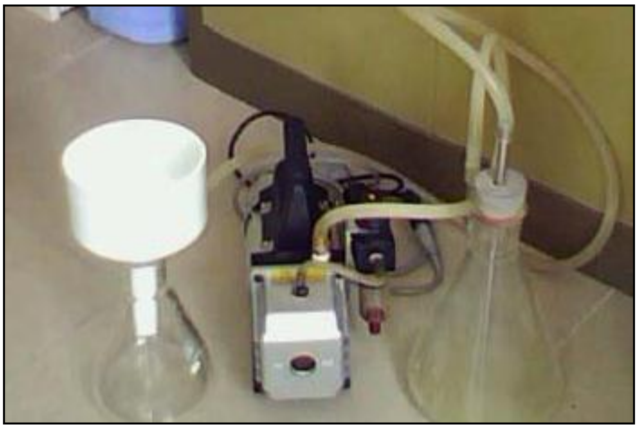


Figure III.5 Filtration system.

III.2.2.2 Compounding Process

Twin-Screw Extruder

Synthesized nano-sized and commercial micron-sized zinc borate powders were blended with EVA and HDPE polymers by melt blending the materials using an intermeshing co-rotating twin screw extruder. The modular PRISM TSE 24 HC (Figure III.6), with 24 mm screw diameter (D) and 28:1 L/D ratio (shaft length over screw diameter) twin screw extruder was used. Several technical specifications of twin screw extruder is given in Table III.2.

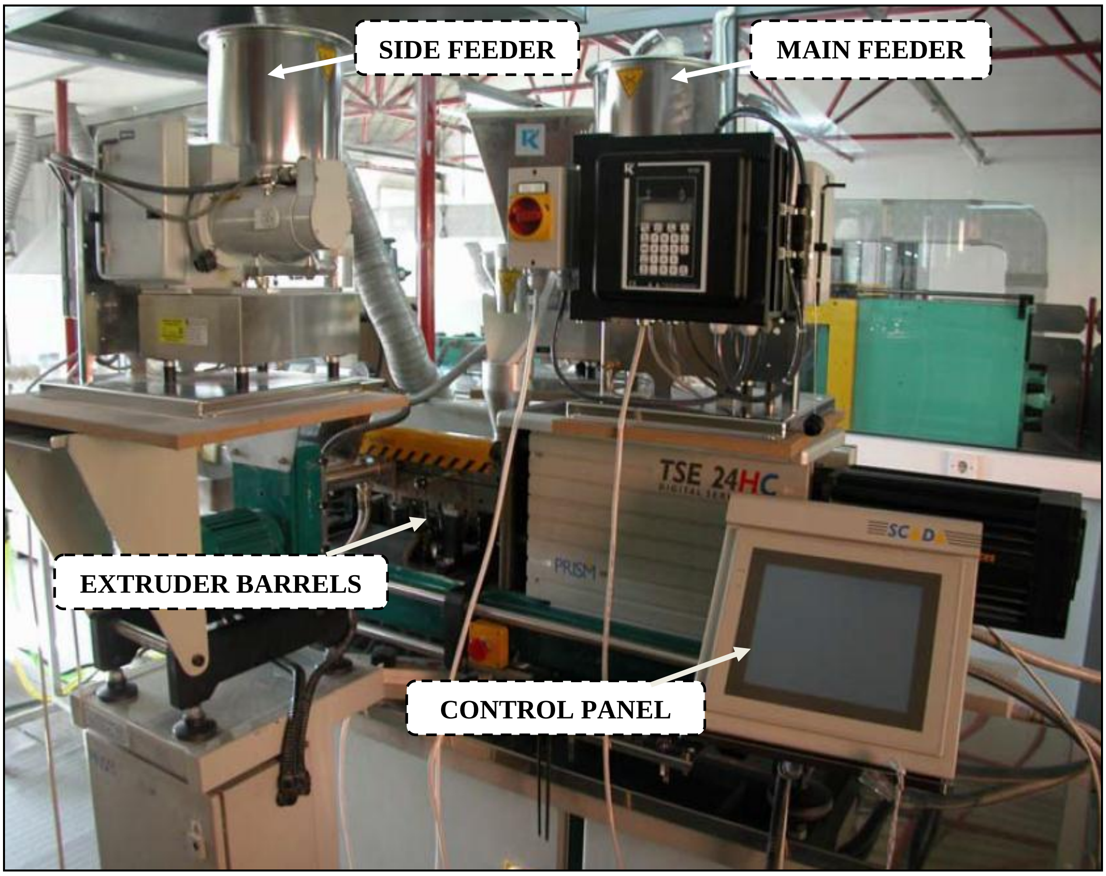


Figure III.6 PRISM TSE24 HC extruder with gravimetric feeder.

Table III.2 Technical specifications of Prism TSE 24 HC 28:1 extruder.

PRISM TSE 24 HC 28:1	Units	Values
Barrel bore diameter	mm	24
Screw diameter	mm	23.6
Channel depth	mm	5.15
Maximum screw speed	rpm	1000
Power at maximum screw speed	kW	9.0
Maximum torque/shaft	Nm	43
Barrel zones	Qty.	7
Extruder dimensions (L x W x H)	cm	165 x 60 x 135

PRISM TSE 24 HC extruder had 7 heat controlled modular barrel segments with length of 96 mm or 4 x screw diameter. Thermo regulator controls the set temperature; electrical resistances and water cooling channels; which are connected to the each modular barrel zone. Thermocouples were mounted in the 3rd, 5th, and 7th zone of barrels to measure the melt temperatures of polymers. Barrels and screws are shown in Figure III.7.

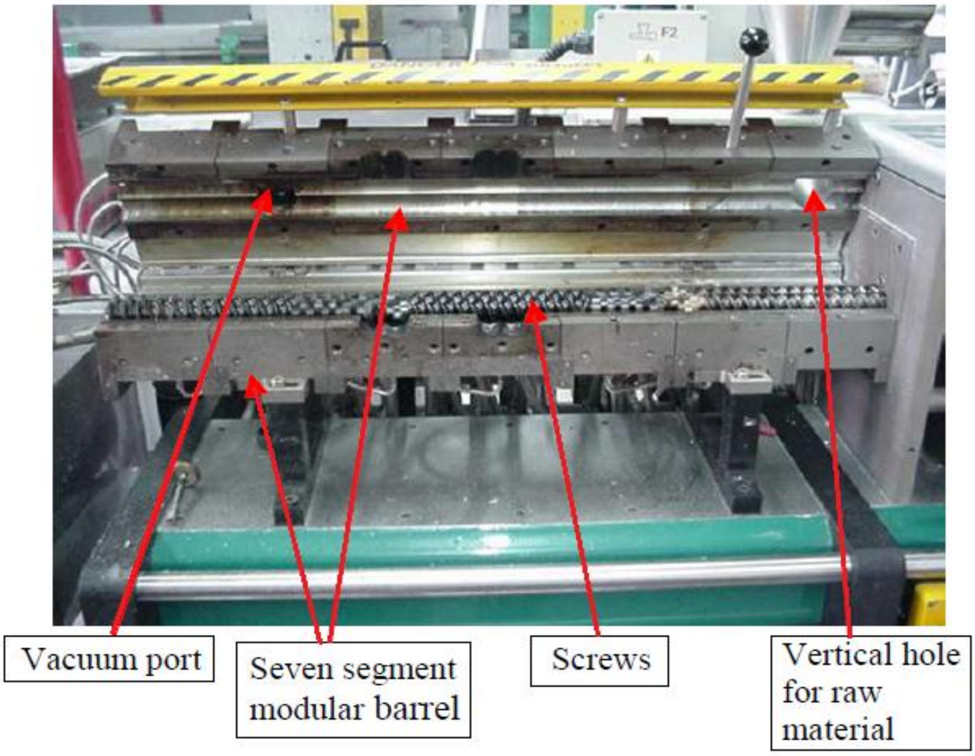


Figure III.7 Prism Twin Screw Extruder Barrels and Screws.

In the first barrel, which is known as inlet zone, polymeric materials start conveying into other zones and melt in the barrels by the effect of heat and work supplied on the polymers. Edwards rotary vacuum pump by hoses at 6th zone of barrel is used to remove the gases occurred during compounding. The barrels finish with a three-strand hole die. Melted polymeric composite can go out of the extruder from hear and it can be cooled down into a water bath and solidified as spaghettis. These spaghettis are cut into small pieces a called granule by Prism Granulating Unit is shown in Figure III.8.

The extruder is equipped with both K-Tron gravimetric feeders are operated by K-Tron computer interfaced software and one Brabender side feeder is operated by Prism own controller system.

Figure III.8 Prism Granulating Unit.

Injection Moulding Machine

Standard specimens for tensile, impact and LOI test specimens according to the ISO standards were produced with an Arburg Allrounder 320C fully hydraulic plastic injection machine (Figure III.9). A plastic injection machine is mainly divided into 2 parts which are injection unit and clamping unit. Plastic granules are fed into the barrel from a feeding hopper. In the barrel, there is a reciprocating screw which can make rotational and linear movements together and plastic is melted in hear and injected into the mold with the linear movement of the screw. Holding pressure which control the shrinkage and maintain the dimensional stability is applied after injection. The mold is kept close for cooling of the injected part after holding pressure. A schematically illustration of an injection machine is given in Figure III.9.

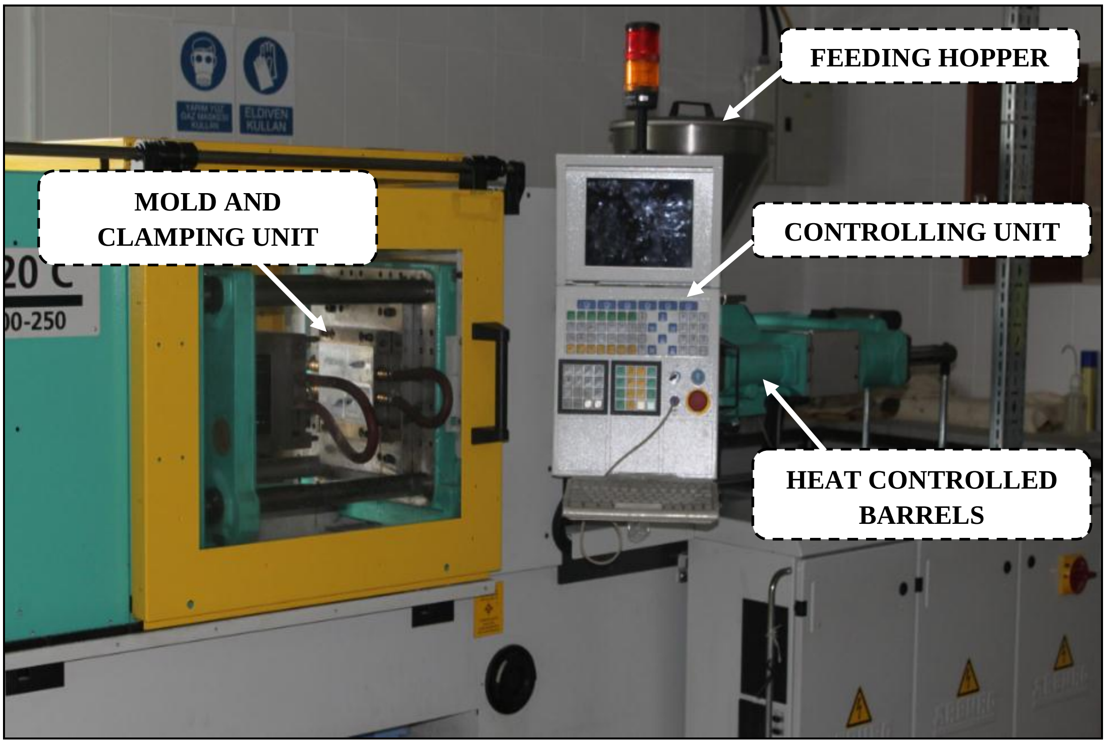


Figure III.9 Arburg Allrounder 320C Injection Machine.

Mold temperature during the injection process was kept constant as 23 °C with a water cooling chiller; Piovan ST092. The Arburg injection machine's specifications are given below in Table III.3.

Table III.3 Arburg Allrounder 320C Injection machine specifications.

Arburg Allrounder 320C	Units	Values
Screw diameter	mm	30
Maximum injection pressure	bar	2000
Maximum volumetric displacement	cm^3	144
Hydraulic motor power	W	1500
Maximum clamping force	tons	50
Maximum screw speed	rpm	154
Screw back pressure	bar	350

Standard for tensile and flexural specimens were prepared according to the International Organization for Standardization (ISO) by means of Arburg Allrounder 320C Injection machine. Mold design of tensile, Izod impact test and LOI test specimens are shown in Figure III.10 [48] and Figure III.11 [49].

Figure III.10 Mold designs of tensile specimens according to the ISO R 527

Figure III.11 Mold designs of Izod Impact test and LOI test specimens according to the ISO 180

III.2.2.3 Characterization of Zinc Borate Powders and Zinc Borate – Polymer Composites

Crystal Structure Analyses

Zinc borate phase analysis was performed by X-ray diffractometer (XRD). Rigaku difractometer was used under the stated conditions; Cu Kα radiation, scanning speed: 2°/min., 2θ: 10-60°.

Thermal Properties

Thermal analysis measurements of synthesized zinc borate powders were carried out by thermogravimetric and differential thermal analysis (DTA-TG) (NETZSCH STA 409C/CD) (Figure III.12.a). DTA-TG instrument was calibrated before measurement. Around 15-20 mg sample was used and the measurement was made between 30-950°C at a heating rate of 10K/min under nitrogen atmosphere.

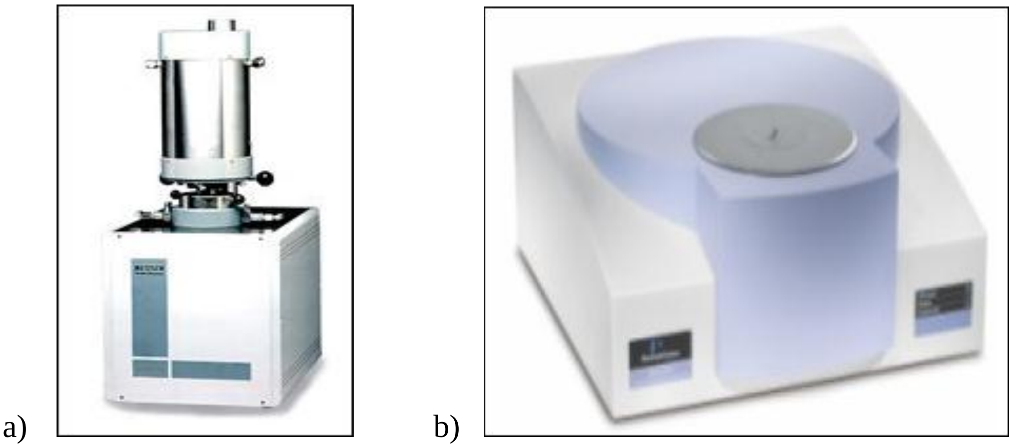


Figure III.12 NETZSCH STA 409C/CD DTA-TG and DSC 4000 analysers.

Oxidative-Induction Time or OIT is a standardized test performed in a DSC to measure the stabilization level of the material. OIT analysis was carried out by Perkin–Elmer DSC 4000 with Pyris software program instrument to understand flame retardation behaviour of zinc borate – EVA and zinc borate – PE composite materials (Figure III.12.b). DSC instrument was periodically calibrated. Samples (15-20 mg) were scanned from 30°C to 200°C at a heating rate of 10°C/min under argon atmosphere and hold at that temperature giving oxygen to identify flame stabilization level of composite's.

Molecular Analysis

IR spectroscopy of the samples were examined in the wave number range from 4000 to 450 cm^{-1} at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 100 spectrophotometer at room temperature (Figure III.13).

Figure III.13 Perkin-Elmer FT-IR Spectrum 100 spectrophotometer.

Particle Size Measurement

Particle size measurement was carried out by Zetasizer (Nano ZS, ZEN 3600) (Figure III.14). Before measurement the sample was dispersed in distilled water.

Figure III.14 Nano Sizer; Nano ZS, ZEN 3600 instrument.

Morphology Investigation

The size and shape of the particles and their morphologies and the degree of agglomeration of synthesized zinc borate powders were investigated by Transmission Electron Microscope (TEM). After dispersing zinc borate powders in ethyl alcohol, a few drop of mixture was poured on the grid, and ethyl alcohol was removed by drying. After cooling the powders, they were analysed by TEM.

The microstructure of zinc borate – EVA and zinc borate – PE composites was examined by Scanning Electron Microscope (SEM, Jeol JSM 6400) and compositional analysis were carried out by NORAN Voyager EDS (Energy Dispersive X-ray Spectrometer) (Figure III.16). Injection molded impact test specimens were immersed in the liquid nitrogen and broken with sudden force to investigate the interface between polymer and zinc borate filler and filler dispersion in the matrix. Fractured surface of the samples were coated with carbon by Polarou E6200 Turbo Coater (Figure III.15) before SEM analysis to provide electron conductivity. Carbon coated fracture surfaces of produced composite‘s were investigated of different magnifications.

Figure III.15 Polarou E6200 Turbo Coater.

Figure III.16 JSM 6400 SEM ve NORAN Voyager EDS instruments.

Mechanical Properties

Tensile and impact test specimens were kept in on air conditioned room with a room temperature of 23±2 °C and the relative humidity of 50% for at least 48 hours.

- Measurement of Tensile Properties

Stress-strain behaviour of the composites was determined using Zwick universal tensile testing machine Z020 equipped with 20 kN load cell as load indicator and a mechanical long stroke extensometer as extension indicator. Injection molded tensile specimens (according to ISO R 527 [48]) were used to measure the tensile properties. Strain-stress tests were performed using dumbbell shaped specimens after measurement of thickness and width. Testing speed was set to 50 mm/min and gauge length (Lo) was set to 70 mm which is shown in the Figure III.17.

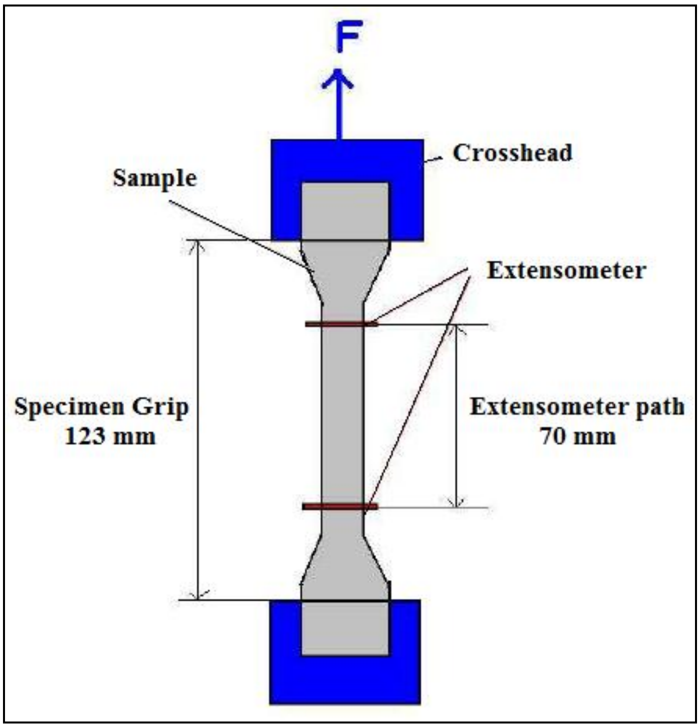


Figure III.17 Tensile test specimen.

A typical stress-strain curve is shown in Figure III.18**.** The elastic strain region and the plastic strain region of the stress-strain curve are divided by the yield point which is an imaginary boundary. Above yield point, stresses cause permanent damage to the bone structure which is called plastic deformation. The amount of post-yield strain occurs in a material before fracture is a measure of the ductility of the material. Brittleness is opposite of ductility and material that sustains very little post-yield strain before fracture is called brittle material.

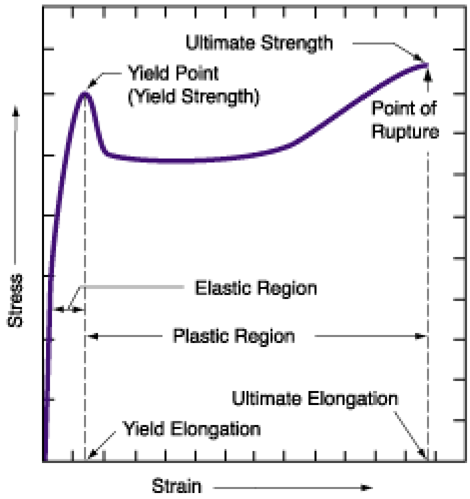


Figure III.18 Important points in the stress-strain graph.

- Measurement of Izod Impact Strength

Izod impact test was carried out according to ISO 180 standard [50]. Injection molded test bars had dimensions of 4 ± 0.2 mm, 10 ± 0.2 mm, 80 ± 0.2 mm. 2 mm notch with notch base radius 0.25 ± 0.05 mm was machined at mid-span of specimen before Izod impact test. The test specimen and the notch are defined in the ISO standard as type 1A. The testing machine was Ceast Impact Tester equipped with 2.75 J pendulum (Figure III.19). The Izod impact strength, in kilojoules per square meter (KJ/m^2), is calculated using the following formula (III.1),

$$\text{Izod Impact Strength} = \frac{Ak}{(X \times Yk) \times 103} \qquad \text{(III.1)}$$

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


Figure III.19 Ceast impact tester.

III.3. EXPERIMENTAL TECHNIQUES

III.3.1. Synthesis of Nano-Sized Zinc Borate

Nano-sized zinc borate powders with the formulas of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$ were prepared by a wet chemical method using $Zn(NO_3)_2.6H_2O$ and $Na_2B_4O_7.5H_2O$ as raw material in aqueous solution, and oleic acid as the modifying agent. 1000 ml three-neck round-bottomed glass reactor equipped with a thermometer, reflux condenser, and mechanical stirrer was charged with 120.0 mL of 0.2 mol dm^{-3} $Na_2B_4O_7.5H_2O$ aqueous solution heated at 70°C and 80.0 mL of 0.2 mol dm^{-3} $Zn(NO_3)_2.6H_2O$ aqueous solution. Certain amount of oleic acid (OA) was added dropwise into the existing solution while being stirred for a period of about 0.5 h. After addition was complete, the mixture was continuously mixed at 70 °C with mixing rate of 250 rpm for 4 h. The final mixture was then filtered, washed repeatedly with distilled hot water to remove unreacted residues and by-products, and dried in the drying oven at 70 °C to obtain the white zinc borate powders. Flow chart for the zinc borate production is given in Figure III.20.

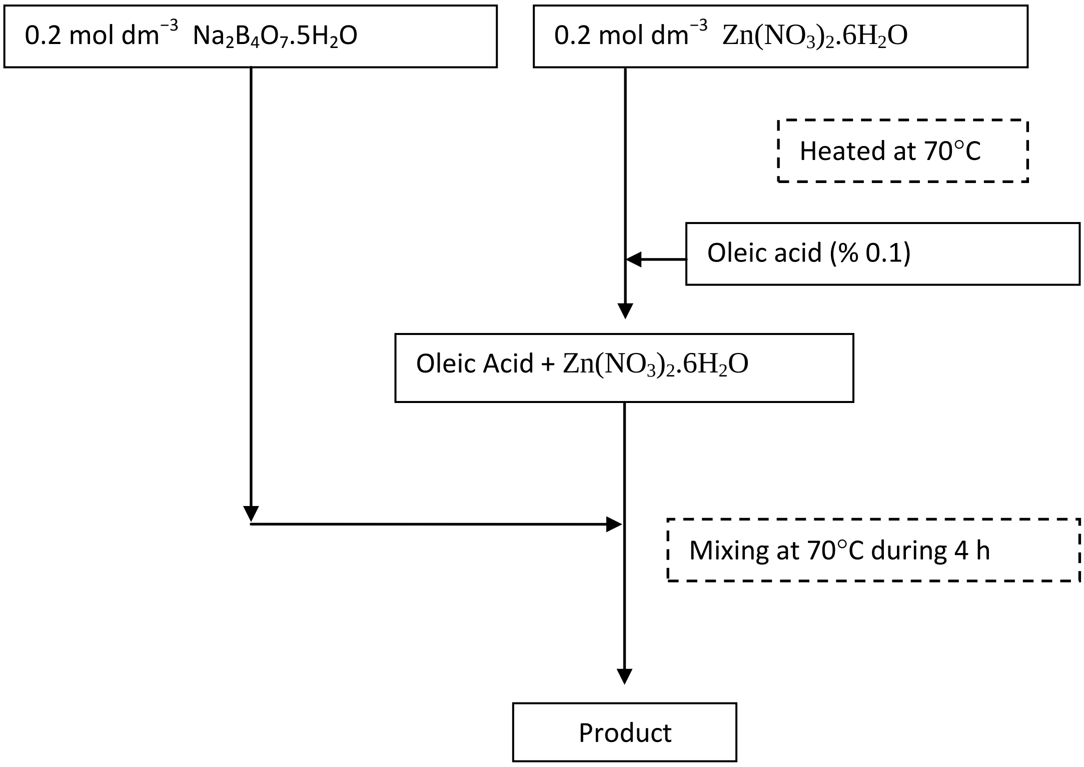


Figure III.20 Flow chart for the production of nano-sized zinc borate powders.

III.3.2. Preparation of Zinc Borate-Polymer Nano Composites

The synthesized powders were blended with EVA and HDPE at different ratios (1-3-5 wt.%) by twin screw extruder and then by injection machine in order to investigate the effect of zinc borate on various properties of composite, mainly flame retardancy and mechanical properties. Compounds for injection molding were prepared by melt blending the materials using an intermeshing co-rotating twin screw extruder. The modular twin screw extruder was PRISM TSE 24 HC with 24 mm screw diameter (D) and 28:1 L/D ratio (shaft length over screw diameter). The operating rate was 100 rpm for both EVA and HDPE and discharged temparature was 145 °C and 160 °C, respectively for EVA and HDPE. Melted compounds were allowed to cool to room temperature and palletized using granulated grinder. The granulates were then injection molded at 165 °C using an Arburg Allrounder 320C fully hydraulic plastic injection machine equipped with a standard ISO mold for tensile and Izod impact test specimens. EVA - zinc borate and HDPE – zinc borate are given respectively in Table III.4 and Table III.5. In the designation of the compositions the capital letters N stand for nano-sized zinc borate powder, the capital letters C stand for commercial micron-sized zinc borate powders (Melos, MA013-ÇB), respectively, and the numbers following the capital letters refer to their amounts in wt %.

Table III.4 Designed EVA-zinc borate composite material compositions.

Composition	**EVA (wt.%)**	**Nano-sized ZB (wt.%)**	**Micron-sized ZB (wt.%)**
NEVA-1 (1 %)	99	1	-
NEVA-3 (3 %)	97	3	-
NEVA-5 (5 %)	95	5	-
CEVA-1 (1 %)	99	-	1
CEVA-3 (3 %)	97	-	3
CEVA-5 (5 %)	95	-	5

Table III.5 Designed HDPE-zinc borate composite material compositions.

Composition	**HDPE (wt.%)**	**Nano-sized ZB (wt.%)**	**Micron-sized ZB (wt.%)**
NPE-1 (1 %)	99	1	-
NPE-3 (3 %)	97	3	-
NPE-5 (5 %)	95	5	-
CPE-1 (1 %)	99	-	1
CPE-3 (3 %)	97	-	3
CPE-5 (5 %)	95	-	5

CHAPTER IV

RESULTS AND DISCUSSION

IV.1. CHARACTERIZATION OF SYNTHESIZED ZINC BORATE POWDERS

IV.1.1. Crystal Structure Analyses

XRD pattern of the synthesized powders revealed that they were crystalline (Figure IV.1). Although XRD peaks did not match with any of the zinc borate in the JCPDS Cards, they were in good agreement with the data in the literature. [38] All diffraction peaks were in good agreement with the data in the literature given in Figure IV.2.

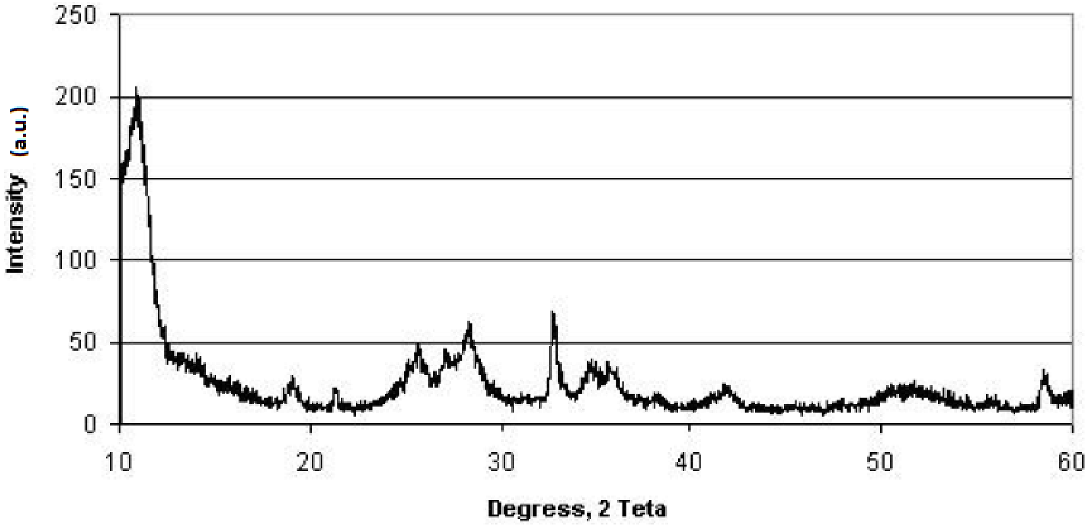


Figure IV.1 XRD of synthesized zinc borate ($2ZnO.3B_2O_3.3\text{-}3.5H_2O$) nano powder.

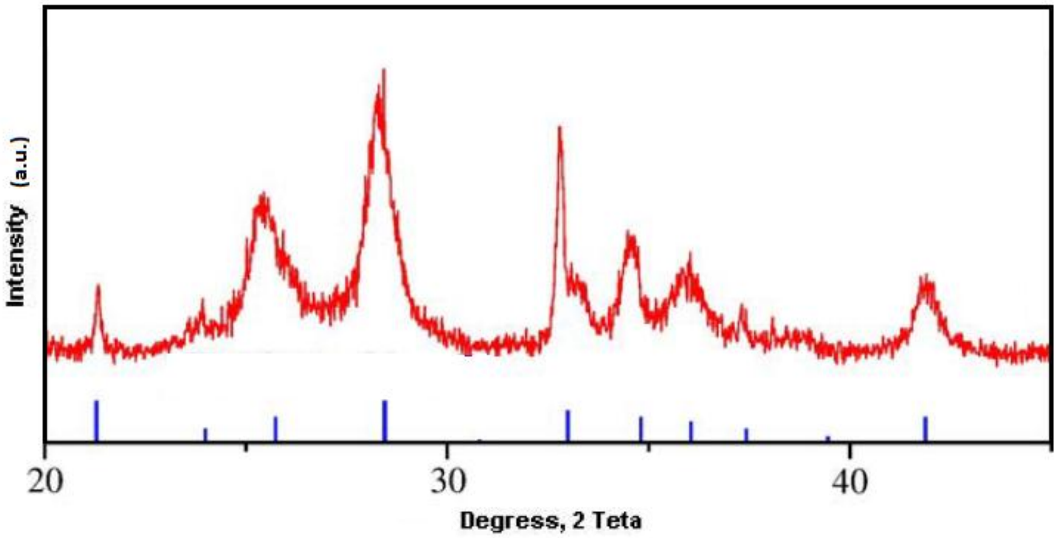


Figure IV.2 XRD of zinc borate nano powder produced by Tian [38].

IV.1.2. Thermogravimetric Analyses

TGA instrument which is a good way in studying dehydration of water in the zinc borate was carried out to have an idea about the thermal behaviour of the zinc borate powders.

A DTA-TG curve of synthesized nano-sized zinc borate is given in Figure IV.3. Low weight loss until 110 °C (~ 3%) was due to the physical water on the zinc borate powders. Then, zinc borate powders started to lose its crystal water at 110ºC and the loss continued until 450ºC with a total mass loss of 12.95% between 110-450ºC. The results were in agreement with theoretical values of zinc borate with chemical composition of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$. (weight loss of zinc borate which has 3 mole water is 12.7% and the weight loss of zinc borate which has a 3.5 mole water is 14.5%) TG results showed that synthesized zinc borate had a 3-3.5 molecular crystal water.

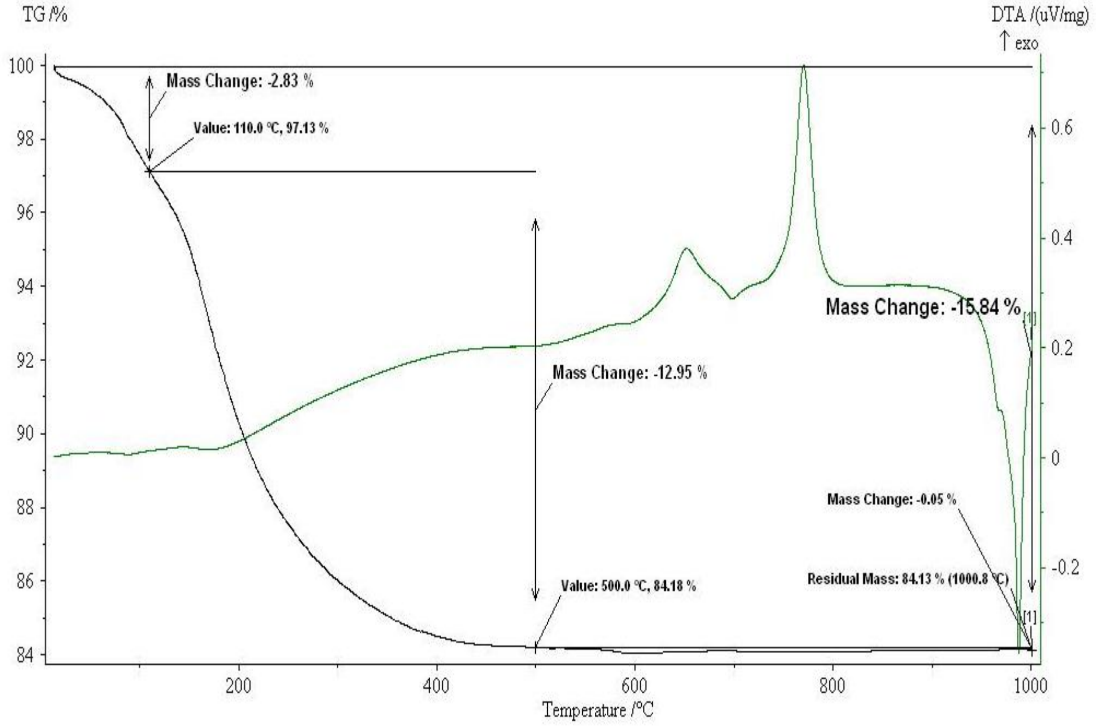


Figure IV.3 DTA-TG curves of synthesized zinc borate powders.

Produced nano-sized zinc borate powders have lower dehydration temperature than micron-sized zinc borate. [50] This result could be explained as nano-sized powders have different physical and chemical properties than micron-sized powders due to smaller particle size and large surface area. [51] For example, nano-sized particles have lower melting temperature than micron-sized particles.

IV.1.3. Molecular Analysis

FT-IR spectra of nano zinc borate powder which is given in Figure IV.4 were identical with the literature. [5, 38] While the band at 3458 cm^{-1} was the stretching of O–H, the band at 1634 cm^{-1} was assigned to the H–O–H bending mode, which indicates that the compound contains the crystal water. T he band at 1382 cm^{-1} could be the asymmetric stretching of B(3)–O and the bands at 1100 and 788 cm^{-1} were assigned as the asymmetric and symmetric stretching of B(4)–O, respectively. The band at 608 cm^{-1} was due to the symmetric pulse vibration of triborate anion indicating that the sample contains the $[B_3O_4(OH)_3]^{2-}$.

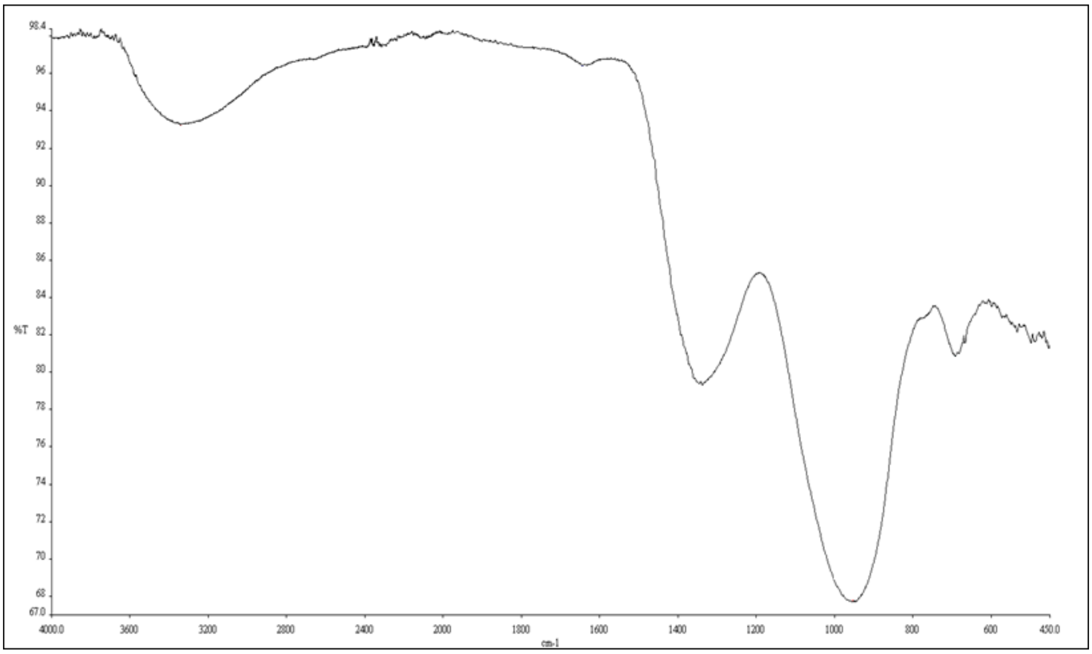


Figure IV.4 FT-IR spectra of nano-sized zinc borate powder.

IV.1.4. Particle Size Measurement

Particle size measurement of synthesized zinc borate powders was carried out by Zetasizer. Particle size measurement results gave a mean particle size of around 68 nm which was in a good agreement with TEM results. Particle size distribution of zinc borate powders are given in Figure IV.5.

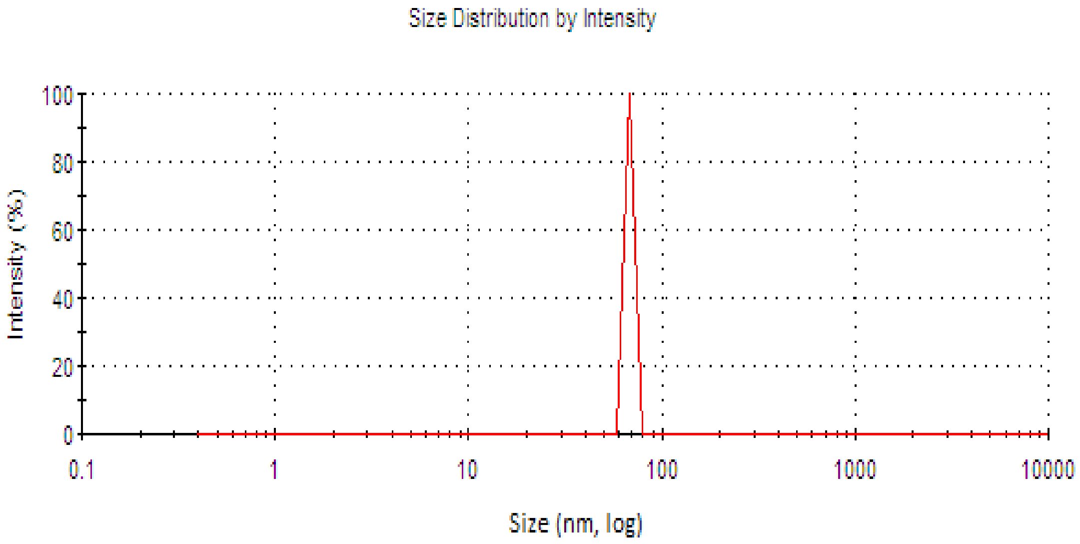


Figure IV.5 Particle size distribution of synthesized zinc borate powders.

IV.1.5. Morphology Investigation

The shape, size of zinc borate particles and their agglomeration were investigated using TEM. Micrographs of powders are given in Figure IV.6. These micrographs indicated that the particle sizes were below 100 nm and nearly spherical in shape, although some degree of agglomeration was also detected due to large surface area.

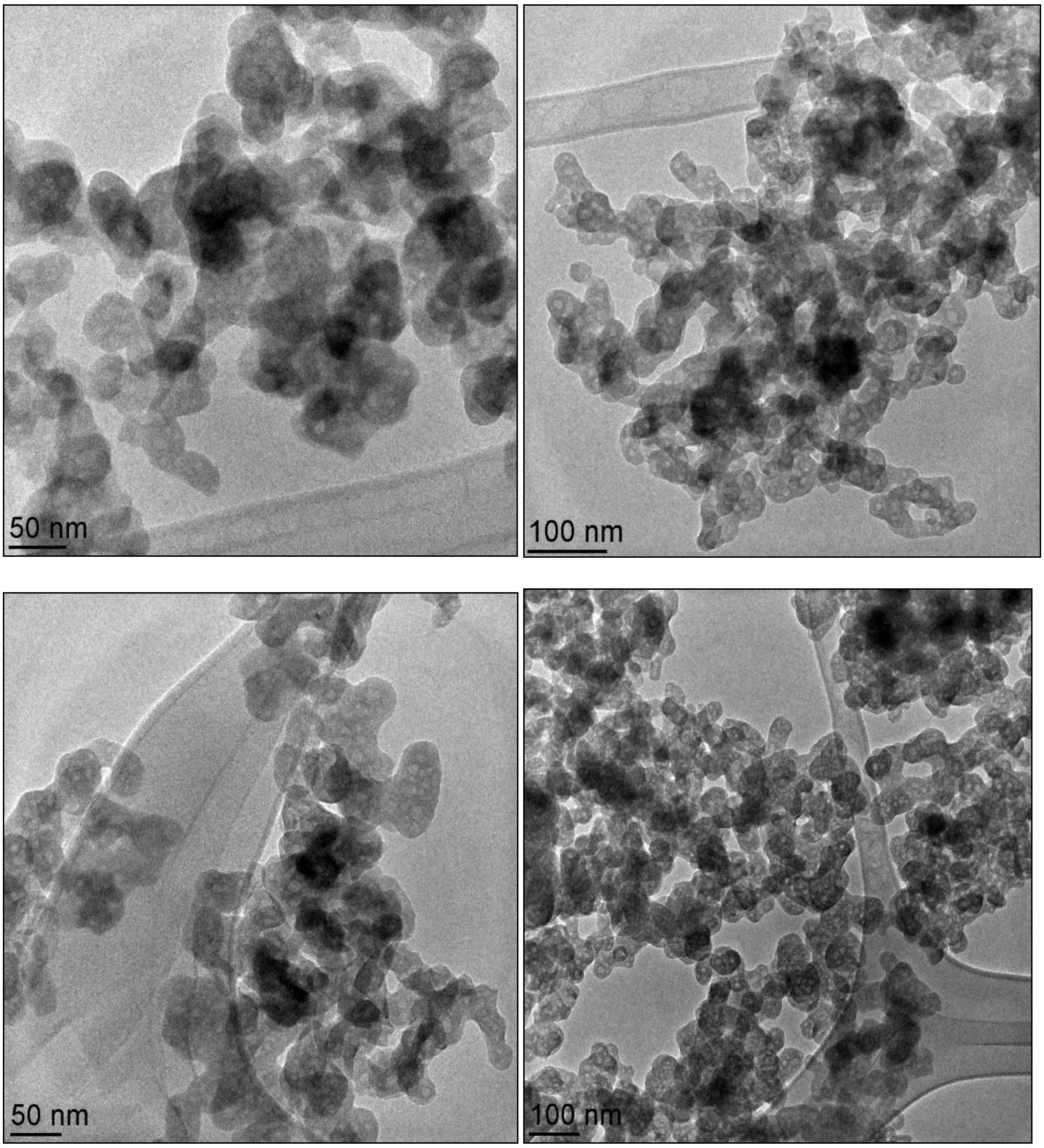


Figure IV.6 TEM micrographs of produced zinc borate powders.

IV.2. CHARACTERIZATION OF ZINC BORATE – POLYMER COMPOSITES

IV.2.1. Thermal Analyses

DSC instrument was used to identify flame retardancy level of nano-sized zinc borate - EVA composite materials. Micron-sized (commercial) zinc borate – EVA composite materials were also analysed to compare the flame retardancy level and mechanical properties with nano-sized composite'. OIT test results of the nano-sized zinc borate – EVA composites are given in Figure IV.7 while OIT results of micron-sized zinc borate – EVA composites is given in Figure IV.8. These results are well agreed well with the LOI test results and demonstrated that the oxidation time of nano-sized zinc borate – EVA composite was lower than virgin EVA. Also, when the amount of zinc borate powder increased, oxidation time decreased. This result indicated that the nano-sized zinc borate powder improved the flame retadancy of the EVA. Moreover, nano-sized zinc borate addition supplied more flame retardant effect than micron-sized zinc borate addition.

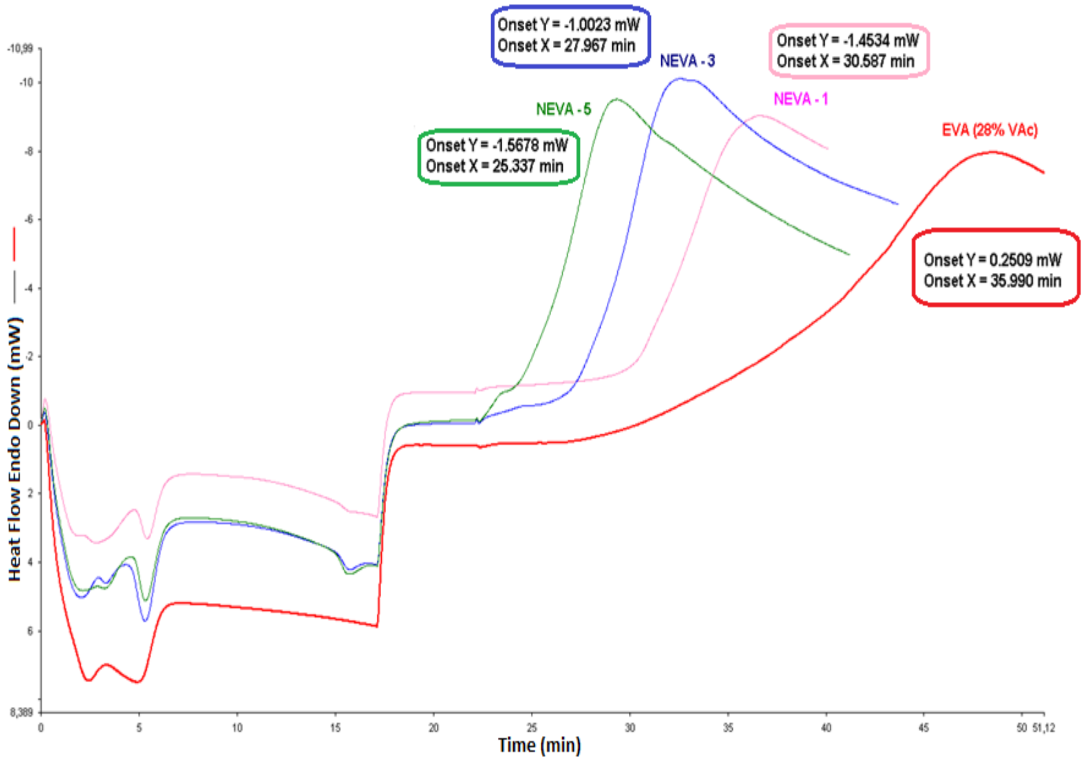


Figure IV.7 OIT test of produced nano-sized zinc borate–EVA composites.

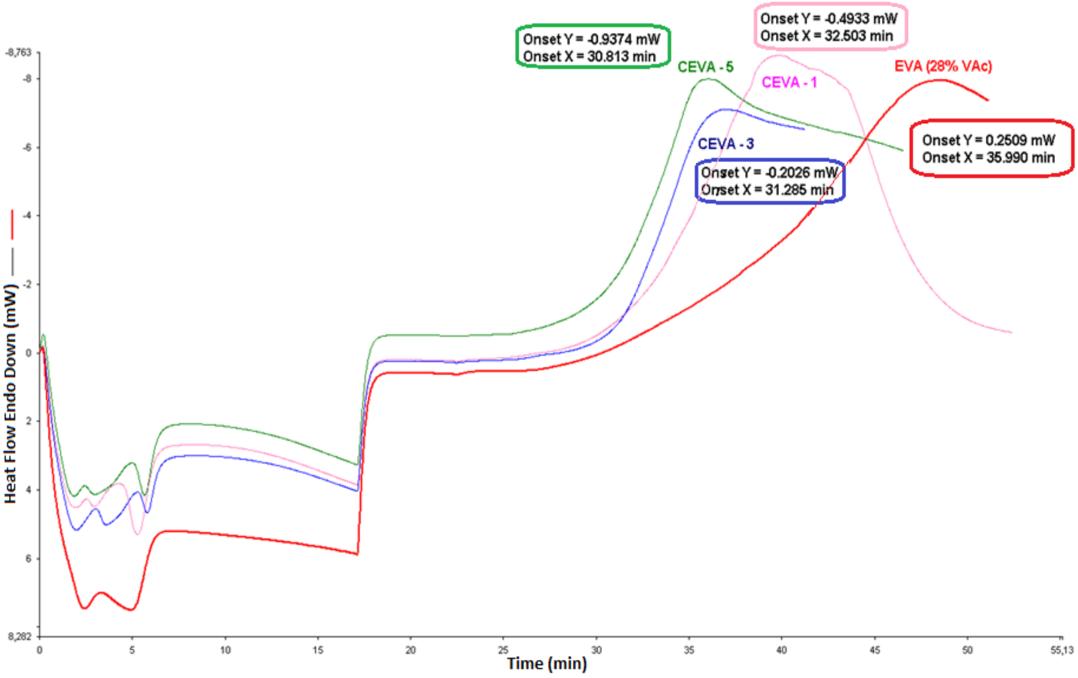


Figure IV.8 OIT test of produced micron-sized zinc borate–EVA composites.

IV.2.2. Microstructural Investigation

Microstructural investigation of zinc borate - EVA and zinc borate - HDPE composite materials were carried out by SEM. In addition, micron-sized zinc borate filled EVA and micron-sized zinc borate filled HDPE composite materials were analysed by SEM to compare with nano-sized composites.

SEM images demonstrated that micron-sized zinc borate powders were homogeneously distributed in EVA matrix. However, in the SEM it was very difficult to observe the zinc borate particles due to their fine sizes. Therefore, it was difficult to decide about distribution of nano zinc borate particles within EVA. SEM micrograph of NEVA-1, NEVA-3, NEVA-5 are given in Figure IV.9, IV.10, and IV.11, respectively. In addition, SEM micrographs of CEVA-1, CEVA-3, CEVA-5 are given in Figure IV.12, IV.13, and IV.14, respectively.

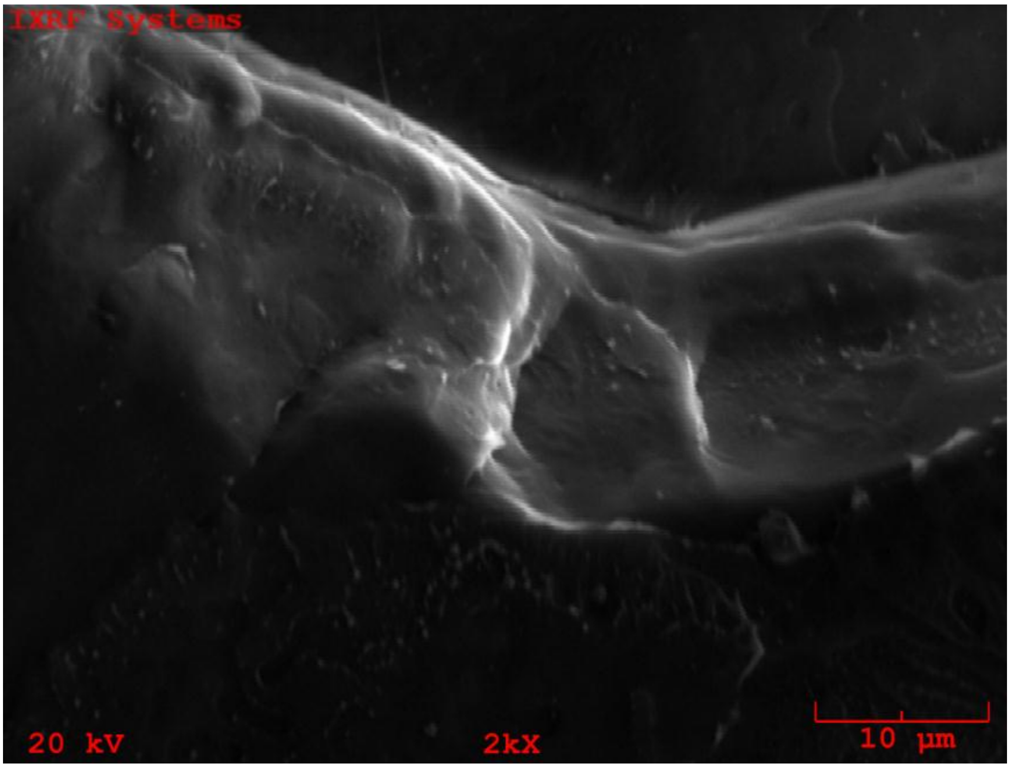


Figure IV.9 SEM micrograph of NEVA-1.

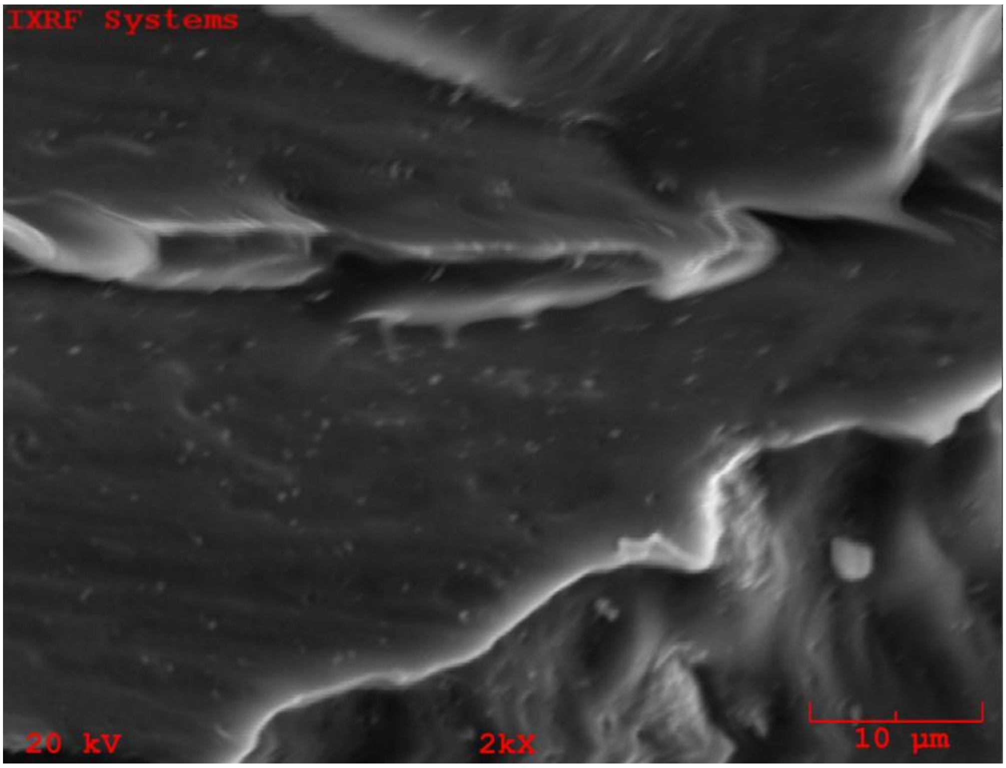


Figure IV.10 SEM micrograph of NEVA-3.

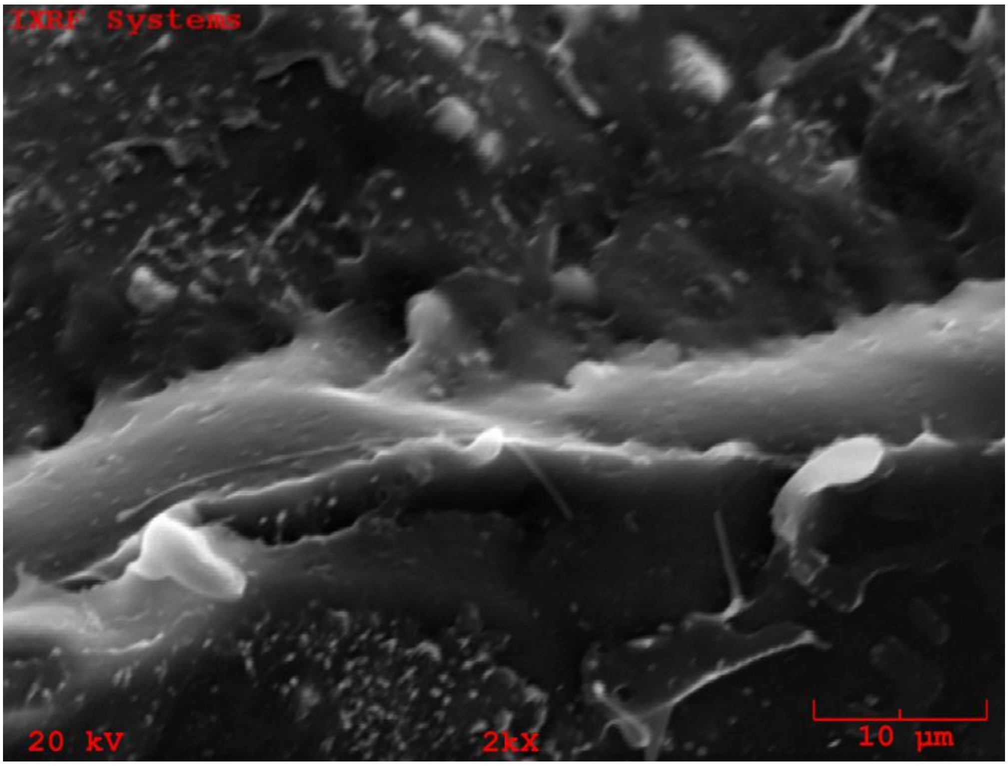


Figure IV.11 SEM micrograph of NEVA-5.

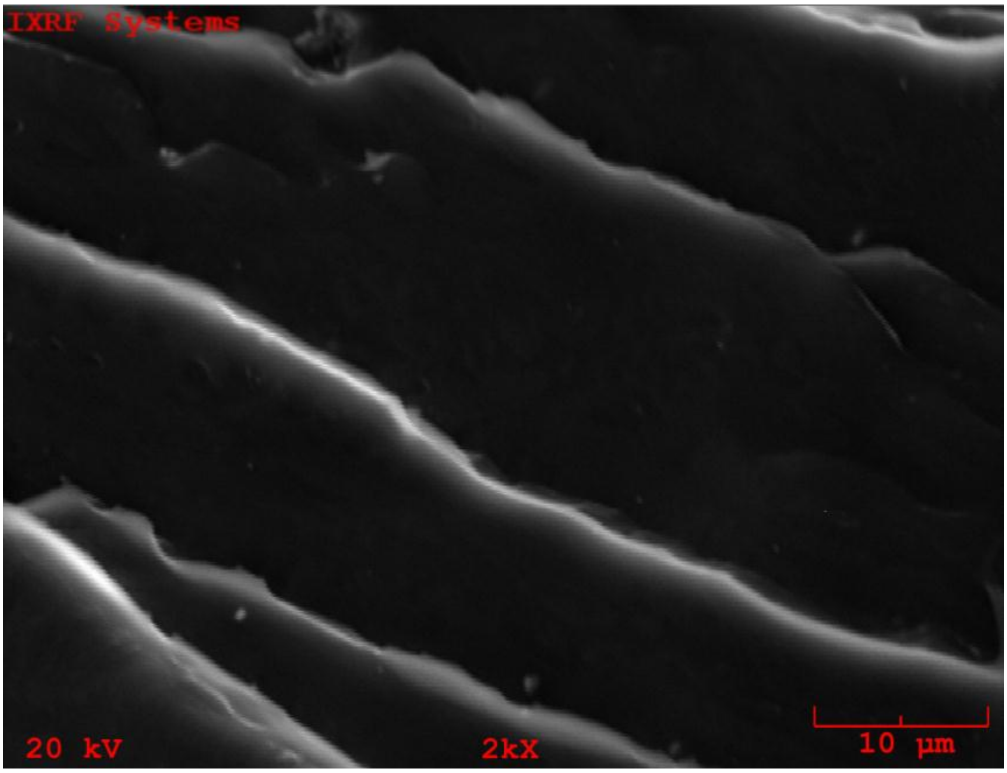


Figure IV.12 SEM micrograph of CEVA-1.

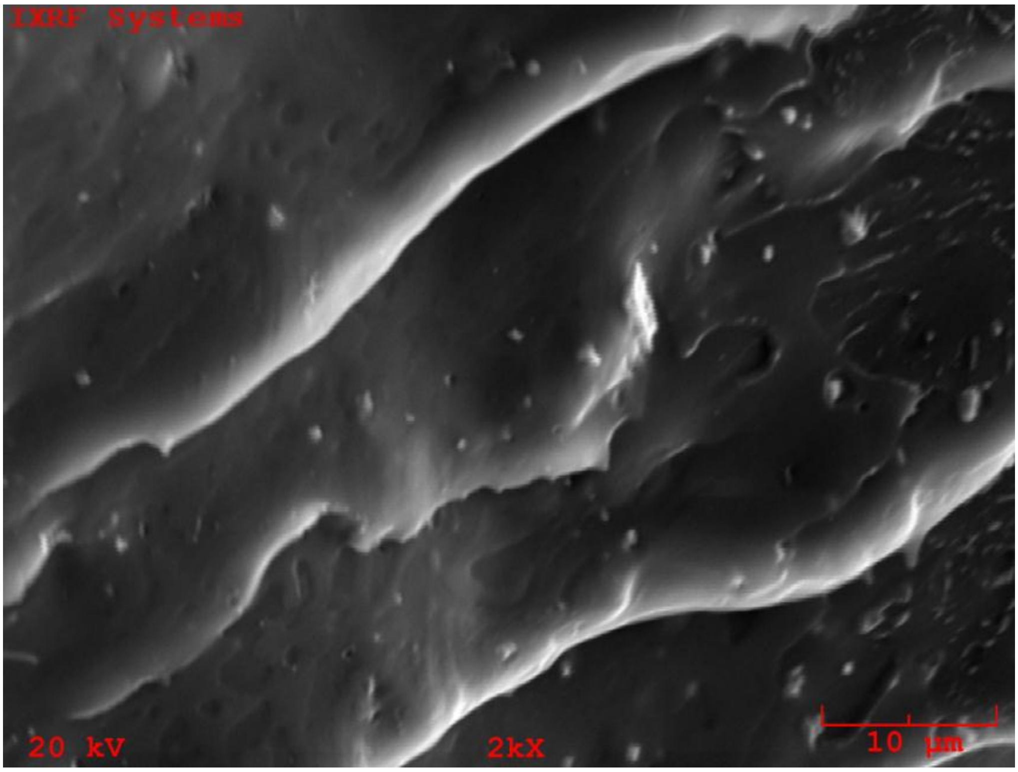


Figure IV.13 SEM micrograph of CEVA-3.

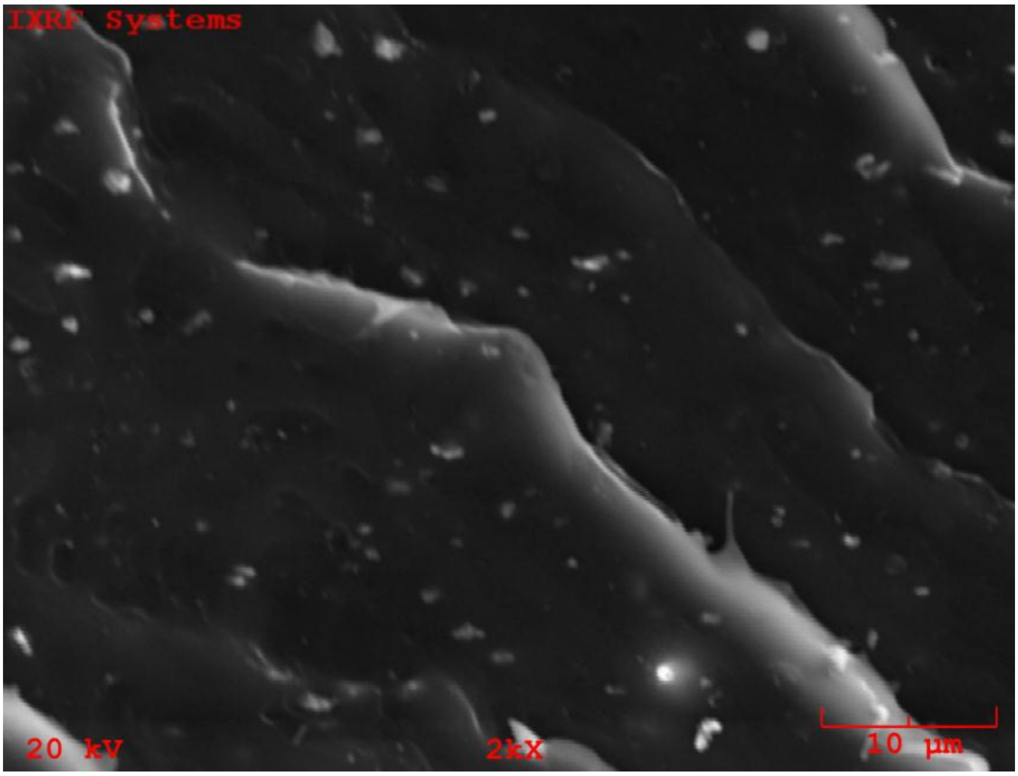


Figure IV.14 SEM micrograph of CEVA-5.

SEM images of zinc borate – HDPE demonstrated that micron-sized zinc borate powders were homogeneously distributed in HDPE matrix but nano-sized zinc borate distribution could not be investigated clearly due to nano sizes. SEM micrograph of NPE-1, NPE-3, and NPE-5 are given in Figure IV.15, IV.16, and IV.17, respectively. In addition, SEM micrograph of CPE-1, CPE-3, and CPE-5 are given in Figure IV.18, IV.19, and IV.20, respectively.

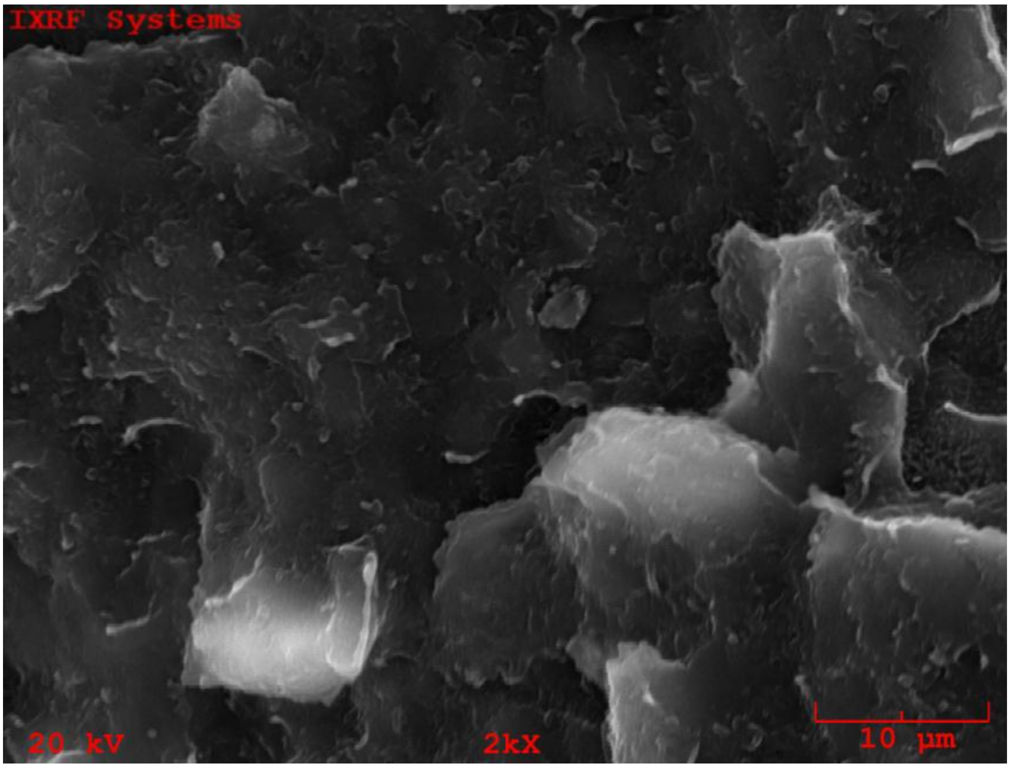


Figure IV.15 SEM micrograph of NPE-1.

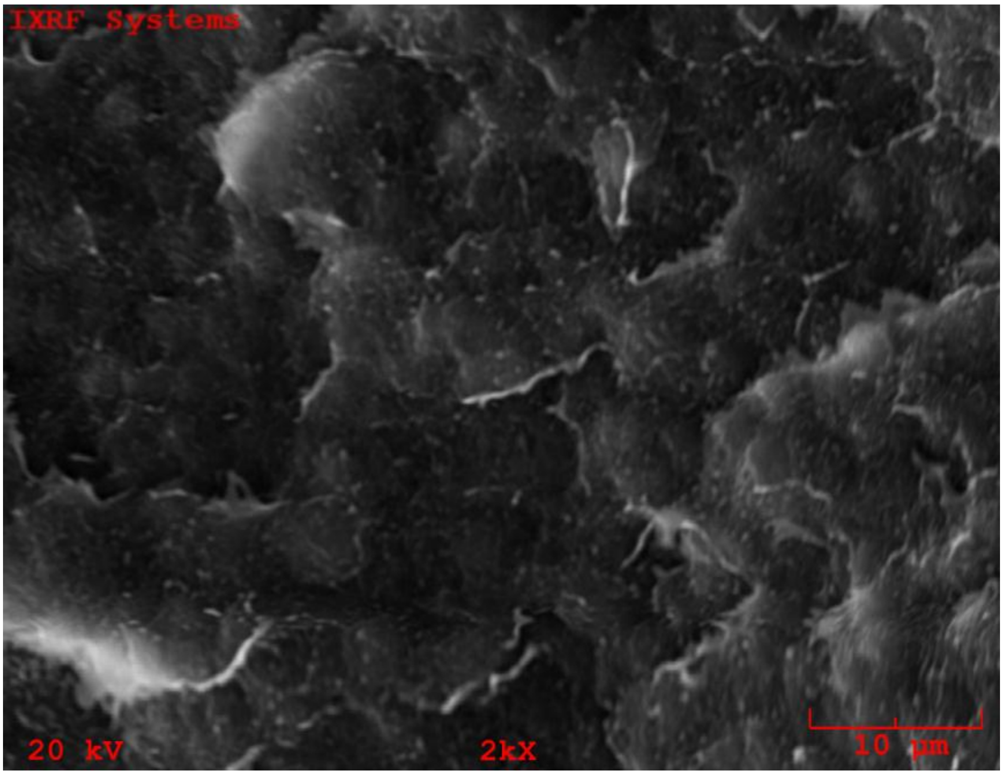


Figure IV.16 SEM micrograph of NPE-3.

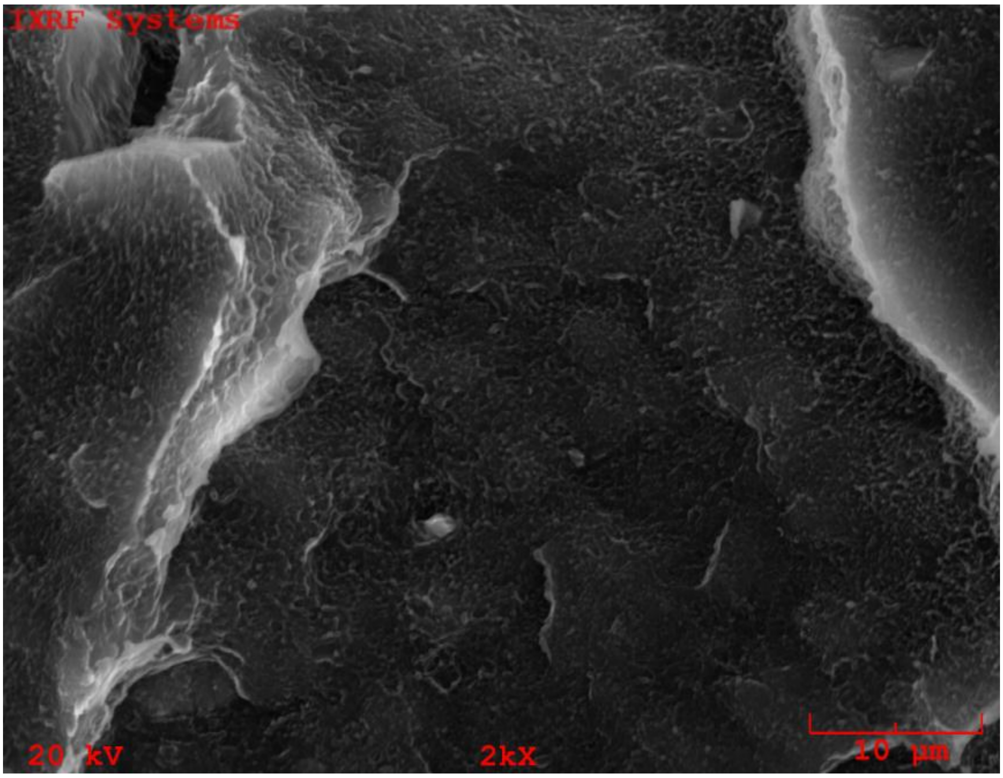


Figure IV.17 SEM micrograph of NPE-5.

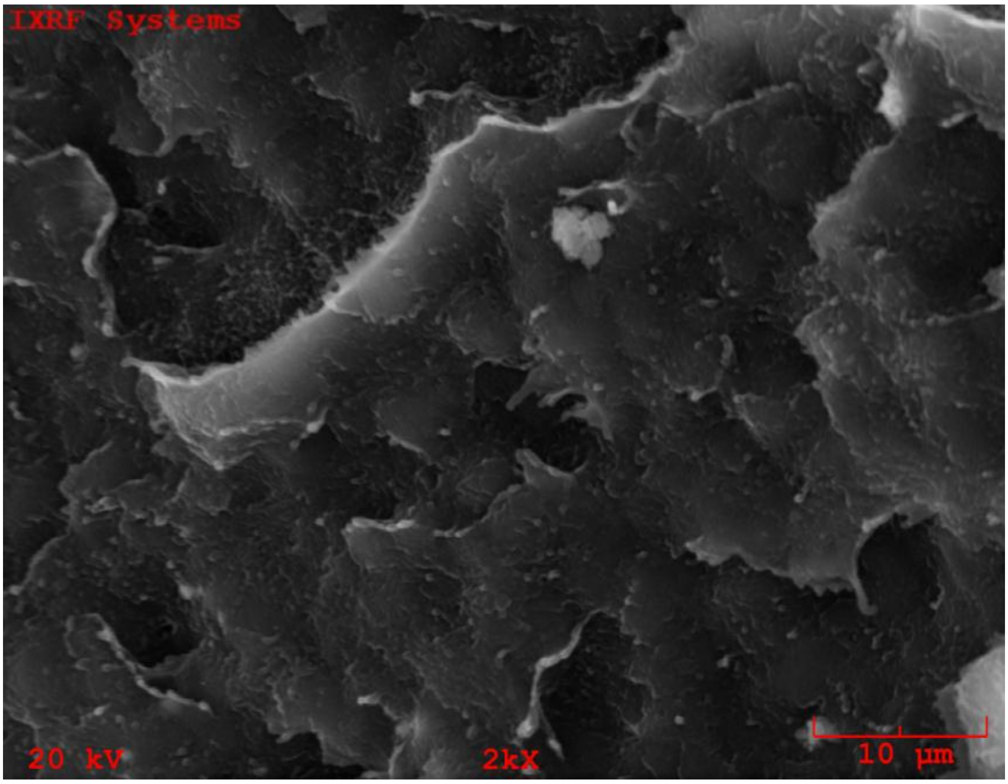


Figure IV.18 SEM micrograph of CPE-1.

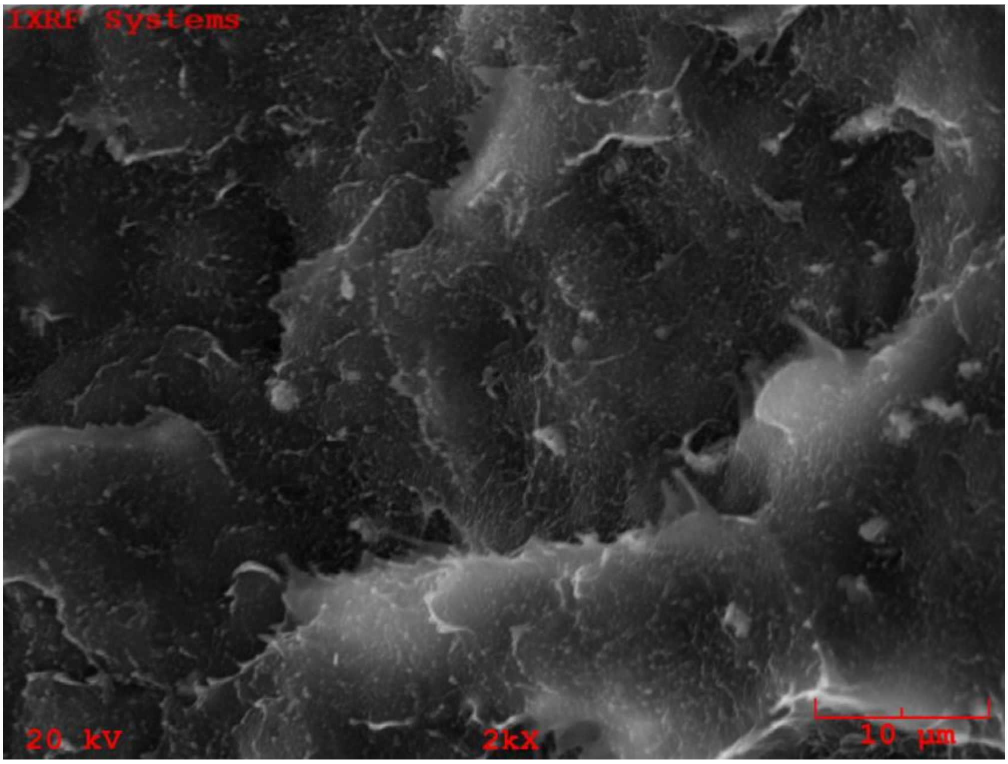


Figure IV.19 SEM micrograph of CPE-3.

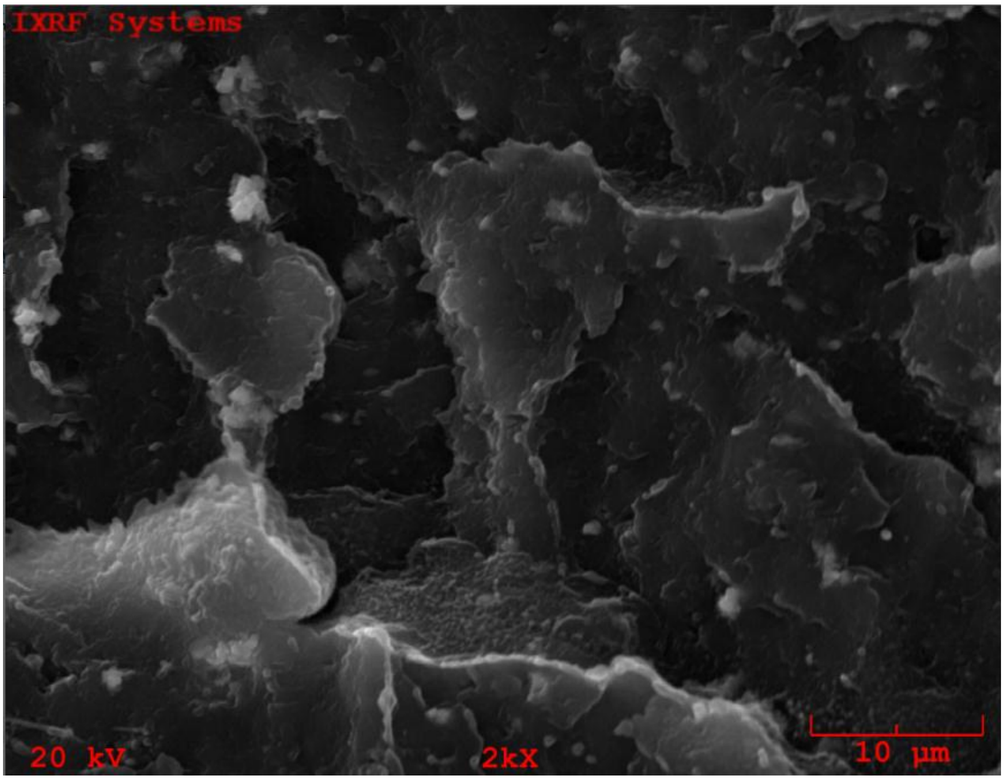


Figure IV.20 SEM micrograph of CPE-5.

IV.2.3. Flame Retardant Properties

Flame retardant properties of zinc borate – EVA and zinc borate – HDPE composites were investigated by LOI test method. While the LOI test results for zinc borate added EVA composites is given in Table IV.1 and Figure IV.21, LOI test results for zinc borate added HDPE composites is given in Table IV.2 and Figure IV.22. These results showed that LOI values of the composites increased with increasing zinc borate content. The main reason for such an increase is possibly due to two reasons:

1) Crystal water content of zinc borate which was released during firing,

2) B_2O_3 content of zinc borate that formed a strong protective layer against oxygen.

Consequently, as the zinc borate content increased the flammability of composites decreased or LOI value increased. In addition, flame retardation effect of nano-sized zinc borate powders was larger than the micron sized powders, although, the differences between LOI values were not significant.

Table IV.1 LOI test results of zinc borate–EVA composites.

Sample	LOI (%)
NEVA - 1	22.8
NEVA - 3	23.1
NEVA - 5	23.9
CEVA - 1	22.6
CEVA - 3	22.9
CEVA - 5	23.7
Virgin EVA	20.8

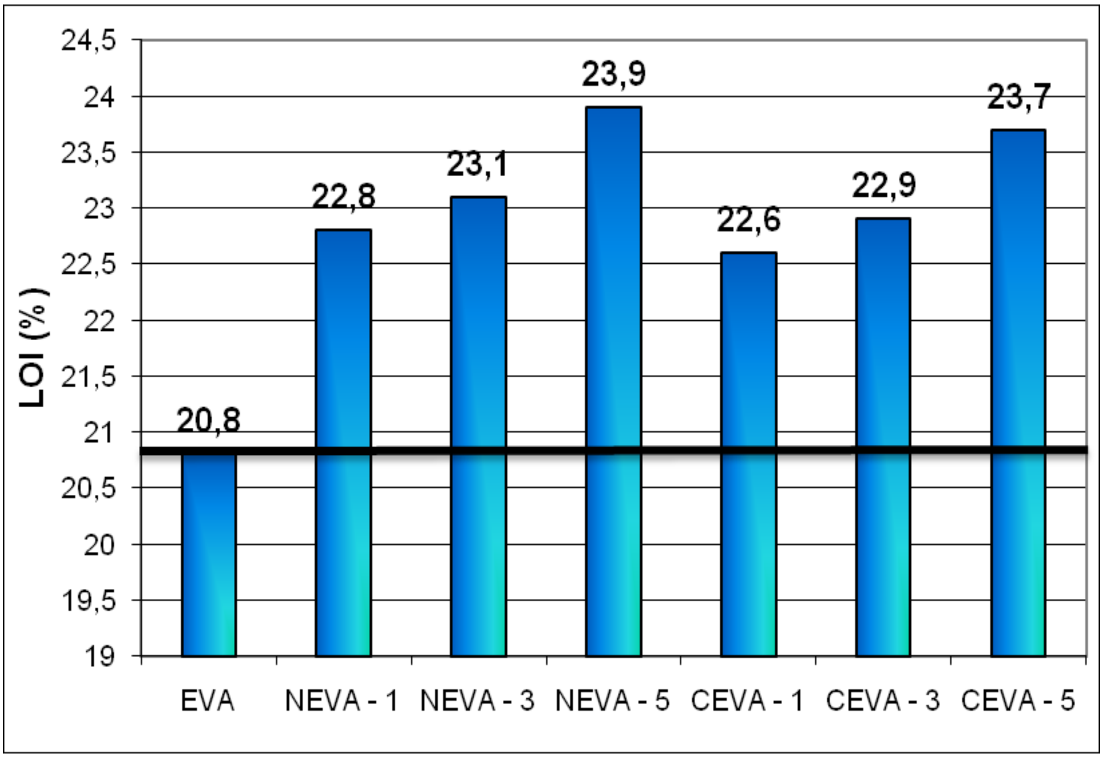


Figure IV.21 LOI test of produced zinc borate–EVA composites.

Table IV.2 LOI test results of zinc borate–HDPE composites.

Sample	LOI (%)
NPE - 1	21.3
NPE - 3	21.7
NPE - 5	22.2
CPE - 1	21.1
CPE - 3	21.8
CPE - 5	22.4
Virgin HDPE	19.6

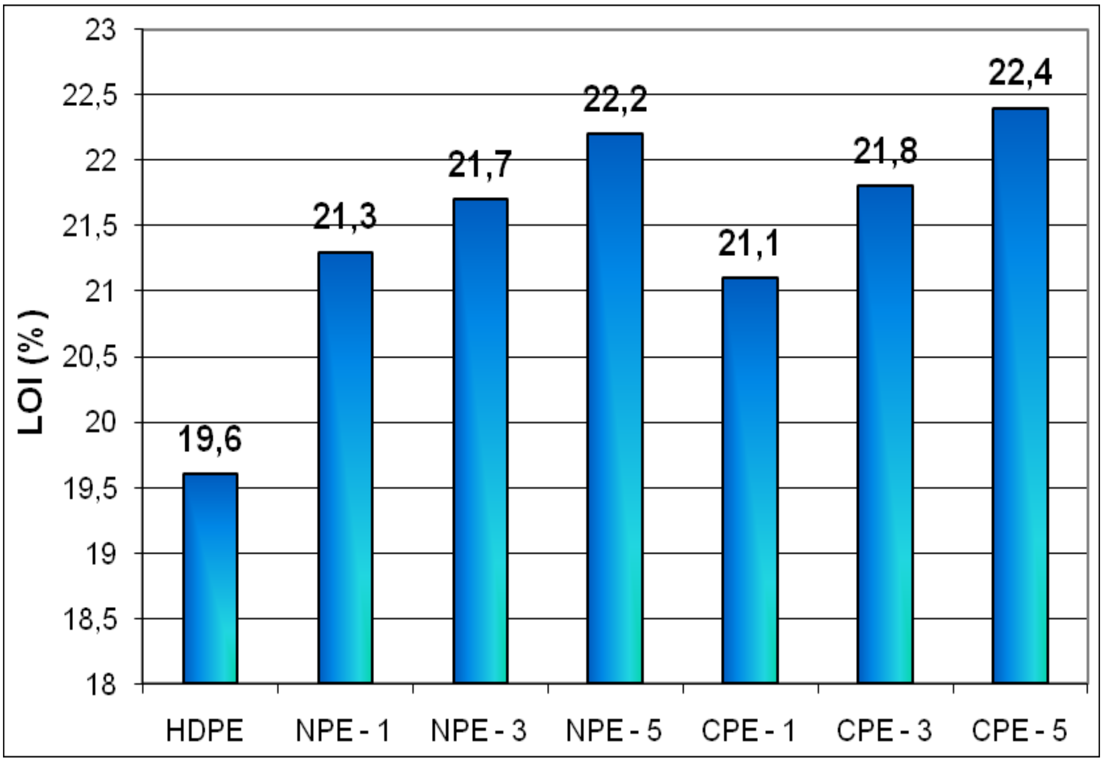


Figure IV.22 LOI test of produced zinc borate–HDPE composites.

IV.2.4. Mechanical Properties

Mechanical properties of composites were determined by mechanical testing methods.

IV.2.4.1 Tensile Properties

The effects of nano-sized zinc borate addition on mechanical properties of EVA and HDPE composites were compared with micron-sized zinc borate-EVA, micron-sized zinc borate-HDPE, virgin EVA and virgin HDPE.

Tensile strength results of zinc borate added EVA and HDPE composites are given in Table IV.3, Table IV.4 and Figure IV.23, Figure IV.24. The increase in the amount of filler, in all cases, has caused a decrease in composites' tensile strength. Furthermore, while the tensile strength of nano-sized zinc borate filled EVA composites' way higher than micron-sized zinc borate filled composites; the tensile strength of nano-sized zinc borate filled HDPE composites' was similar to micron-sized zinc borate filled composites.

Table IV.3 Tensile strength of zinc borate–EVA composites.

Sample	**Tensile Strength (N/mm^2)**
NEVA - 1	7.13
NEVA - 3	7.47
NEVA - 5	7.01
CEVA - 1	6.28
CEVA - 3	6.35
CEVA - 5	6.34
Virgin EVA	8.35

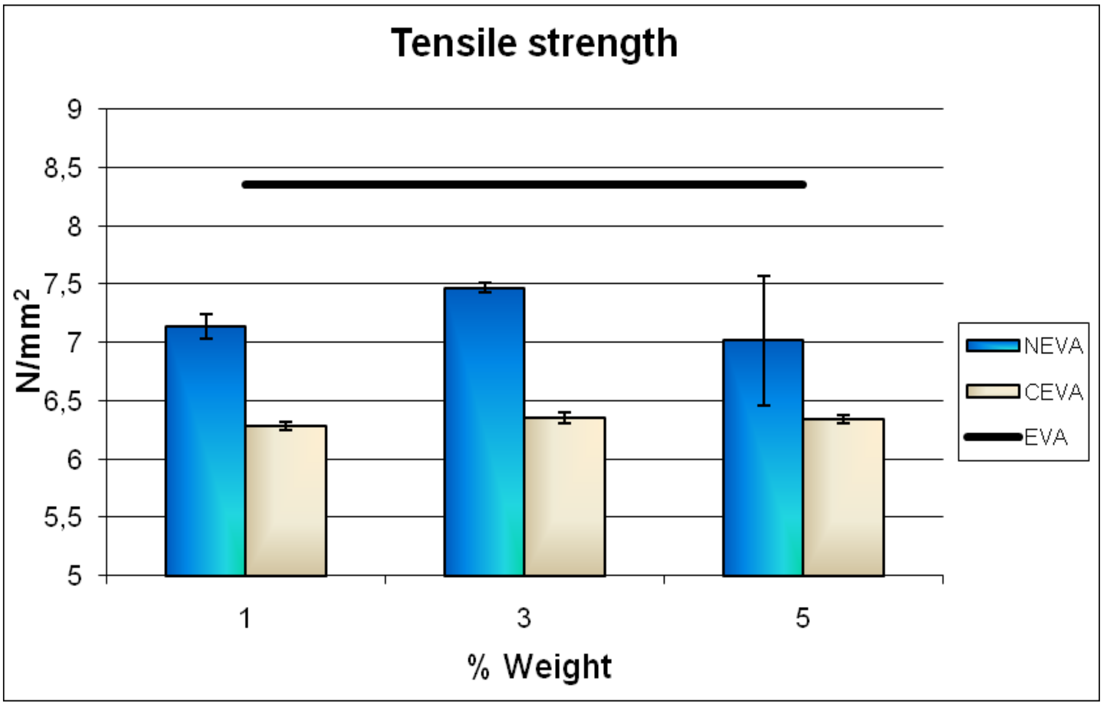


Figure IV.23 Tensile strength of zinc borate–EVA composites.

Table IV.4 Tensile strength of zinc borate–HDPE composites.

Sample	**Tensile Strength (N/mm^2)**
NPE - 1	27.44
NPE - 3	27.45
NPE - 5	27.40
CPE - 1	27.86
CPE - 3	27.83
CPE - 5	28.08
Virgin HDPE	26.97

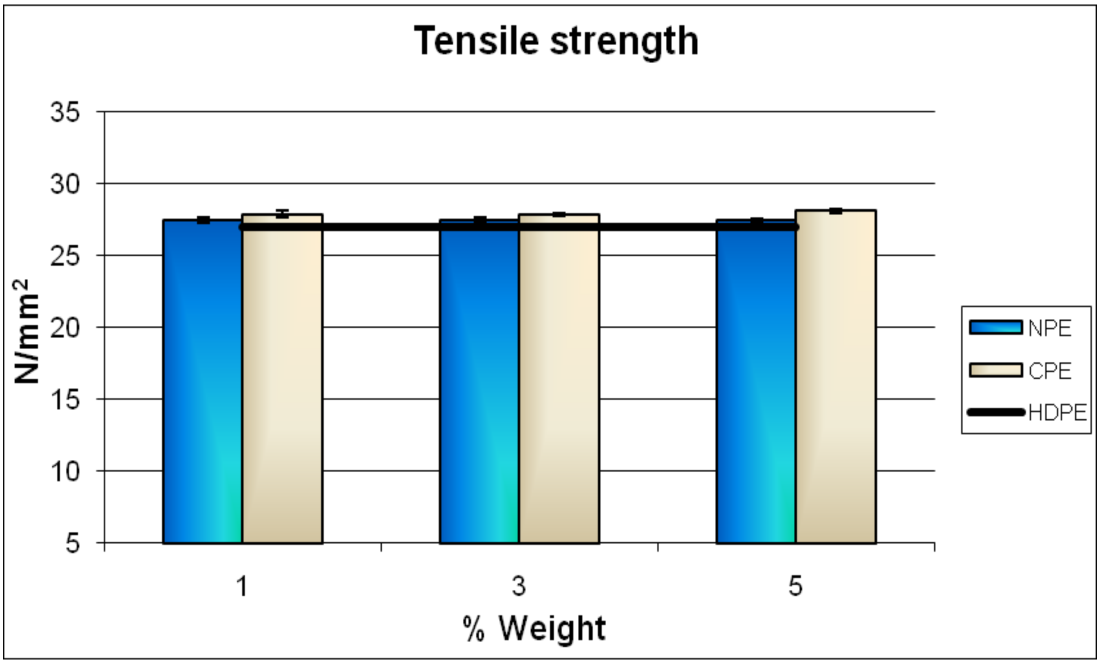


Figure IV.24 Tensile strength of zinc borate–HDPE composites.

Fracture strength of zinc borate added EVA composites and zinc borate edded HDPE composites are given in Table IV.5 and IV.6 and Figure IV.25 and IV.26, respectively. These results indicated that both nano and micron sized zinc borate addition caused a decrease in fracture strength in EVA. But the effect of micron sized zinc borate addition was more significant that nano sized. However, addition of micron and nano sized zinc borate into HDPE gave identical results in fracture strength.

Table IV.5 Fracture strength of zinc borate–EVA composites.

Sample	**Fracture Strength (N/mm^2)**
NEVA - 1	6.98
NEVA - 3	7.26
NEVA - 5	6.87
CEVA - 1	6.18
CEVA - 3	6.17
CEVA - 5	6.19
Virgin EVA	8.15

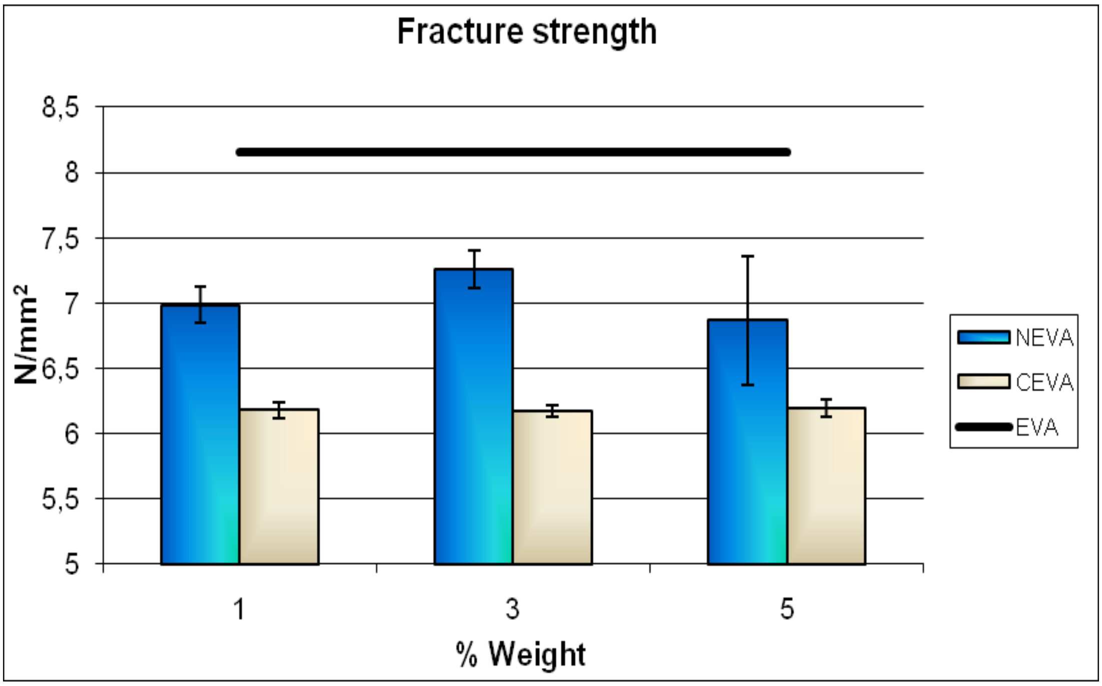


Figure IV.25 Fracture strength of zinc borate–EVA composites.

Table IV.6 Fracture strength of zinc borate–HDPE composites.

Sample	**Fracture Strength (N/mm^2)**
NPE - 1	5.55
NPE - 3	4.21
NPE - 5	4.12
CPE - 1	4.42
CPE - 3	4.17
CPE - 5	4.37
Virgin HDPE	4.08

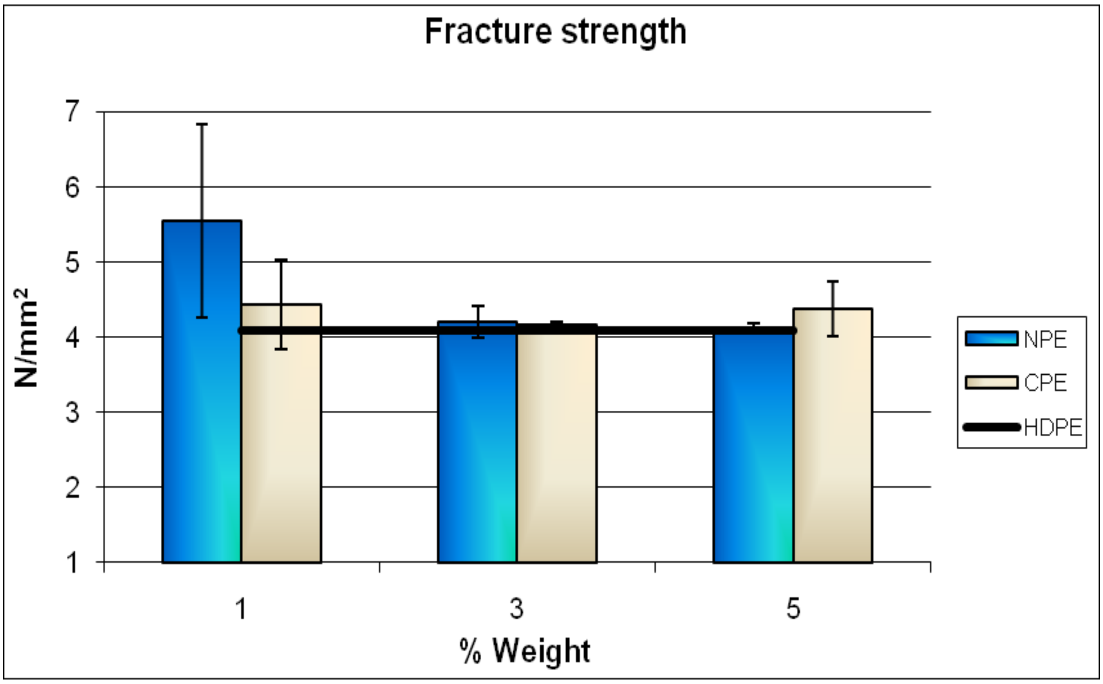


Figure IV.26 Fracture strength of zinc borate–HDPE composites.

Elastic modulus test results for zinc borate added EVA and HDPE composites are given in Table IV.7, IV.8 and Figure IV.27, IV.28, respectively. Zinc borate addition into EVA decreased the elastic modulus. But the decrease was higher in case of micron sized zinc borate. So it on be said that nano zinc borate addition had less effect on elastic modulus. Moreover, modulus of nano-sized zinc borate filled HDPE composites' was similar to micron-sized zinc borate filled composites and addition of zinc borate slightly increased the elastic modulus.

Table IV.7 Elastic modulus of zinc borate–EVA composites.

Sample	Elastic Modulus (N/mm^2)
NEVA - 1	18.59
NEVA - 3	19.59
NEVA - 5	18.78
CEVA - 1	15.80
CEVA - 3	15.40
CEVA - 5	16.11
Virgin EVA	21.74

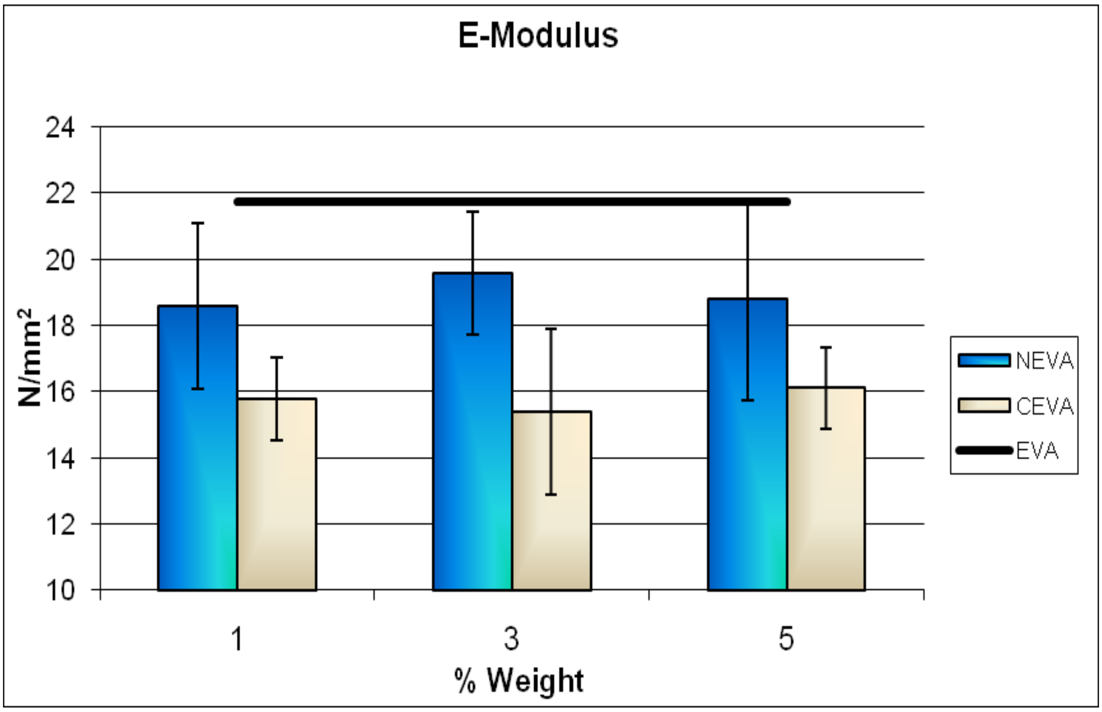


Figure IV.27 Elastic modulus of zinc borate–EVA composites.

Table IV.8 Elastic modulus of zinc borate–HDPE composites.

Sample	**Elastic Modulus (N/mm^2)**
NPE - 1	1595.74
NPE - 3	1610.39
NPE - 5	1621.12
CPE - 1	1563.81
CPE - 3	1583.07
CPE - 5	1645.56
Virgin HDPE	1517.28

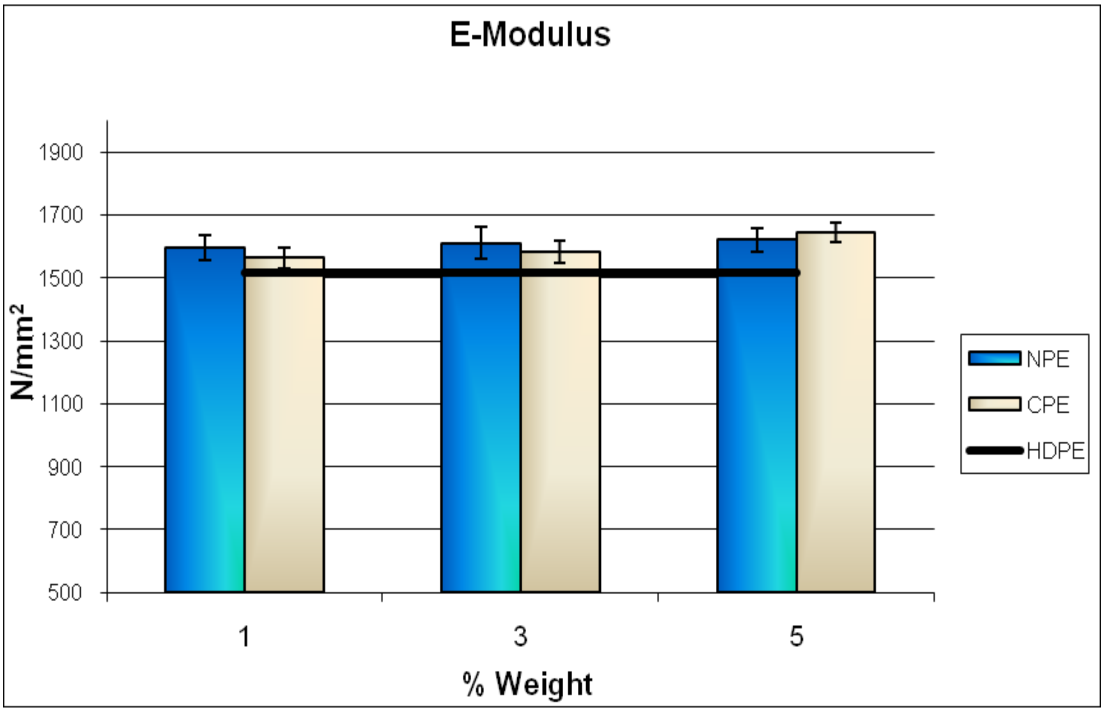


Figure IV.28 Elastic modulus of zinc borate–HDPE composites.

The elongation values at break are given in Table IV.9 and IV.10 and in Figure IV.29 and IV.30 for zinc borate added EVA and HDPE composites Elongations of composites were higher than virgin EVA's and virgin HDPE. It is also found that elongation did not change with addition of zinc borate. But micron-sized zinc borate added composites had higher elongations than nano-sized composites.

Table IV.9 Elongation at break results of zinc borate–EVA composites.

Sample	Elongation at Break (%)
NEVA - 1	471.14
NEVA - 3	456.70
NEVA - 5	476.92
CEVA - 1	485.08
CEVA - 3	477.82
CEVA - 5	480.72
Virgin EVA	440.93

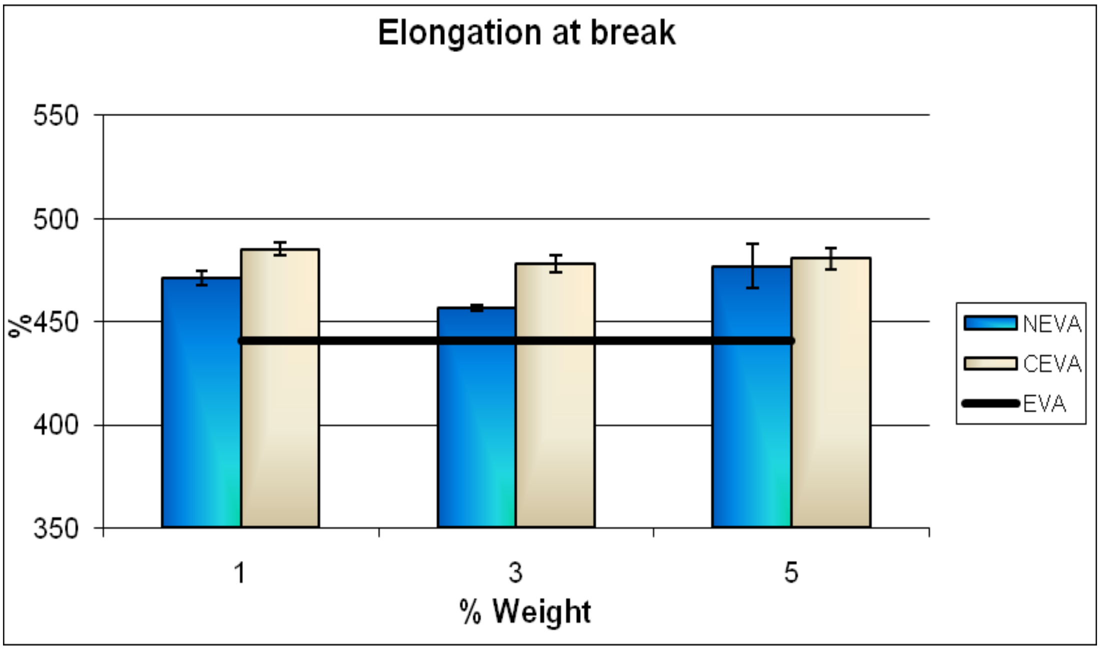


Figure IV.29 Elongation at break results of zinc borate–EVA composites.

Table IV.10 Elongation at break results of zinc borate–HDPE composites.

Sample	**Elongation at Break (%)**
NPE - 1	160.81
NPE - 3	163.25
NPE - 5	77.44
CPE - 1	178.29
CPE - 3	114.96
CPE - 5	149.77
Virgin HDPE	76.92

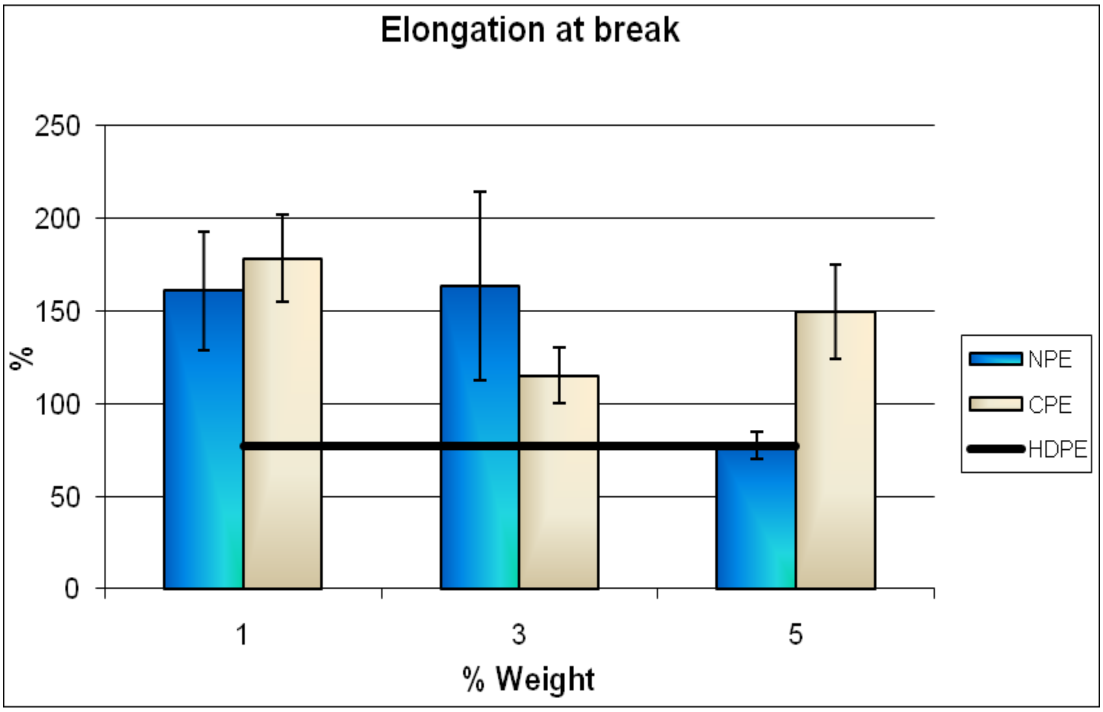


Figure IV.30 Elongation at break results of zinc borate–HDPE composites.

In conclusion, while the elastic modulus, tensile strength and fracture strength values of zinc borate filled composites were lower than the virgin EVA and HDPE, elongation at fracture was slightly higher for the zinc borate filled composites than virgin EVA and HDPE. The increases in the amount of filler from 1% to 5% did not cause a considerable change in mechanical properties. However, micron-sized zinc borate filled EVA composites had significantly lower elastic modulus, and tensile and fracture strengths but slightly higher elongation at fracture. Furthermore, micron-sized zinc borate filled HDPE composites had similar mechanical properties of nano-sized filled composites. Inverse effect of 1% micron-sized zinc borate addition on elastic modulus and tensile and fracture strengths was even higher than that of 5% nano-sized zinc borate added EVA and HDPE composites. These results indicated that the addition of micron-sized zinc borate on mechanical properties led to higher negative effect. Although elongation at fracture of zinc borate-EVA and HDPE composites was higher than virgin EVA and virgin HDPE, no substantial difference was observed in elongation at fracture of micron and nano-sized zinc borate added EVA and HDPE composites. Polymer composites filled with inorganic materials may have higher and lower mechanical properties depending on the filler–matrix interactions and filler dispersion in the matrix. [52] For example, if stress is transferred from matrix to filler completely, then mechanical properties increases. But some filler like aluminium trihydrate and zinc borate may decrease the mechanical properties due to their inherent incompatibility with matrix.

IV.2.4.2 Impact Properties

Impact test results are given in the Table IV.11 and Figure IV.31. The increase in the amount of filler, in all cases, caused a decrease in composites' impact strength. Furthermore, the impact property of nano-sized zinc borate filled HDPE composites' was slightly higher than micron-sized zinc borate filled composites. The reduction of impact strength with zinc borate addition into HDPE could be explained by the increase in bond formation and restriction of chain mobility.

Table IV.11 Izod impact test results of zinc borate–HDPE composites.

Sample	Izod Impact Strength (kJ/m^2)
NPE - 1	4.28
NPE - 3	3.84
NPE - 5	3.75
CPE - 1	3.84
CPE - 3	3.76
CPE - 5	3.50
Virgin HDPE	5.18

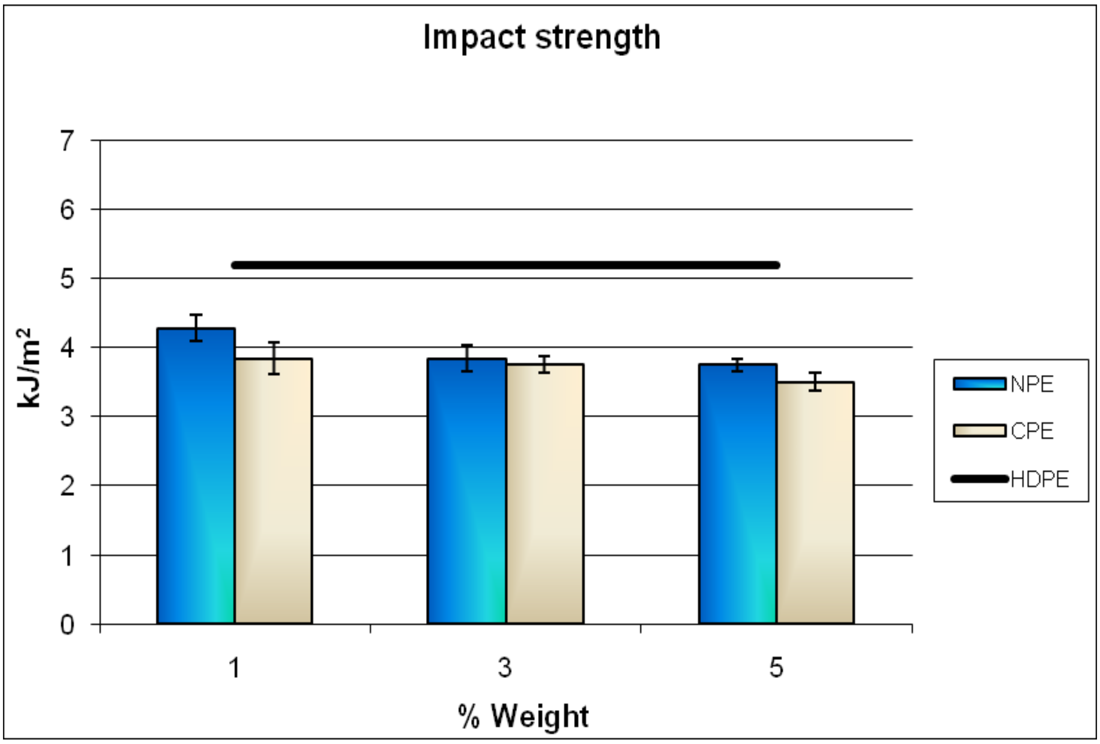


Figure IV.31 Izod impact test results of produced zinc borate–HDPE composites.

CHAPTER V

CONCLUDING REMARKS AND RECOMMENDATIONS

Nano-sized zinc borate powders with the formula of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$ were successfully synthesized by a wet chemical method using oleic acid as surfactant. XRD, FT-IR and DTA-TG results indicated that the powder had the zinc borate formula of $2ZnO.3B_2O_3.3\text{-}3.5H_2O$. TEM and particle size measurements gave a particle size below 70 nm with nearly spherical particles. SEM micrograph of a zinc borate - polymer composites revealed that distribution of zinc borate in polymer matrix was nearly homogeneous. LOI results demonstrated that zinc borate addition into EVA matrix improved the flame retardancy of virgin EVA from 20.8% to 23.9% with addition of 5% nano-sized zinc borate. Furthermore, zinc borate addition into HDPE matrix improved the flame retardancy of virgin HDPE from 19.6% to 22.2% with addition of 5% nano-sized zinc borate. In addition, flame retardancy of nano-sized zinc borate-EVA composites was a slightly higher than micron-sized zinc borate-EVA composites. Flame retardancy of nano-sized zinc borate - HDPE composites was similar to micron-sized zinc borate - HDPE composites. Nano-sized zinc borate addition into EVA had less negative effect on mechanical properties than micron sized zinc borate. Although zinc borate addition into HDPE decreased the mechanical properties the results nano and micron sized zinc borate addition gave identical results.

In the future studies, synergistic effect of commercially available inorganic flame retardant materials with nano sized zinc borate should be investigated. In addition, effect of nano zinc borate higher than 5% on flame retardancy and mechanical properties of EVA and HDPE should be investigated.

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- NanoTR VII, Nanoscience and Nanotechnology Conference, İstanbul, Turkey, 2011 (Poster Presentation).
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