PREPARATION OF EPOXY-BASED COMPOSITES CONTAINING BARIUM METABORATE AND THEIR CHARACTERIZATION

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES
OF
MIDDLE EAST TECHNICAL UNIVERSITY

BY

ELİF YÜREKLİ

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR
THE DEGREE OF MASTER OF SCIENCE
IN
CHEMICAL ENGINEERING

AUGUST 2014

Approval of the thesis:

PREPARATION OF EPOXY-BASED COMPOSITES CONTAINING BARIUM METABORATE AND THEIR CHARACTERIZATION

submitted by **ELİF YÜREKLİ** in partial fulfillment of the requirements for the degree of **Master of Science in Chemical Engineering Department, Middle East Technical University** by,

Prof. Dr. Canan Özgen
Dean, Graduate School of **Natural and Applied Sciences**

Assoc. Prof. Dr. Halil Kalıpçılar
Head of Department, **Chemical Engineering**

Prof. Dr. Göknur Bayram
Supervisor, **Chemical Engineering Dept., METU**

Examining Comitee Members:

Prof. Dr. İnci Eroğlu
Chemical Engineering Dept., METU

Prof. Dr. Göknur Bayram
Chemical Engineering Dept., METU

Prof. Dr. Cevdet Kaynak
Metallurgical and Materials Engineering Dept., METU

Assoc. Prof. Dr. Ayşen Yılmaz
Chemistry Dept., METU

Assist. Prof. Dr. Erhan Bat
Chemical Engineering Dept., METU

Date: 27 AUGUST 2014

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Name, Last name : Elif YÜREKLİ

Signature :

ABSTRACT

PREPARATION OF EPOXY-BASED COMPOSITES CONTAINING BARIUM METABORATE AND THEIR CHARACTERIZATION

Yürekli, Elif

M.S., Department of Chemical Engineering

Supervisor: Prof. Dr. Göknur Bayram

August 2014, 147 pages

Epoxy resin is one of the most important thermosetting polymers, widely used in various fields of industry. However, like most of the polymeric materials, epoxy resins are flammable and this restricts their application areas.

The purpose of this thesis is to increase flame retardant property of epoxy-based composites using various flame retardant additives mainly including barium metaborate.

This thesis consists of three main parts. In the first part, preliminary composites, which containing barium metaborate (BaM), zinc borate (ZnB), melamine phosphate (MP), melamine polyphosphate (MPP), red phosphorus (RP), pentaerythritol (PER) and dipentaerythritol (DPER), were given. In accordance with the results of preliminary experiments, the information about the flame retardant types and amounts was obtained to create formulations of final composites.

In the second part of the thesis, the final composites were prepared using MP, DPER, ZnB, and calcium borate (CaB) in addition to BaM and methacrylate epoxy cyclosiloxane (MEC). The produced composites were characterized by scanning electron microscopy (SEM), limiting oxygen test (LOI) test, the vertical burning test (UL-94), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), tensile and impact tests. The LOI value of neat epoxy was measured as 19%. 10% MP and 1% BaM containing epoxy-based composite was 27% in LOI value and UL-94 test result was determined as V-0. Also, when concentration of the additives increased in the epoxy matrix, it was seen that tensile strength and elongation at break value of the composites decreased; however tensile moduli of the composites increased in general.

In the last part of the thesis, pure epoxy and epoxy-based composites were subjected to accelerated weathering test. They were exposed to UV radiation and moisture for 300 hours. Exposed samples were characterized by SEM and impact test. Furthermore, samples were photographed before and after the accelerated weathering test in order to show physical change that occurred in the samples. According to the impact test results, the impact strength of all the weathered composites decreased when compared to unweathered composites.

Keywords: Flame retardancy, composite, epoxy, barium metaborate, methacrylate epoxy cyclosiloxane

ÖZ

BARYUM METABORAT İÇEREN EPOKSİ BAZLI KOMPOZİTLERİN HAZIRLANMASI VE KARAKTERİZASYONU

Yürekli, Elif

Yüksek Lisans, Kimya Mühendisliği

Tez Yöneticisi: Prof. Dr. Göknur Bayram

Ağustos 2014, 147 sayfa

Epoksi reçine sanayinin çeşitli alanlarında kullanılan en önemli termoset polimerlerinden biridir. Ancak çoğu polimerik malzemeler gibi epoksi reçineler yanıcıdır ve bu onların kullanım alanlarını kısıtlar.

Bu çalışmanın amacı, baryum metaborat başta olmak üzere çeşitli alev geciktiriciler kullanılarak epoksi bazlı kompozitlerin alev geciktirme özelliğini arttırmaktır.

Bu tez üç ana kısımdan oluşmaktadır. İlk kısmında, baryum metaborat (BaM), çinko borat (ZnB), melamin fosfat (MP), melamin polifosfat (MPP), kırmızı fosfor (RP), pentaeritritol (PER) ve dipentaeritritol (DPER) içeren ön denemeler verilmiştir. Ön deneylerin sonuçları doğrultusunda, final kompozitlerinin formülasyonlarının olusturulmasında kullanılacak alev geciktiriciler ve konsantrasyonları hakkında bilgi edinilmiştir.

Tezin ikinci kısmında, BaM ve metakrilat epoksi siklosilokzan (MEC) ile birlikte MP, DPER, ZnB ve kalsiyum borat (CaB) kullanılarak final kompozitleri hazırlanmıştır. Hazırlanan kompozitler taramalı elektron mikroskopisi (SEM), sınırlayıcı oksijen indeksi (LOI), dikey yanma testi (UL-94), fourier dönüşümlü kızılötesi spektroskopisi (FTIR), termogravimetrik analiz (TGA), çekme ve darbe testleri ile karakterize edilmiştir. Saf epoksinin LOI değeri %19 olarak ölçülmüştür. %10 MP ve %1 BaM içeren epoksi bazlı kompozitin LOI değeri %27, UL-94 test sonucu ise V-0 olarak belirlenmiştir. Ayrıca, genel olarak hazırlanan kompozitlerin mekanik özelliklerinde numunelere eklenen katkı maddesi miktarı arttıkça, çekme gerilimi ve kopmada uzama değerlerinin düştüğü fakat elastik modülü değerlerinin arttığı görülmüştür.

Tezin son kısmında ise, saf epoksi ve epoksi bazlı kompozitler atmosferik yaşlandırma testine tabii tutulmuştur. 300 saat boyunca UV radyasyona ve neme maruz bırakılmışlardır. Atmosferik yaşlandırma testinin sonucunda, numuneler SEM ve darbe testleri ile karakterize edilmiştir. Ayrıca numunelerde oluşan fiziksel değişimleri göstermek amacıyla yaşlandırma testinden önce ve sonra numunelerin fotoğrafları çekilmiştir. Darbe dayanımı test sonuçlarına göre, atmosferik yaşlandırma testine maruz bırakılan bütün numunelerin darbe dayanımları, atmosferik yaşlandırma testine maruz bırakılmayanlarla karşılaştırıldığında azalmıştır.

Anahtar kelimeler: Alev geciktiricilik, kompozit, epoksi, baryum metaborat, metakrilat epoksi siklosilokzan

To my precious family…

ACKNOWLEDGEMENTS

I would like to express my deepest gratitude to my thesis supervisor Prof. Dr. Göknur Bayram for her guidance, endless support, advices and great encouragement throughout my thesis. Without her patience and understanding, completing this thesis would have been almost impossible.

I gratefully thank Prof. Dr. Cevdet Kaynak from Metallurgical and Materials Engineering Department for letting me use the accelerated weathering test machine; Prof. Dr. İnci Eroğlu from Chemical Engineering Department for providing me barium metaborate and Mihrican Açıkgöz from Chemical Engineering Department for the TGA analysis.

I specially thank Yiğit Genç from IMCD Group for providing me the epoxy and the hardener; Zeynep Su Karagöz from Üçgen Pigments and Polymer Additives and Dilek Sayrav from Univar Chemistry for providing me flame retardant additives.

I would like to also thank the Middle East Technical University (METU) for supporting this study by the BAP-07-02-2012-101-204 project.

I also would like to thank my friends from polymer group of METU; Miray Yaşar, İrem Şengör, Eda Açık and Erdem Balık for their friendship and help during my experiments and researches.

I especially thank Hülya Yürekli for her support and encouragement every step of my thesis.

Last but not least, I would like to thank my parents, Ziya and Songül Yürekli, and my sisters and brother, Emel, Pınar, Yasemin and Gökhan Yürekli, for their endless love, trust and support in every step of my life. My success wouldn’t have been possible, without their encouragement and love.

TABLE OF CONTENTS

CHAPTERS

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURES

NOMENCLATURE

E	Young’s Modulus, MPa
F	Maximum Force, N
S	Cross Sectional Area, cm^2
Δl	Gauge Length, mm
l_0	Initial Gauge Length, mm

Greek Letters

σ	Tensile Strength, MPa
ε	Strain

Abbreviations

BaM	Barium Metaborate
CaB	Calcium Borate
DPER	Dipentaerythritol
FR	Flame Retardant
FTIR	Fourier Transformed Infrared Spectroscopy
IFR	Intumescent Flame Retardant
LOI	Limiting Oxygen Index, %
MEC	Methacrylate Epoxy Cyclosiloxane
MP	Melamine Phosphate
MPP	Melamine Polyphosphate
RP	Red Phosphorus
PER	Pentaerythritol
SEM	Scanning Electron Microscope
TGA	Thermogravimetric Analysis
UV	Ultraviolet
ZnB	Zinc Borate

CHAPTER 1

INTRODUCTION

In our daily life, polymeric materials find many uses due to the low weight, exceptional combination, and easily processable feature. On the other hand, polymers as being organic materials are also known for their relatively high flammability; usually associated with the production of toxic and corrosive gases and smoke during combustion. As a result, developing the fire retardant behavior of polymers is an important challenge to extend the use of the polymers to most applications, and this thesis proposes to improve the fire retardant behavior of polymers [1, 2].

In order to enhance flame retardancy of polymeric materials, different strategies have been developed. These strategies are the polymer backbone alteration, the use of inherently flame retardant polymers or the incorporation of flame retardant additives into polymers [3]. By modifying the polymer backbone through including phosphorus (P), silicon (Si), nitrogen (N) or boron (B), the newly synthesized polymer would have outstanding fire properties. The disadvantage of this method is the mechanical properties of the obtained copolymer are often needed to be modified unlike to the reference material. Another strategy is to use of inherently flame retardant polymers like poly(vinyl chloride), which may cause to high production costs. Among these strategies; the incorporation of flame retardant additives into polymers is the most widely used method due to its simplicity and cost effectiveness [3].

Flame retardant additives decrease the ignitability of polymers and inhibit the combustion process by limiting the amount of heat released. Depending on their nature, flame retardants act physically and/or chemically in the solid or gas phase. They interfere with the combustion during heating, decomposition, ignition, or flame spread. The combustion process can be retarded by the cooling, by the formation of a protective layer, and by the dilution in physical action. The most important chemical reactions that interfere with the combustion process occur in the solid and gas phase [4].

There are many types of flame retardants. These are halogen containing flame retardants, mineral flame retardants (e.g. metal hyroxides), antimony compounds, phosphorus, nitrogen, boron, and silicon containing flame retardants.

Epoxy matrix have many attractive properties like excellent moisture, chemical and solvent resistance, ease of cure, perfect electrical and mechanical properties, low shrinkage, good adhesive strength and ease of modification to optimize its properties [5]. It is widely used for surface coatings, composites and laminates, insulating material for electrical devices, adhesives, encapsulants for semiconductors and pottings. However, flammability is a major limitation and this restricts their application areas.

In general, halogen containing compounds together with antimony oxide are efficient flame retardants for epoxy polymers. However, toxic smoke and corrosive products are formed during combustion, which affects the environment and human beings. Also, metal hydroxides are used as flame retardant additives for epoxy due to having lower cost and being environmentally friendly additives. However, in order to obtain flame retardancy, metal hydroxides should be used at high concentrations, that decrease mechanical properties of epoxy. Therefore, the recent tendency in research studies for polymeric materials is to use halogen-free flame retardants, such as compounds that include boron, silicon, phosphorus, nitrogen, and sulphur [6].

Barium metaborate (BaM) is an inorganic additive with a chemical formula $Ba(BO_2)_2$. It is the main boron compound which is used for the flame retardant plastic formulations and it is an excellent afterglow suppressant. In addition, it is resistant to ultraviolet radiation. It can act as UV stabilizer for poly(vinyl chloride) [7].

The main objective of this thesis is to improve flame retardant properties of epoxy polymer. In addition to the main objective, this thesis also aimed to preserve the mechanical properties of epoxy. Therefore, by using various flame retardant additives such as barium metaborate, methacrylate epoxy cyclosiloxane, melamine phosphate, dipentaerythritol, zinc borate and calcium borate, epoxy-based composites were prepared and the effects of additives on flammability, mechanical and thermal properties of the composites were investigated. Also, the effects of additives on UV radiation and moisture stability of epoxy-based composites were studied with accelerated weathering test.

This thesis includes three main parts. In the first part, preliminary composites were prepared using different flame retardant additives such as barium metaborate, melamine phosphate, red phosphorus, etc. The prepared samples were characterized in terms of flame retardancy and mechanical properties. Preliminary experiments have clarified the formulations and the preparation of the final composites.

In the second part, the final composites were prepared through different routes. In the first step, epoxy-based composites were prepared using barium metaborate in concentration of 0.5%, 1% and 3% by weight. In the second step, epoxy systems were formed using methacrylate epoxy cyclosiloxane with loading of 0.5%, 1% and 3%. Lastly, inherent flame retardant additives, which are melamine phosphate and dipentaerythritol containing composites, were prepared. After selecting the optimum concentrations from these routes according to flammability and mechanical properties, binary and ternary combinations were produced using the above mentioned additives. Also, the effect of borates on flammability of epoxy-based composites was investigated by adding zinc borate and calcium borate alternative to BaM into the selected combinations. Composites were characterized in terms of their flame retardant, mechanical and thermal properties using limiting oxygen index test (LOI) and UL-94 vertical burning tests, tensile and impact tests and TGA analysis, respectively.

In the third part, accelerated weathering test was applied to the selecting composites. The samples were exposed to UV radiation and moisture for 300 hours. For characterization of the composites, impact test was applied to the samples. Also, color change was observed through photography.

CHAPTER 2

BACKGROUND

2.1 Fire

Fire is a rapid oxidation exothermic process. During this process light, heat and different reaction products are released. Fire occur when three main elements; an oxidizer, fuel and source of ignition interact together. If one of these elements is removed, fire cannot exist [8]. This is called the fire triangle, which is given in Figure 2.1.

To start a fire, an adequate amount of oxidizer, e.g. oxygen gas or other oxygen-rich compounds, and a flammable and/or a combustible material are needed. When the material or the flammable is exposed to heat temperature above the flash point, the fuel/oxidizer mixture is capable to sustaining a rate of rapid oxidation which creates a chain reaction.

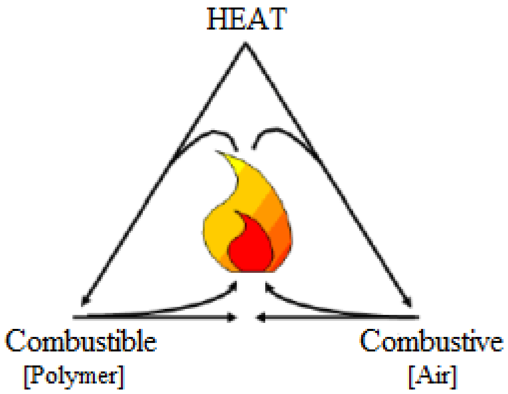

Figure 2.1 The fire triangle [1]

2.2 Flame Retardancy

2.2.1 Polymer Combustion and Thermal Degradation Process

Polymers are combustible materials because of their chemical structure, which generally contain carbon and hydrogen.

Two factors are involved in combustible reactions: one or more combustibles (reducing agents) and a combustive (oxidizing agent). Mostly, the oxygen in the air is the combustive. The polymeric materials are long chain molecules. Generally, this process starts when the temperature of the polymer increases. For thermal degradation of polymeric material, energy barrier can be handled which leads to wide changes in the chemical structures. Thermal decomposition initiated by main chain or side group scission, which causes to small volatile fragments to form. A combustible gaseous mixture is generated by the diffusion of the volatile fragments into the air. When the auto ignition temperature (temperature at which the activation energy of the combustion reaction is reached) is attained, this gaseous mixture ignites. This mixture can also ignite at a lower temperature which is also called the flash point with an external source such as spark or flame [1]. The typical combustion cycle of polymers is given in Figure 2.2.

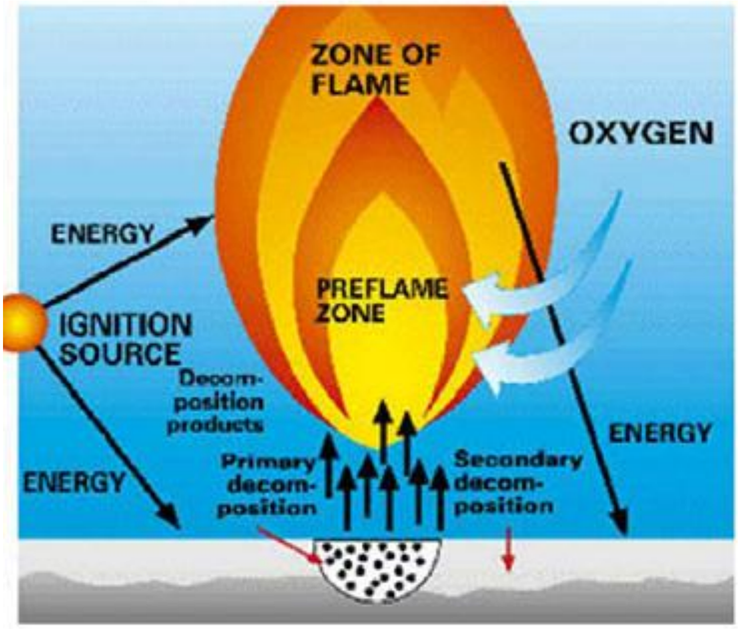

Figure 2.2 The combustion cycle of polymers [1]

The thermal decomposition of a polymer is an endothermic phenomenon. For this an input energy is needed. The energy which is provided to the system must be higher than the binding energy between atoms which atoms linked (200 to 400 kJ/mol for most C-C polymers). The decomposition mechanism depends on the weakest bonds, and the presence or the absence of oxygen (thermo-oxidative decomposition) or oxygen (pyrolysis) in the gas and solid phases. It is important to separate non-oxidizing thermal decomposition and oxidizing thermal decomposition [9].

In thermo-oxidative degradation, the polymer molecules react with oxygen and form various lower molecular weight products such as alcohols, ketones, acids, etc. Also, very reactive species, i.e. H• and OH•, release in this degradation.

On the other hand, according to some researchers, polymer degradation occurs via non-oxidizing thermal degradation at combustion temperatures exceeding 300 ^{o}C. In these circumstances, in the solid phase, the diffusion of oxygen is slower than pyrolysis. Since there is a presence of low molecular compounds, which are produced by thermal degradation, oxidation takes place in the gas phase [1].

2.2.2 Flame Retardant Mechanism

The polymer combustion process acting in a physical or chemical manner can be inhibited or stopped using flame retardant additives. They act physically by cooling, which is a formation of a protective layer or fuel dilution. Conversely, they act chemically by a reaction occurred in the condensed or gas phase. They may interfere with the combustion processes such as ignition, pyrolysis, heating, etc. [2].

2.2.2.1 Physical Action

Some flame retardant additives decompose endothermically. Therefore, they cause a temperature decrease by heat consumption. This involves cooling of the reaction medium to below the combustion temperature of polymer. Magnesium hydroxide and hydrated tri-alumina are examples that start releasing water at almost 300 and 200 ^{o}C, respectively. Such a prominent endothermic reaction is known to act as a “heat sink”.

Flammable gas mixture is diluted, when the flame retardant materials decompose and form inert gases (CO_2, H_2O, NH_3, etc.). This case limits the possibility of ignition and the concentration of reagents. Also, a way to stop spreading of the fire is the formation of an insulation barrier (protective layer) between the solid phase (thermal degradation takes place) and the gaseous phase (combustion occurs). This insulation barrier limits the transfer of agents such as flammable volatile gases and oxygen. As a result of this, the amount of decomposition gases produced is considerably decreased. In addition, oxygen can be extracted from the fuel gases. This procedure prevents the combustion process from being sustained [1].

2.2.2.2 Chemical Action

In the gaseous or the condensed phases, flame retardancy can occur by the chemically modified fire process. In order to stop the free-radical mechanism of the combustion process, halogenated flame retardants, releasing specific radicals such as Cl• and Br• are incorporated in the gas phase. When these radicals have a reaction with highly reactive species like H• and OH•, less reactive or even inert molecules are formed. This modification of the combustion reaction pathway leads significant temperature decrease, which causes a reduction in the produced fuel [1].

Flame retardants trigger the chemical reactions in the condensed phase in two types: firstly, the flame retardants can increase the rupture of the polymer chains. In this situation, there is a drip in the polymer, which causes the polymer to move away from the flame action zone. Next, in the degrading polymer chains, a carbonized (perhaps expanded) or vitreous layer at the polymer surface is formed by the flame retardant via a chemical transformation. This glassy layer or char performs as if it is a physical insulating layer between the condensed phase and the gas phase [1].

2.2.3 Flame Retardant Additives

Flame retardant additives can be grouped into two categories: reactive flame retardants and additive flame retardants. Reactive flame retardants are integrated in the polymer chains and they are chemically bound to the raw materials. Additive flame retardants are added to a polymer without bonding or reacting with the polymer. This type of flame retardants are generally mineral fillers, organohalogen, and organophosphate compounds.

In the following sections, various flame retardants, especially the ones that were used in this thesis are described, and their types and mechanisms are explained.

2.2.3.1 Intumescent Flame Retardants

Intumescent flame retardants (IFR) can be used as additives for polymeric materials and act as char promoters [10]. The advantages of IFR are low smoke, low corrosion, low toxicity, and no molten dripping during combustion. In general, intumescent flame retardant systems require three main components: an acid source, a carbon source, and a blowing agent. An acid source degrades to form char layer before the polymer decomposes during a fire. Generally, phosphorus containing compounds are used as an acid source. A carbon source is dehydrated by the acid source because of the acid attack to form a char. Polyhydroxy compounds like pentaerythritol and its derivatives are used as a carbon source. A blowing agent release non-combustible gas, such as HCl, NH_3 and CO_2, when it degrades. The heat gases can swell, which leads to the expansion of a polymer, and the formation of the swollen char can isolate the transfer of heat and mass between the flame and the materials. In general, nitrogen containing compounds like melamine are used as blowing agents. The acid source, carbon source and blowing agent often come from different compounds in the intumescent system [1, 11]. The typical mechanism for an intumescent system is shown in Figure 2.3.

The most commonly used intumescent flame retardant system is the one which includes melamine derivatives due to containing two out of three sources (the acid source and the blowing agent). In addition, when melamine derivatives degrade, they form the acid source and melamine in melamine derivatives behave as a blowing agent [12].

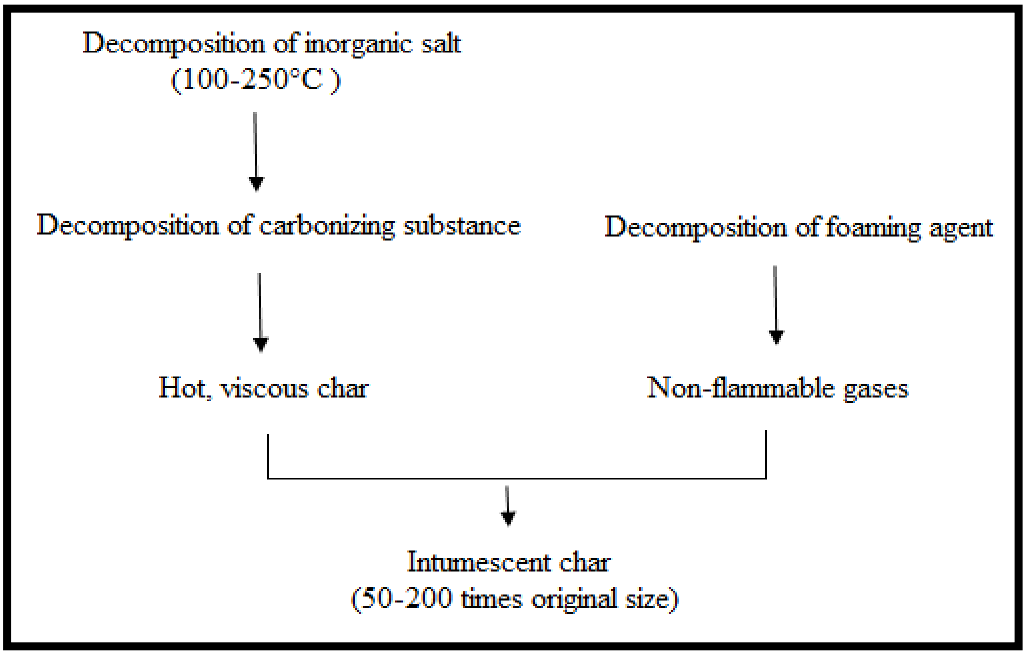

Figure 2.3 The mechanism for an intumescent system [10]

2.2.3.2 Phosphorus-based Flame Retardants

Nowadays significant attention in the studies of flame retardancy has focused on the phosphorus based flame retardants. The phosphorus containing flame retardants, having phosphates, phosphinates, phosphonates, phosphine oxides and red phosphorus are widely studied. These flame retardants can be used as additives in the direct mixing or incorporated into the polymer chain, during synthesis. Also, they are active in the condensed and/or vapor phases [1].

Phosphorus containing flame retardants can volatilize into the gas phase to create active radicals, such as PO•, PO_2•, HPO•. These species act as scavengers of H• and OH• radicals. Volatile phosphorated compounds are the most effective combustion inhibitors [1, 11].

Phosphorus based flame retardants can also act in the condensed phase which are especially effective in polymers containing oxygen. Thermal degradation causes to the formation of phosphoric acid. Pyrophosphate structures are produced and water is liberated by most of this condensed phosphoric acid. The oxidizing gas phase is diluted by the released water. Furthermore, the terminal alcohols' dehydration reaction can be catalyzed by phosphoric and pyrophosphoric acids. This catalyzation leads to carbocations and carbon-carbon double bonds to form, which results in the crosslinked or carbonized structures formation at high temperatures.

The pyrophosphate, the polyphosphate, and the carbonized residues are the parts of char formation. The benefits of the char (carbonized layer) are insulating and protecting the polymer from the flames, limiting the fuel volatilization and preventing the new free radicals' generation. In other words, the polymer underneath from the heat is insulates and oxygen diffusion, reducing combustion, is limited by the char.

Phosphorus-based flame retardants are considerably more effective in oxygen or nitrogen containing polymers. When the absence of suitable reactive groups occurs, the polymer cannot contribute to charring. In this case, a highly charring co-additive in combination with the phosphorated flame retardant has to be introduced. In this case, polyol like pentaerythritol and its derivations can be used as a co-additive [1].

2.2.3.3 Nitrogen-based Flame Retardants

Nitrogen-based flame retardants are less toxic and environmentally friendly. During combustion, they do not contain dioxin and halogen acids side products and they lead to low smoke evolution. Nitrogen containing flame retardant material is also suitable for recycling [13].

The most commonly used nitrogen-based flame retardants are melamine and its derivatives. Urea, guanidine, triazines, isocyanurates, and cyanuric acid derivatives can also be used as nitrogen-based flame retardants [14].

Melamine which contains 67% nitrogen atoms is a crystalline product, which is thermally stable. Melamine has a melting point as high as 345 ^{o}C [15]. Upon sublimation of melamine at about 350 ^{o}C, a considerable amount of energy is absorbed, and decrease in the temperature occurs. When ammonia is eliminated from melamine, combustible gases and oxygen are diluted, which causes to the formation of condensates, which are thermally stable at high temperatures [16].

These contend for melamine volatilization. If there is an inhibition in melamine volatilization, for instance by the formation of a protective layer, these decomposition reactions are more pronounced. The residues are generated by the thermally stable condensates formation in the condensed phase. This formation results in endothermic processes, and this is also efficient for the process of flame retardancy. Furthermore, thermally stable salts with strong acids, like melamine phosphate, melamine pyrophosphate and melamine cyranurate can be formed by melamine. Different flame retardant mechanisms characterize melamine and their salts. Melamine based salts are dissociated and melamine volatilizes, such as neat melamine, are reformed. However, a large amount of melamine undergoes more progressive condensation than in the case of neat melamine [16]. Therefore, the salts' action is substantially higher in the condensed phase.

The thermal degradation of melamine phosphate brings the melamine polyphosphate formation, and phosphoric acid and melamine release [17]. The released phosphoric acid is known as phosphorylate.

In the occurrence of melamine release, melamine phosphate thermal decomposition cause the ammonium polyphosphate formation. However, melamine struggles with the forming of its condensation products in the gaseous phase. Thus, the formation of polyphosphoric structures goes along with the melamine condensation. During thermal degradation, melamine is developed by the melamine pyrophosphate. However, the thermal performances of the melamine pyrophosphate are different than melamine and its other salts, the carbonaceous structures formation of the melamine pyrophosphate is more noticeable, and the action mode of the melamine pyrophosphate is similar to the action mode of ammonium polyphosphate.

2.2.3.4 Boron-based Flame Retardant

Boron-based flame retardants are other inorganic additives, which have flame retardant properties. Zinc borate, boric acid, and boroxide are widely used boron-based flame retardant additives. When, water of hydration is evaporated, swelling occurs in the polymers and a formation occurs in intumescent coating on the surface. This coating insulates the polymer from the heat source. The reasons for the flame retardancy of boron-containing additives could be the enhancement of the char formation, the endothermic dehydration process, and the dilution of the gaseous breakdown products by the water released.

Among them, zinc borate with the chemical formula of $2ZnO \cdot 3B_2O_3 \cdot 3.5H_2O$ is the most widely used. Its endothermic decomposition (503 kJ/kg) between 290 and 450 ^oC releases water, boric acid and boron oxide (B_2O_3). The B_2O_3 formed softens at 350 ^oC and flows above 500 ^oC which leads to the formation of a protective vitreous layer. The presence of boric acid leads to dehydration and leads to the formation of a carbonized layer in the cases where polymers contain oxygen atoms. The polymer is protected from heat and oxygen by this layer. Thus, the release of combustible gases is reduced [1].

Barium metaborate monohydrate has a potential of use as a flame retardant in plastic formulation. It is a synergist for phosphorus and halogen compounds, and it can be used as a partial or complete replacement for antimony oxide. It is also excellent as an afterglow suppressant. Barium metaborate monohydrate has a specific gravity of 3.25-3.35 and a fusion point of 900-1050 ^oC [18]. It has also greater transparency and brighter colors in formulated plastics, due to its low refractive index [19].

2.2.3.5 Silicon-containing Flame Retardants

Silicon-containing additives like silicones, silicates, silicas, organosilanes, and silsesquioxanes are used to improve flame retardancy properties of polymeric materials. Because of their non-toxicity, non-generation of toxic gases during combustion, and heat resistance, silicone and its derivatives can be preferred as flame retardants. They can also be used as additives, which are incorporated into the polymer or as copolymers [1, 20]. In general, silicon-containing flame retardants such as silicone and silica systems form a protective surface layer.

Methacrylate epoxy cyclosiloxane is a kind of epoxy monomer which includes silicon atoms. This unique monomer can be used in a free radical polymerization as well as epoxy related cures. The monomer can be used as an adhesion promoter to mold compound, metal surfaces and polyimide surfaces. It can also act as a multifunctional diluent. It is soluble in most resins [21]. In this research, this monomer is also used as a flame retardant due to the silicon atoms in its structure.

2.3 Epoxy

In this study, epoxy resin is used as a polymer matrix. Pierre Castan, a chemist in Switzerland, discovered epoxy resin in 1938. Epoxy resins are a kind of thermosetting resin which is a low molecular weight organic liquid including epoxide groups. As epoxy resin has perfect bonding property, also after curing, excellent mechanical, electrical properties and chemical resistance, epoxy resin has been commonly used in coating, painting, civil engineering, and electronics applications [22-24].

Epoxy resin is generally produced by the reaction of bisphenol A with epichlorohydrin. When these two raw materials are reacted in a basic compound (NaOH), linear epoxy resins are formed. This reaction is given in Figure 2.4.

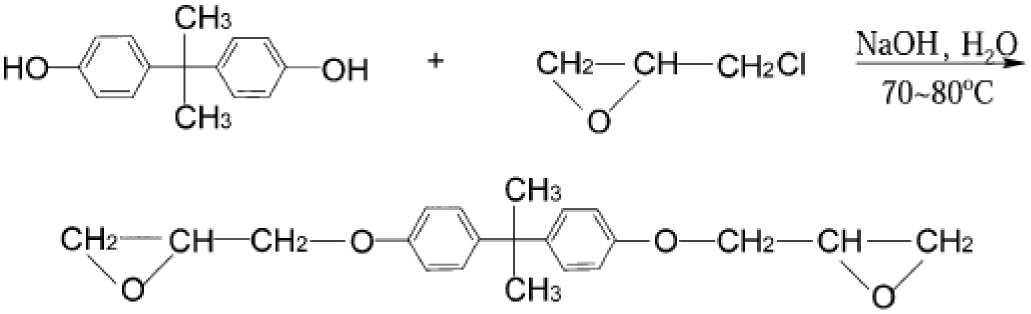

Figure 2.4 The reaction mechanism of Bisphenol A with epicholorohydrin [25]

Hardeners or curing agents are used to form crosslinked structure with epoxy resins. Amines and its derivatives are widely used curing agents. The curing mechanism of epoxy resin with amines is shown in Figure 2.5. The advantage of epoxy resins is that by using different epoxy and curing agent combinations, suitable epoxy system can be obtained according to design requirements. Glass transition temperature, cure kinetics, chemical resistance and mechanical performance can be controlled by using different type of epoxy and hardener combinations [23, 25].

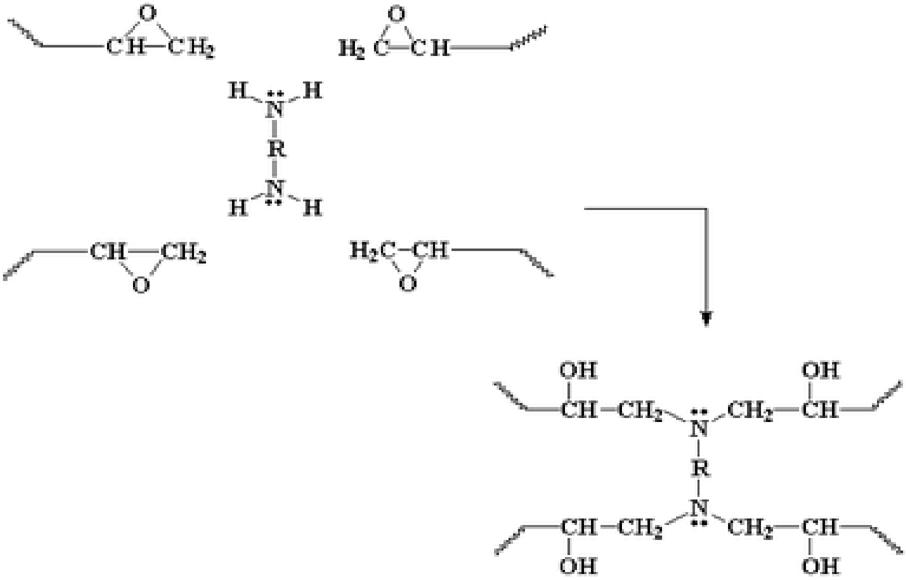

Figure 2.5 The curing mechanism of epoxy resin with diamines [26]

In the middle chain, epoxy contains two phenol ring groups. This provides better absorbing mechanical and thermal stresses than aliphatic chains. This also provides high stiffness, high thermal stability, and toughness.

Like other polymeric materials, when epoxy is exposed to high temperatures like 300-400 °C, the cured epoxy decomposes releasing smoke, toxic volatiles, heat and soot [27]. In general, there are four different reactions that occur in the condensed phase during the fire. The main reactions are end or random chain scissions, which are forming radical species. Simultaneously, atoms or different functional groups which are not part of the polymer backbone can be removed, which is known as *chain stripping*. The last occurring dominant reaction is the different radicals' crosslinking. During the chain scission this crosslinking is produces, which generates new polymers or char that thermally stable. An amine cured epoxy resin's thermal decomposition paths are given in Figure 2.6. In the first stage, during the crosslinking reaction, the formation of the dehydration or dehydrogenation of the secondary alcohol occurs, which yield allylic amides (a) [28-30]. Then, isomerization may be experienced by the unsaturated moiety (c). Next, allylic-oxygen bond scission follows (d) [28]. In the case of amine curing agents the formation of the weak C-N bond occurs during curing. Then, allylic-nitrogen bond scission will be experienced (b) in order to contribute charring or to form volatile particles [31].

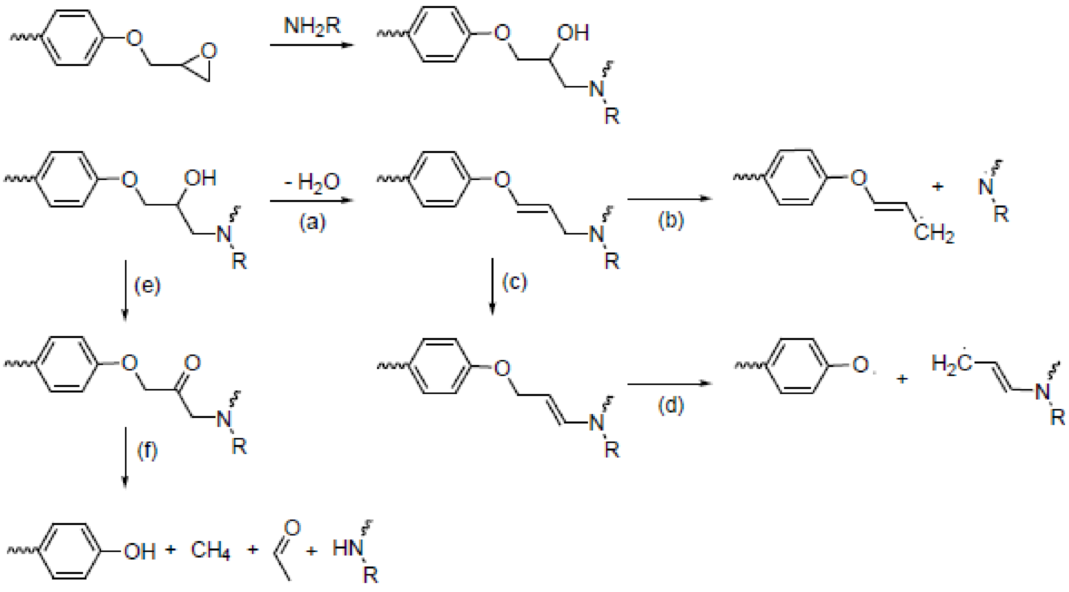

Figure 2.6 Thermal decomposition of an amine cured epoxy resin [3]

2.4 Environmental Degradation of Epoxy Composites Due to Ultraviolet (UV) Radiation and Moisture Exposure

It is advantages to use composite materials for structural applications that requires high stiffness and strength to weight ratios. In spite of its beneficial use, there are concerns about their overall long-term durability. Especially, under environmental conditions, which are harsh and changing, they have a limited capacity for sustained performance [32]. For example, in aerospace applications, environmental effects, such as UV radiation, moisture, hot and cold weather and its combination, mechanical properties to some degrees are reduced, based on the system and particular design application [33].

Tipton (2008) implied that the composite matrix is one of the components that are the most undefended to environmental attack, where UV light and moisture are the two of the primary environmental factors, which contributes to material decomposition. Generally, matrix decomposition, which is caused by environmental exposure, is manifested as matrix cracking and erosion, leading to matrix properties' reduction [33-35].

The ability to form bonds between the molecules of individual chains (crosslinks) characterizes thermosetting resins, like epoxy. This is possible when the certain molecules on the polymer chains are activated in order to form reaction sites. These crosslinks' formation restricts the polymer chains, movement, and increase the resistance to temperature, stiffness and strength. Under extreme temperatures, these materials cannot be melted, because of crosslinks that are formed during cure.

Epoxy is very sensitive to UV light. Thus, its photo-degradation mechanism depends on its chemical structure [36]. The uncured epoxy resins' basic structure has two parts: the first part is a three member ring oxirane group (epoxy group) and the remaining is the rest of polymer chain. This epoxy group is regarded an active site. Upon cure, the increased crosslinking ability will lead to a material having higher stiffness, strength, and temperature resistance [37].

Nakamura et al. (2006) explained that when the epoxy matrix exposes to the environment, which may have harmful effects on the epoxy composite structure's overall mechanical properties, moisture is absorbed. The diffusion of moisture into the matrix leads to dilatation expansion and also causes changes, e.g., hydrolysis [35].

In degradation when moisture entrance, there is a controlling factor, which is the water vapor' diffusion constant. Since water is a very polar molecule, involves hydrogen bonding with polar sites in the polymer are includes in the diffusion mechanism. Since epoxy resin contain ether groups, hydroxyl groups and C-N bonds, they are the most polar of the normal resins. For this reason, epoxy resins have the highest water permeability, which may cause either reversible or irreversible damage to the epoxy matrix. One of the reversible damages is plasticization because of the moisture desorption. The permanent irreversible damage is chemical bonds' hydrolysis. Microcracking may be included by moisture desorption gradients since the surface desorbs, and shrinks, the surface is put in tension [32, 34].

The epoxy is sensitive for incident light attacks. The UV component of light has the most important interaction with the polymer matrix. The solar radiation incident's UV components on the earth surface are in the 290-400 nm bands. The energy of these UV photons is comparable to the dissociation energies of covalent bonds of polymer, which are typically 290-460 kJ/mole. For this reason, the interactions between this UV light and the electrons are strong, which often results in excitation of the electrons and a resultant breaking of the bond. Therefore, UV light can decompose polymeric materials [32, 37]. The nature of the atoms in polymer matrix has some effects on the tendency of the electrons to become excited by the UV light and degradation. In general, UV light is decomposed the aromatic polymers more easily than the aliphatic polymers. The high aromatic content which is very common to most high performance epoxies makes them especially susceptible to UV radiation which is induced by degradation [34, 37].

The polymers absorb the UV photons, which produce photo-oxidative reactions. These reactions change the chemical structure which causes material deterioration. In general, the chemical reactions lead to molecular chain scission and/or chain crosslinking. Chain scission decreases the molecular weight of the polymer, which causes reduced heat and strength resistance. Chain crosslinking causes ultra brittleness and can result in microcracking.

When some polymer, including epoxy, exposed to UV radiation, show a color change [32].

According to Kumar et al. (2008), moisture exposure together with UV radiation can enhance the degradation of the epoxy-based composites [32]. When the epoxy is exposed to UV radiation, a thin surface layer is formed. Due to following water condensation leaches away soluble UV degradation product, a fresh layer is exposed which can be attacked by UV radiation. Thus, a repetitive process is established that causes to significant epoxy matrix erosion. Additionally, it is also possible that absorbed water molecules in the epoxy matrix enhance the photo-oxidation reactions because more OH^- and H^+ ions are available. This would increase the chain scission and crosslinking reactions which occur on the epoxy polymer surface which increase matrix brittleness [32, 35].

2.5 Characterization of Composites

2.5.1 Morphological Analysis

2.5.1.1 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is the most commonly used electron microscope to investigate surface morphology by scanning the surface of the materials with a high resolution and high magnification. SEM provides information by sending a high energy beam over the surface of materials. The most considerable feature of SEM is the three dimensional appearance of the surface because of the great depth of field [38]. The magnification range can change between 10x and 300000x.

In scanning electron microscopy, the surface of the sample is scanned by an electron beam sent from electron gun and the beam passes through lenses and electromagnetic fields under vacuum in the vertical direction. The lenses focus the electron beam up to the surface of the material. From the surface of material, x-rays and electrons are discarded; and by using detector secondary electrons or x-rays backscattered electrons are collected, and they are converted to signals. The view of the surface appears on a monitor. The illustration of SEM is given in Figure 2.7 [39].

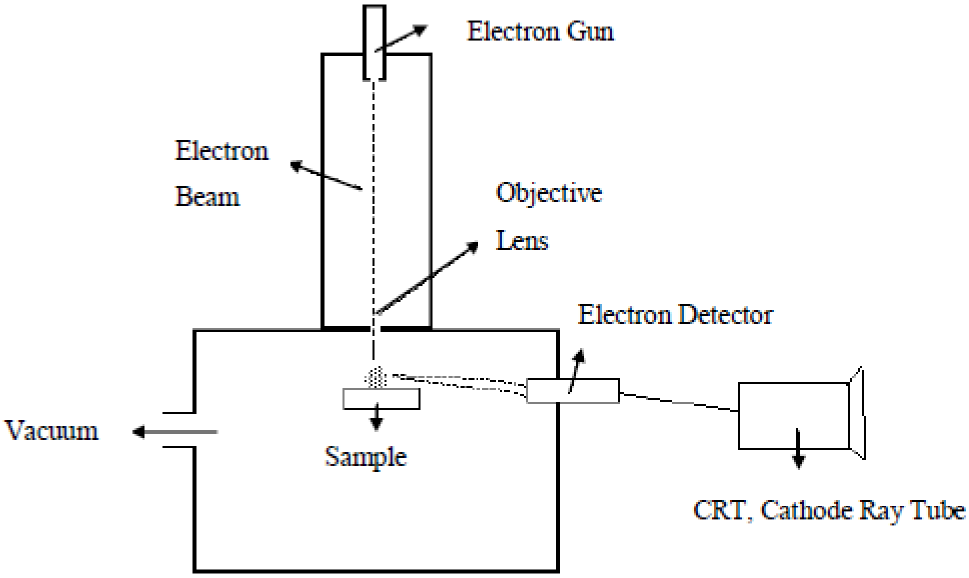

Figure 2.7 The illustration of SEM [39]

The scanning electron microscopy provides us chemical information from material by using different techniques such as X-ray energy dispersive spectrometer (EDS). In addition, SEM gives information about dispersion of fillers in the sample when the composite material is analyzed.

2.5.2 Flame Retardancy Characterization

2.5.2.1 Limiting Oxygen Index (LOI) Test

Limiting oxygen index (LOI) test was suggested by Fenimore and Martin in 1966 and it is used for showing flammability of materials [40, 41]. It was standardized in France (NF T 51-071) and in the United States (ASTM D2863), and is also subject to an international Standard (ISO 4589). The LOI value means that the minimum oxygen concentration (O_2) in the oxygen and nitrogen mixture (O_2+N_2) which either maintains the material's flame combustion for three minutes or consumes a length of five centimeters of the specimen. The top of the specimen is ignited by a heat source in a vertical position. The LOI is determined using Equation 2.1:

$$\mathrm{LOI} = 100 \times \frac{[\mathrm{O_2}]}{[\mathrm{O_2}] + [\mathrm{N_2}]} \tag{2.1}$$

According to ISO 4589, the dimension of the LOI sample is 4×10×80 mm. The sample is placed vertically in the middle of the glass chimney. The homogeneous gas mixture (O_2+N_2) comes below into the chimney which is purged 30 seconds. The sample is inflamed at the top [1].

LOI values below 21 are classified as “combustible” and LOI values above 21 are classified as “self-extinguishing” which cannot be sustained at ambient temperature without an external energy contribution. Higher LOI values represent better flame retardant property of material [1].

LOI test is the most remarkable screening and quality control method used in the plastic industry while it is phased-out due to the new technologies [1]. The illustration of limiting oxygen index experimental set-up is shown in Figure 2.8.

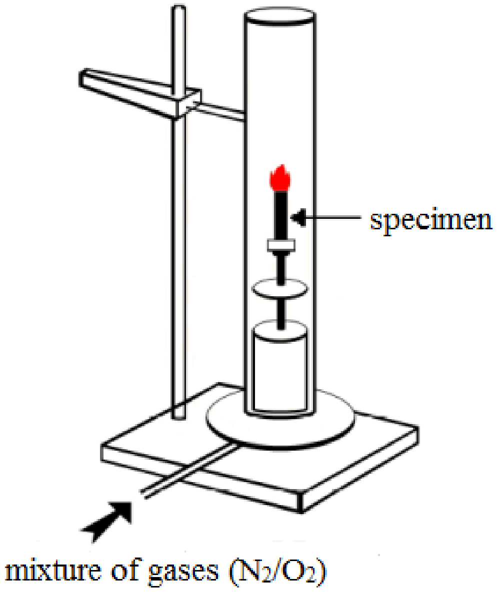

Figure 2.8 The illustration of limiting oxygen index experimental set-up [1]

2.5.2.2 UL-94 Vertical Burning Test

UL-94 test is improved by “Underwriters’ Laboratories” for the flammability of plastic materials for parts in devices and appliances. It is used to measure the flammability and flame spread of polymeric materials exposed to a small flame, and materials are classified as V-2, V-1 or V-0. The schematic of UL-94 test apparatus is given in Figure 2.9.

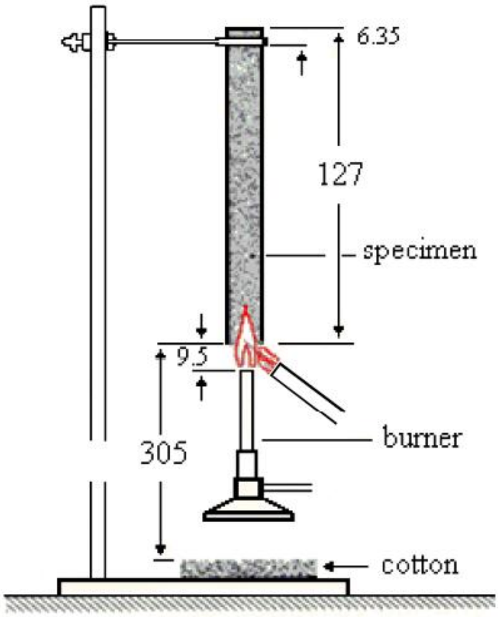

Figure 2.9 The schematic of UL-94 test apparatus [1]

The burner is adjusted to produce 20 mm-high blue flame. It is used for ignited to the sample, and it is placed at 10 mm under the bottom edge of the sample. Flame is applied to the polymer for 10 seconds and removed, the afterflame time (t_1) which is the length of time to a material continues to flame is recorded. After extinction, flame is applied for another 10 seconds and removed, the afterflame time (t_2) and afterglow time which is the time for a material to continue to glow are noted. During the test, cotton is placed below the sample and if it is ignited, this must be noted. The samples are classified according to the criteria in Table 2.1. The test is repeated at least for five specimens for each formulation [1].

Table 2.1 The criteria for classification of samples for UL-94 vertical burning test [42]

Criteria	**V-0**	**V-1**	**V-2**
For each specimen afterflame time, t_1 or t_2	$\leq$ 10 s	$\leq$ 30 s	$\leq$ 30 s
For 5 specimens total afterflame time (t_1+t_2)	$\leq$ 50 s	$\leq$ 250 s	$\leq$ 250 s
For each specimen afterflame time plus afterglow time after second ignition	$\leq$ 30 s	$\leq$ 60 s	$\leq$ 60 s
Afterflame or afterglow of any specimen up to the holding clamp	No	No	No
Cotton ignited by flaming drips or particles	No	No	Yes

2.5.3 Infrared Spectroscopy

2.5.3.1 Fourier Transformed Infrared Spectrum Analysis

Fourier transformed infrared spectroscopy (FTIR) is the most commonly used spectroscopic technique. In this technique, IR radiation is passed through a sample, some of it is transmitted and the remaining is absorbed. The molecular absorption and transmission shows the resulting spectrum. This molecular absorption and transmission creates the molecular fingerprint of the specimen. FTIR can be used for quality control, purity control, for defining of the chemical groups in the molecular structure and for identifying the reaction. The FT-IR components are given in Figure 2.10.

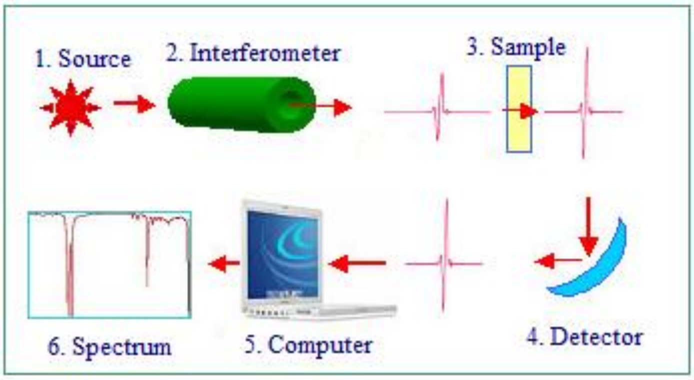

Figure 2.10 The FT-IR components [43]

2.5.4 Thermal Characterization

2.5.4.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a kind of analytical technique that measures mass change of materials as a function of temperature. The main applications of TGA are in chemical phenomena such as decomposition, dehydration, oxidation, reduction, etc. and in physical phenomena such as sublimation adsorption, desorption, vaporization, sublimation, etc.

Since the different components of the sample are decomposed, the sample is heated using the thermogravimetric analysis instrument and the mass change of the sample is measured. The results are plotted as a graph where x and y axes represent temperature and weight loss, respectively. Data are adjusted using the curve smoothing technique. Also, first derivatives can be plotted in order to determine points of inflection [44].

2.5.5 Mechanical Characterization

2.5.5.1 Tensile Test

Tensile test is one of the common ways to measure material strength. Tensile test, also known as, tension test is used for quality control, and to get information about final product's performance.

In tensile testing, specimens are placed in the grips and pulled at a constant speed until the failure of the material. The schematic view of tensile test system is given in Figure 2.11 [45]. The applied force and changing of gauge length data were obtained from the tensile test. Using this data; tensile strength, elastic modulus, and elongation at break value were calculated. Generalized stress-strain curve for polymeric materials is given in Figure 2.12.

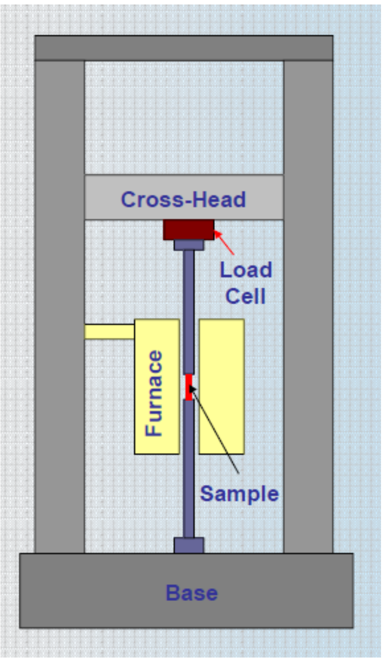

Figure 2.11 The illustration of tensile test system [45]

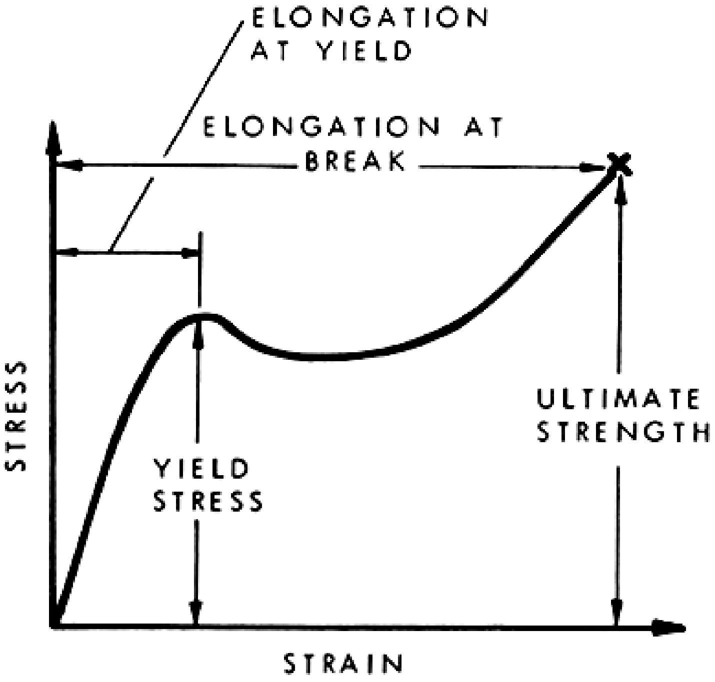

Figure 2.12 Generalized stress-strain curve for polymeric materials [46]

Tensile strength (σ) is the maximum stress which a material can withstand. Tensile strength is calculated using Equation 2.2, where F is the maximum force and S is the cross sectional area of the sample.

$$\sigma = \frac{F}{S} \tag{2.2}$$

Strain (ε) is determined using Equation 2.3 where Δl is the change in gauge length and l_0 is the initial gauge length.

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{l - l_0}{l_0} \tag{2.3}$$

Young's modulus or elastic modulus (E) is a measure of stiffness which is obtained from the initial slope of the stress-strain curve [45]. It is determined from Equation 2.4.

$$E = \frac{\sigma}{\varepsilon} \tag{2.4}$$

2.5.5.2 Impact Test

Impact test is measured to determine the toughness of the polymers. The specimen is placed and failed with the pendulum. The absorbed energy by the specimen which is equal to the potential energy difference of the hammer between before and after the fracture is measured as impact energy [47]. The illustration of impact test system is given in Figure 2.13 [48]. The most commonly used types of the tests are Charpy and Izod impact tests.

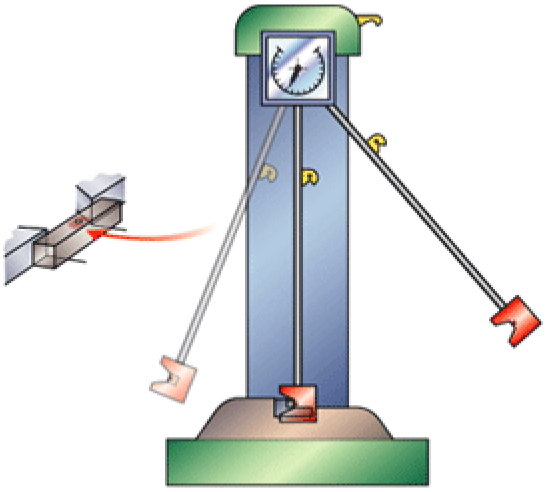

Figure 2.13 The illustration of impact test system [48]

2.5.6 Accelerated Weathering Test

Accelerated weathering test is a kind of outdoor environment simulation of the damaging forces of weather to predict the relative durability of materials. Specimens are placed in racks in the QUV chamber. Sunlight's damaging effects are simulated by fluorescent type lamps and also rain and dew are simulated by condensation systems and pressurized spray. Weather conditions cycle and the exposure temperature are controlled automatically. The commonly used fluorescent lamps are UVA and UVB. These lamps do not produce any infrared or visible lights but UV lights. Since the lamp was used in this study, the produced wavelength of UV light might affect the final degradation results. Actually, natural sunlight includes radiation in many areas of the spectrum which contains UVA and UVB. UVB radiation is less predominant than UVA and the UVB radiation is at the lowest end of natural light. Because it has a shorter wavelength, it also has a higher energy. UVB increases chemical reaction kinetics and initiates chemical reaction to occur [49]. Figure 2.14 represents the accelerated weathering test machine system [50].

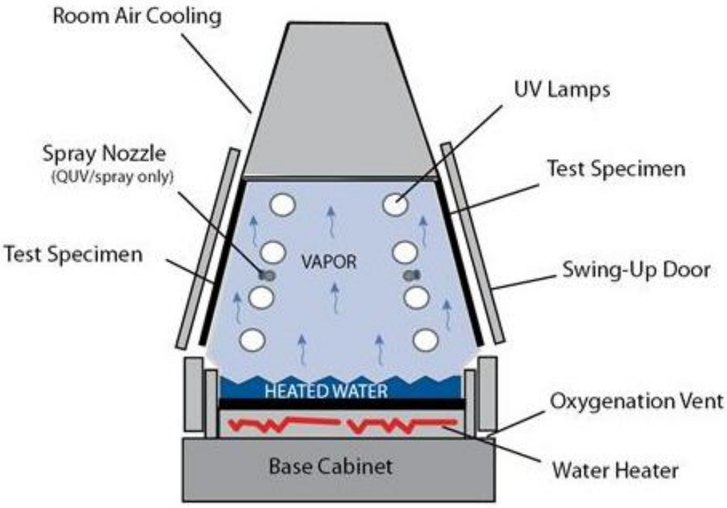

Figure 2.14 Accelerated weathering test machine system [50]

2.6 Literature Survey

This section reviews the literature related with the methods to develop flame retardant property of epoxy. Furthermore, the studies about the additives, which are used as flame retardants in this study, are also summarized.

Cowan and Manley (1976) studied the effects of inorganic borates on the flame retardancy properties of PVC. The flammability of PVC sheet containing barium borates, calcium borates and zinc borates, alone and together with antimony oxide, was measured by limiting oxygen index test and Stanton Redcroft F.T.B. Unit test. They demonstrated that all borates were effective in reducing smoke. Barium borates and calcium borates, with or without antimony oxide, showed little or no effect on flame retardancy of PVC, but zinc borate showed a synergistic effect with antimony oxide [51].

Baltacı et al. (2013) synthesized zinc borate from the reaction of zinc oxide and boric acid. The synthesized zinc borate was used as a flame retardant additive together with boron phosphate for poly(ethylene terephthalate), PET. The addition of 2% zinc borate and 3% boron phosphate increased the LOI value of composite from 22.5% to 26% [52].

Kılınç et al. (2009) synthesized 3.5 hydrated zinc borate and boron phosphate and evaluated the flame retardancy effect of these additives for PET. LOI value of PET was determined as 21%. 8% zinc borate addition into PET resulted in a LOI value of 23.5%. Using 5% zinc borate together with 5% triphenyl phosphate increased the LOI value of PET to 29.9% [53].

Ishii et al. (2006) studied the flame retardant effect of calcium borate on application to semiconductor packaging for epoxy molding compounds. They found that although with a small amount of calcium borate the flammability decreased, the flammability did not decrease proportionally with the amount of calcium borate added. For this system, calcium borate showed cooling effect by water released and the sealing effect by the glassy layer formed from B_2O_3 at high temperature. The char formation by calcium and calcium oxide was also considered [54].

Lv et al. (2005) conducted a research on flammability and thermal decomposition properties of polypropylene (PP) composites including melamine phosphate and pentaerythritol derivatives. They investigated the intumescent effect of melamine phosphate (MP) with or without the addition of pentaerythritol (PER), dipentaerythritol (DPER), and tripentaerythritol (TPER) on the polypropylene flammability. It was found that PP composites including only MP did not show good flame retardancy even at 40% additive loading. Compared to flame retardancy of the PP/MP binary composites, the LOI values of PP/MP/PER, PP/MP/DPER, PP/MP/TPER composites at the same additive level were increased for all of them. Also, UL-94 test results of most ternary composites studied were increased from no rating to V-0 for PP/MP composites [55].

Chen et al. (2004) synthesized epoxy resins containing melamine phosphate (MP) and investigated their thermal and flame retardation properties. MP was used as a hardener for epoxy resin and was also used as a flame retardant additive for epoxy to enhance the flame retardation properties of epoxy resin. According to the LOI results, MP was effective in increasing LOI in both reactive and additive modes. Also, MP in its reactive modes was better than its additive modes. According to thermogravimetric analysis (TGA) results, MP containing epoxy resin decomposed at lower temperature than neat epoxy resin; and this decomposition resulted in a protective layer formation that prevented the epoxy resin from decomposing further by combustion [56].

Jumahat et al. (2012) in studied the tensile properties of epoxy/nanosilica nanocomposites. Epikote 828 was used as epoxy matrix and HY960 was used as curing agent. Tensile test was applied to characterize the composite. Their findings indicated the tensile strength, tensile strain at break, and elastic modulus of neat epoxy were 70.84 MPa, %3.28 and 2750 MPa, respectively [57].

Chang and Chow (2010) prepared epoxy/glass fiber composites with various loading of organomontmorillonite (OMMT) and investigated the effect of UV exposure on fracture toughness and flexural properties of epoxy/glass fiber/OMMT nanocomposites with using accelerated weathering test. The composites were exposured to UV radiation for 100 hours at 50 ^{o}C, and moisture was applied as well. Their results showed that the presence of the combination of moisture, heat, and UV radiation weakened the interface adhesion between the glass fiber and epoxy matrix, causing to lower retention of fracture toughness [58].

2.7 Motivation of the Thesis

Since ancient times, fire has been causing deaths or fatal injuries and economic damage. Therefore, flame retardancy subject has been an important issue all the time.

Epoxy is one of the most important thermosetting polymers, widely used in coating, adhesives, electronics, aerospace industries and high-performance composite materials due to its excellent mechanical and chemical properties. On the other hand, like most of the polymeric materials, epoxy resins are flammable which restricts their application areas.

There are three challenging parts of this thesis. In many researches about flame retardancy, zinc borate is used as flame retardants for polymeric materials. Although barium metaborate (BaM) is also the main boron compound, which has potential for the flame retardant plastic formulations and it is excellent afterglow suppressant, the effects of BaM on epoxy have not been investigated yet. The first challenging part of this study is the use of barium metaborate to increase flame retardant properties of epoxy composites.

The second one is that the utilization of barium metaborate, also with the aim of increasing resistance to ultraviolet radiation for epoxy-based composites by applying accelerated weathering test. Because BaM is known to be resistant to ultraviolet radiation based on the aforementioned literature.

The last challenging part is the use of methacrylate epoxy cyclosiloxane (MEC) which is an epoxy modifier, and has not been studied before in the composites. In this thesis, the effect of MEC on flame retardancy, thermal and mechanical properties of epoxy-based composites were also investigated.

This study has given us the experience about preparation of epoxy-based composites, developing their flammability properties and also overlooking on materials science and industrial point of view together.

CHAPTER 3

EXPERIMENTAL

This section summarizes the materials that have been used, and explains the experimental procedures and characterization methods. Firstly, the materials and their properties are given. Secondly, preparation of epoxy-based composites and their flowcharts are explained. Lastly, characterization methods are described.

3.1 Materials

3.1.1 Epoxy Resin

The epoxy resin, EPIKOTE 828 (MOMENTIVE) was purchased from IMCD Group. EPIKOTE 828 is a medium viscosity liquid epoxy resin which produced from reaction of bisphenol A and epichlorohydrin. Application areas of this resin are building and civil engineering industries (floorings, adhesives, mortars), electrical and electronic industries (potting, casting, impregnating) and filament winding for composites. The chemical structure of EPIKOTE 828 which is taken from its technical data sheet is given in Figure 3.1. The properties of EPIKOTE 828 are given in Table 3.1 [59].

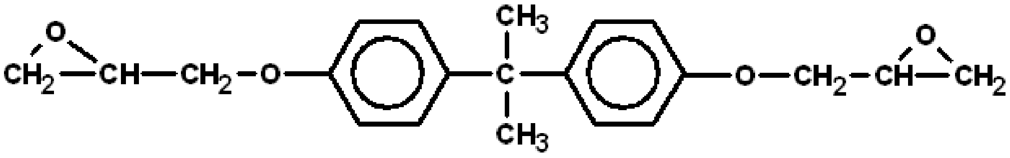

Figure 3.1 Chemical Structure of EPIKOTE 828

Table 3.1 The properties of EPIKOTE 828 [59]

Property	**Unit**	**Value**
Epoxy Group Content	mmol/kg	5260-5420
Epoxy Molar Mass	G	184-190
Viscosity at 25 ^oC	Pa.s	12-14
Density at 25 ^oC	kg/L	1.16
Color	Pt/Co Scale	100 max
Flash Point	^oC	>150

3.1.2 Curing Agent

The curing agent, EPIKURE F205 (MOMENTIVE), was purchased from IMCD Group. It is a low viscosity, modified cycloaliphatic amine curing agent. The chemical structure of EPIKURE F205 is shown in Figure 3.2. The properties of EPIKURE F205 are given in Table 3.2 [60].

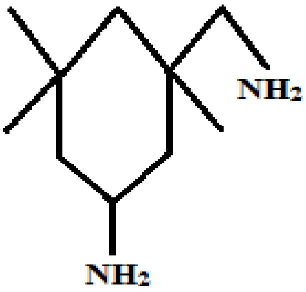

Figure 3.2 Chemical Structure of EPIKURE F205

Table 3.2 The properties of EPIKURE F205 [60]

Property	**Unit**	**Value**
Based nitrogen content	% (m/m)	6.0-8.0
Hydrogen equivalent weight	G	102-106
Viscosity at 25 ^{o}C	Pa.s	0.5-0.7
Density at 25 ^{o}C	kg/L	1.04
Colour	Gardner scale	2 max
Flash Point	^{o}C	100-106

3.1.3 Flame Retardant Additives

3.1.3.1 Barium Metaborate

Barium metaborate monohydrate (BaM) was used as a flame retardant additive which was ordered from Acros Organics. Figure 3.3 shows the chemical formula of BaM, and information on BaM is given in Table 3.3.

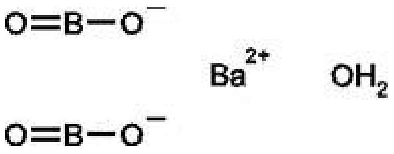

Figure 3.3 Chemical Structure of BaM [61]

Table 3.3 The information on BaM [61]

Property	**Value**
Molecular formula	$B_2BaO_4.H_20$
Molecular weight	240.97 g/mol
Particle size	3.5 microns
Purity	>90%
Form	White powder

3.1.3.2 Melamine Phosphate

Melamine phosphate (MP), which was ordered from BASF is a halogen free melamine based flame retardant component. The property of MP is given in Table 3.4.

Table 3.4 The properties of MP [62]

Property	Value
Specific gravity	1.74 g/cm^3
Molecular weight	224.12 g/mol
Particle size	116 microns
Form	White powder

3.1.3.3 Melamine Polyphosphate

Melamine Polyphosphate (MPP), which is purchased from BASF, is a kind of halogen free melamine based flame retardant. The information on MPP is given in Table 3.5.

Table 3.5 The properties of MPP [62]

Property	Value
Specific gravity	1.85 g/cm^3
Form	White powder

3.1.3.4 Pentaerythritol

Pentaerythritol (PER) which was supplied by Sigma Aldrich, was used as a carbon source. Chemical structure and some properties of PER are given in Figure 3.4 and Table 3.6, respectively.

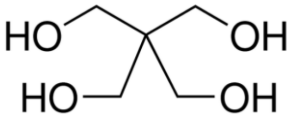

Figure 3.4 Chemical Structure of PER [63]

Table 3.6 The properties of PER [63]

Property	**Value**
Molecular Formula	$C(CH_2OH)_4$
Molecular weight	136.15 g/mol
Purity	98%
Form	White powder

3.1.3.5 Dipentaerythritol

Dipentaerythritol (DPER), which was ordered from Sigma Aldrich, was used as a carbon source. Chemical structure and some properties of DPER are given Figure 3.5 and Table 3.7, respectively.

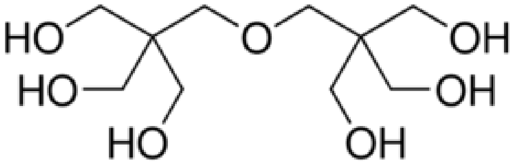

Figure 3.5 Chemical Structure of DPER [64]

Table 3.7 The properties of DPER [64]

Property	**Value**
Molecular Formula	$C_{10}H_{22}O_7$
Molecular weight	254.28 g/mol
Particle size	2.8 microns
Form	White powder

3.1.3.6 Zinc Borate

Zinc borate (ZnB) was used as flame retardant additive and was supplied by Great Lakes. Table 3.8 shows the properties of ZnB.

Table 3.8 The properties of ZnB [65]

Property	**Value**
Molecular Formula	$4ZnO.6B_2O_3.7H_2O$
Particle size	5 microns
Form	White powder

3.1.3.7 Calcium Borate

Calcium borate (CaB), which was purchased from Portaflame, was used as a flame retardant additive. Table 3.9 shows the properties of CaB.

Table 3.9 The properties of CaB

Property	**Value**
Density	2.4 g/cm^3
Particle size	4.3 microns
Form	White powder

3.1.3.8 Methacrylate Epoxy Cyclosiloxane (MEC)

Methacrylate epoxy cyclosiloxane (MEC) is an epoxy modifier which can be used as an adhesion promoter to mold compound, metal surfaces and polyimide surfaces. Due to the silicone atoms in its structure, it is used as a flame retardant. It was ordered from Sigma Aldrich. Chemical structure and some information on MEC are given Figure 3.6 and Table 3.10, respectively.

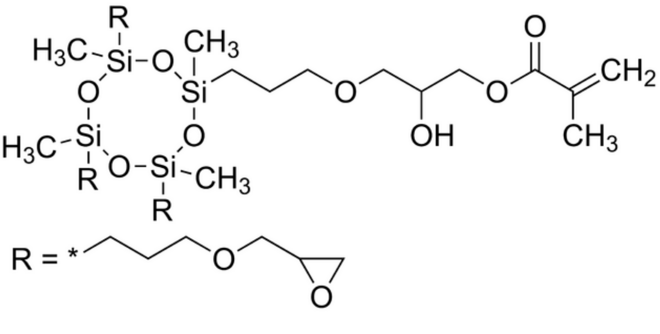

Figure 3.6 Chemical Structure of MEC [66]

Table 3.10 Some information on MEC [66]

Property	**Value**
Molecular Formula	$C_{32}H_{62}O_{14}S_4$
Molecular weight	783.17 g/mol

3.1.3.9 Red Phosphorus

Red phosphorus (RP), was purchased from Riedel-de Haen which was used as a flame retardant additive and the information on RP are given in Table 3.11 [14].

Table 3.11 The information on RP [67]

Property	**Value**
Molecular Formula	P_4
Molecular weight	123.89 g/mol

3.1.4 Solvent

Ultra pure acetone was used as a solvent and was supplied by Sigma Aldrich. Physical properties of acetone are given in Table 3.12.

Table 3.12 The properties of acetone [68]

Property	**Value**
Boiling Point	56 ^{o}C
Melting Point	-94 ^{o}C
Purity	>99%

3.2 Preparation of Epoxy Polymer

Three kinds of flowcharts for the preparation of neat polymer and the composites are shown in further sections. These are the preparation of neat epoxy, the preparation of epoxy composite containing flame retardant additive and the preparation of epoxy composite containing flame retardant additive and MEC.

3.2.1 Preparation of Neat Epoxy

The flowchart for the preparation of neat epoxy is given in Figure 3.7. Firstly, epoxy was degassed in a vacuum oven at 80 ^{o}C and -0.8 bar for 3 hours to remove air bubbles. Next, acetone was used as a solvent which was used as the same weight ratio with epoxy. Later, ultrasonication was applied to acetone for 1 hour. After removing epoxy from the vacuum oven, it was mixed with acetone. Mixing and ultrasonication was applied together for 30 minutes more. After that, the mixture was mixed using mechanical stirrer and heated at 80 ^{o}C at 60 rpm for 2 hours. At the same time ultrasonication was also applied. After 2 hours, mechanical mixing was continued at room temperature to cool the mixture. Curing agent was kept in a vacuum oven at 70 ^{o}C and -0.8 bar for 1 hour. Then, epoxy and curing agent were kept at room temperature for 30 minutes for cooling. Epoxy and curing agent were mechanically mixed at 40 rpm for 25 minutes. The mixing ratio of epoxy and curing agent was taken 100:55 by weight. The mixture was poured into on aluminum molds and curing for 30 minutes at room temperature. Then, curing was continued at 90 ^{o}C for 17 hours and postcured at 130 ^{o}C for 3 hours [69].

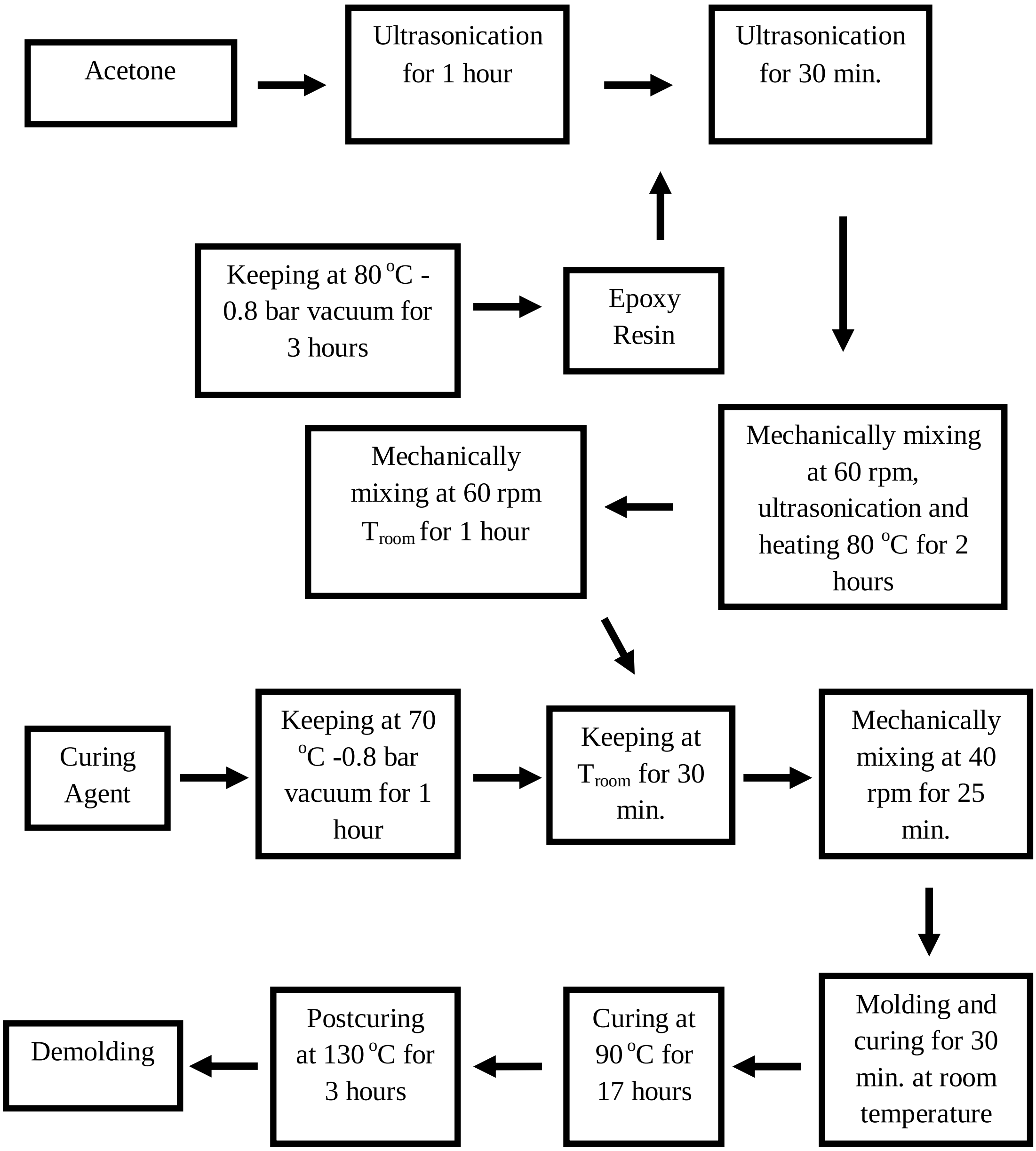

Figure 3.7 Flowchart of Neat Epoxy Preparation

3.2.2 Preparation of Epoxy Composite Containing Flame Retardant Additive

The flowchart for preparation of epoxy composite containing flame retardant additive is shown in Figure 3.8. The only difference from neat epoxy preparation flowchart is the addition of flame retardant (FR) additives. First, epoxy was kept in a vacuum oven at 80 ^{o}C and -0.8 bar for 3 hours. Next, ultrasonication was applied to acetone and FR additive for 1 hour. After removing air bubbles, epoxy was mixed with acetone and FR additive. Then ultrasonication was applied for more 30 minutes to provide homogeneous distribution. The other steps and curing cycle were the same as the neat epoxy preparation.

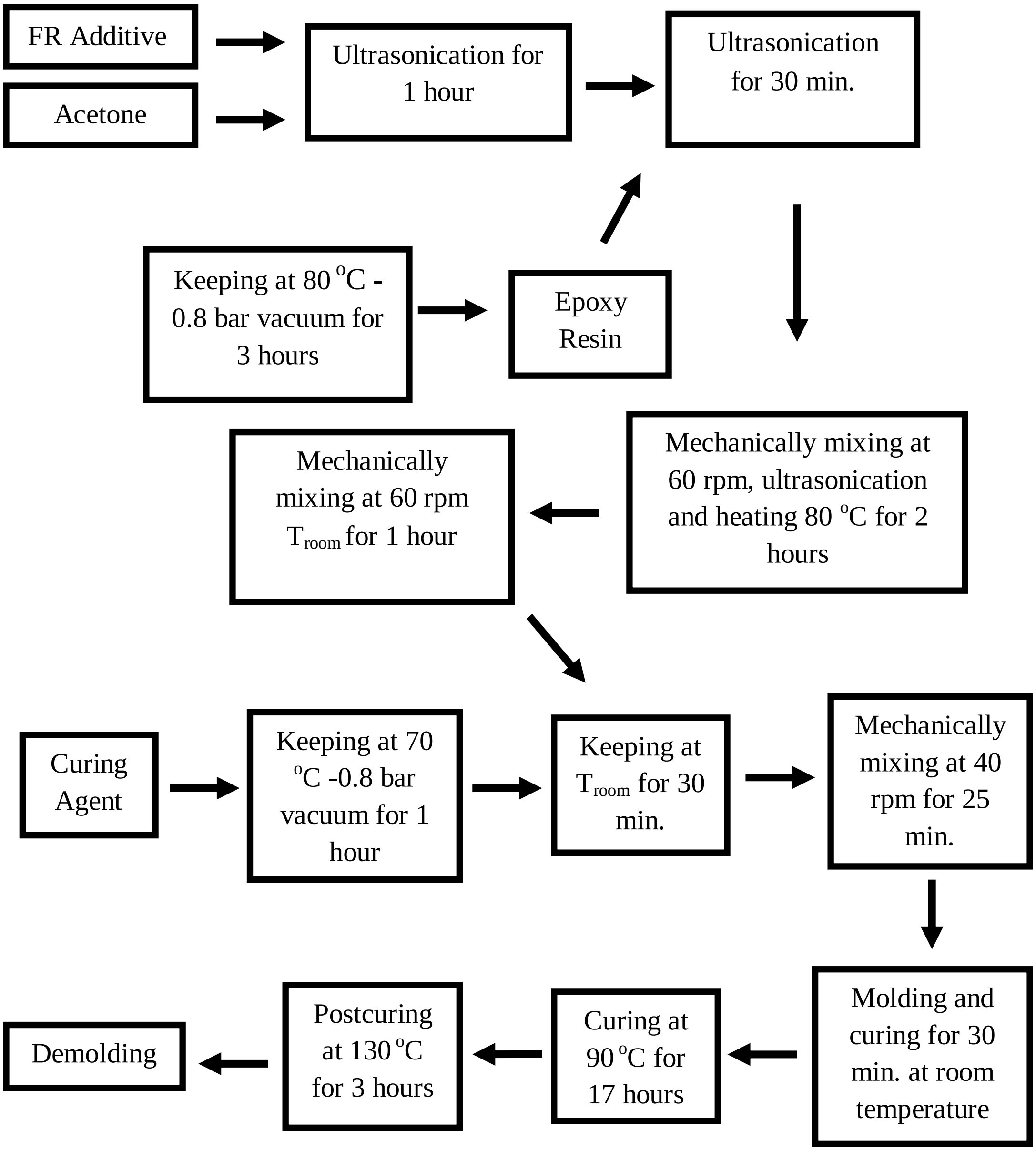

Figure 3.8 Flowchart of Epoxy Composite Containing Flame Retardant Additive

3.2.3 Preparation of Epoxy Composites Containing Flame Retardant Additive and MEC

The flowchart for the preparation of epoxy composite containing flame retardant additive and MEC is given in Figure 3.9. This procedure is same as the other procedures given before except the MEC addition. MEC was added into the mixture which containing acetone and FR additive together with epoxy resin. The other parts of the flowchart were the same as the neat epoxy preparation.

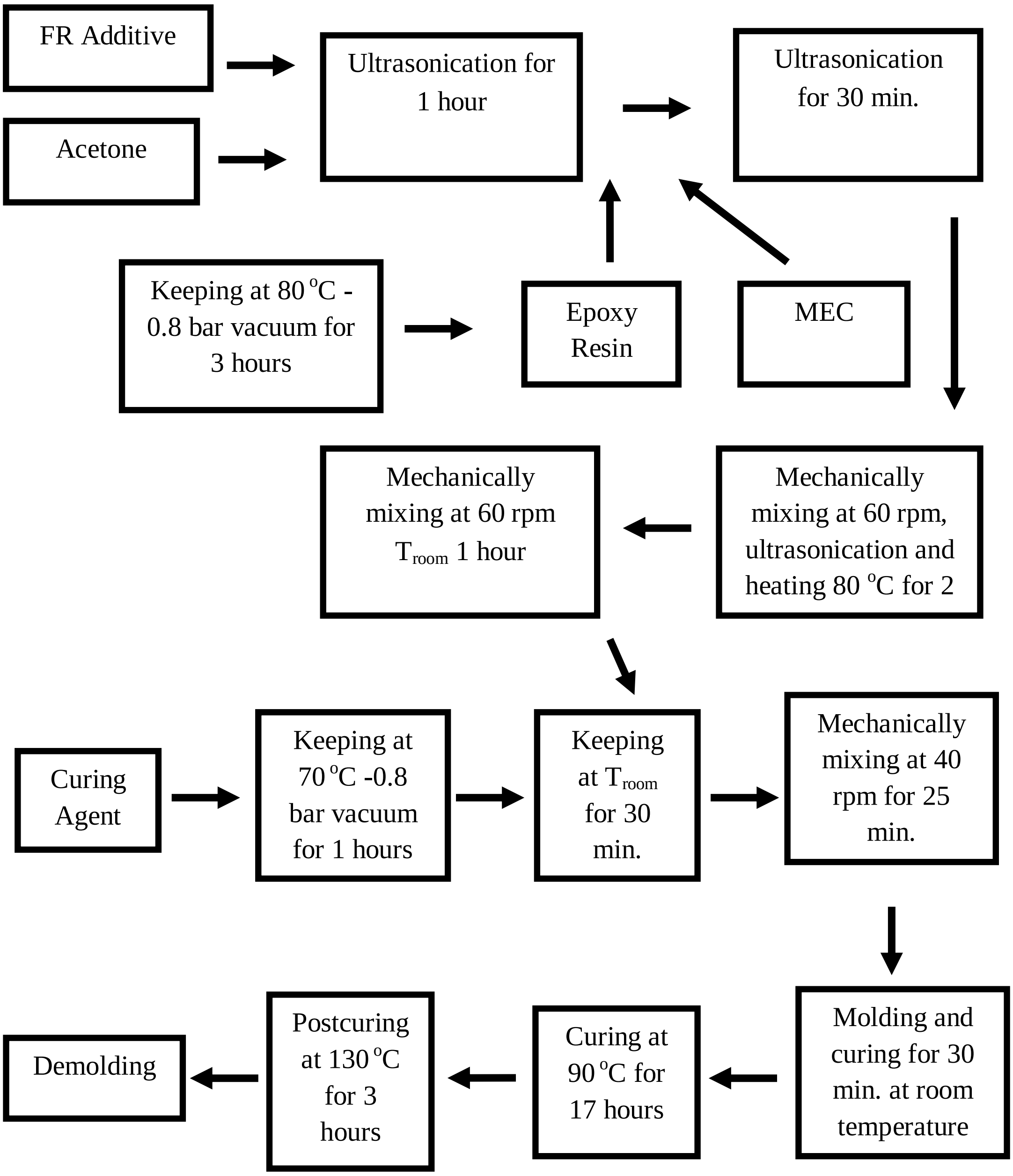

Figure 3.9 Flowchart of Epoxy Composite Containing Flame Retardant Additive and MEC

The compositions of epoxy-based composites are given in Tables 3.13 and 3.14. The preliminary composites are shown in Table 3.13. The final composites formulations were formed according to the flammability and mechanical test results of preliminary composites which are listed in Table 3.14.

Table 3.13 The compositions of preliminary composites

Composite (wt%)	**BaM**	**ZnB**	**MP**	**MPP**	**RP**	**PER**	**DPER**
EP/5BaM	5	-	-	-	-	-	-
EP/10BaM	10	-	-	-	-	-	-
EP/20BaM	20	-	-	-	-	-	-
EP/1ZnB	-	1	-	-	-	-	-
EP/10MPP	-	-	-	10	-	-	-
EP/1BaM/1ZnB	1	1	-	-	-	-	-
EP/10MP/1ZnB	-	1	10	-	-	-	-
EP/5RP/3ZnB	-	3	-	-	5	-	-
EP/10MP/5RP	-	-	10	-	5	-	-
EP/10MP/5RP/1BaM	1	-	10	-	5	-	-
EP/15MP/5PER	-	-	15	-	-	5	-
EP/15MP/5DPER	-	-	15	-	-	-	5

Table 3.14 The compositions of final composites

Composite (wt%)	BaM	MEC	MP	DPER	ZnB	CaB
EP	-	-	-	-	-	-
EP/0.5BaM	0.5	-	-	-	-	-
EP/1BaM	1	-	-	-	-	-
EP/3BaM	3	-	-	-	-	-
EP/0.5MEC	-	0.5	-	-	-	-
EP/1MEC	-	1	-	-	-	-
EP/3MEC	-	3	-	-	-	-
EP/10MP	-	-	10	-	-	-
EP/7.5MP/2.5DPER	-	-	7.5	2.5	-	-
EP/5MP/5DPER	-	-	5	5	-	-
EP/2.5MP/7.5DPER	-	-	2.5	7.5	-	-
EP/10DPER	-	-	-	10	-	-
EP/10MP/0.5BaM	0.5	-	10	-	-	-
EP/10MP/1BaM	1	-	10	-	-	-
EP/10MP/3BaM	3	-	10	-	-	-
EP/1BaM/1MEC	1	1	-	-	-	-
EP/10MP/1MEC	-	1	10	-	-	-
EP/10MP/1MEC/1BaM	1	1	10	-	-	-
EP/10MP/1MEC/1ZnB	-	1	10	-	1	-
EP/10MP/1MEC/1CaB	-	1	10	-	-	1

3.3 Characterization Methods

3.3.1 Morphological Analysis

3.3.1.1 Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM) was used for morphological analysis. The SEM analysis was carried out with a QUANTA 400F Field emission. The impact fractured surfaces of samples were investigated through SEM analysis in order to obtain conductive surface. Samples were coated with palladium (Pa) – gold (Au).

3.3.2 Flame Retardancy Characterization

3.3.2.1 Limiting Oxygen Index (LOI) Test

The limiting oxygen index (LOI) test was carried out with a Dynisco Polymer LOI test instrument to determine the minimum oxygen concentration. The test instrument is illustrated in Figure 3.10. This test was carried out according to ASTM D2863. Dimensions of the samples were 4×10×80 mm^3.

Figure 3.10 The limiting oxygen index test instrument [70]

3.3.2.2 UL-94 Vertical Burning Test

UL-94 vertical burning test was used to investigate flammability property of epoxy-based composites, according to the ASTM D3801. The specimen dimensions were 4×10×80 mm^3.

3.3.3 Fourier Transformed Infrared Spectroscopy with Attenuated Total Reflectance Apparatus

Fourier transform infrared spectroscopy was used to understand interactions between epoxy and the flame retardant additives, and to compare the influence of the radiation and moisture on degradation behavior between unweathered and weathered samples. Samples were scanned from 750 cm^{-1} to 4000 cm^{-1}. Fourier transform infrared spectroscopy was performed using a Shimadzu IR Prestige21 with attenuated total reflectance apparatus (ATR).

3.3.4 Thermal Characterization

3.3.4.1 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the thermal stability, the thermal degradation and the char yield of epoxy-based composites. TGA was carried out with a Shimadzu DTG-60/DTG-60A instrument. Analyses were performed from room temperature to 900^{o}C under nitrogen atmosphere. The heating rate was 10^{o}C/min.

3.3.5 Mechanical Characterization

3.3.5.1 Tensile Test

The tensile test was carried out with a Shimadzu Autograph AG-100 KNIS MS universal tensile testing machine which is pictured in Figure 3.11. ASTM D638 standard was used for characterization. The shape and the dimensions of the sample are given in Figure 3.12. The gauge length, the width, and the thickness were taken 65 mm, 6 mm, and 4 mm, respectively. The crosshead speed was taken at 4 mm/min. The data which were obtained from the tensile test was used for determination of tensile strength, elastic modulus and elongation at break values. For each composition of final composites, tensile test was repeated for five samples. The average results and the standart deviation of the composites are given in Appendix A.

Figure 3.11 The universal tensile testing instrument

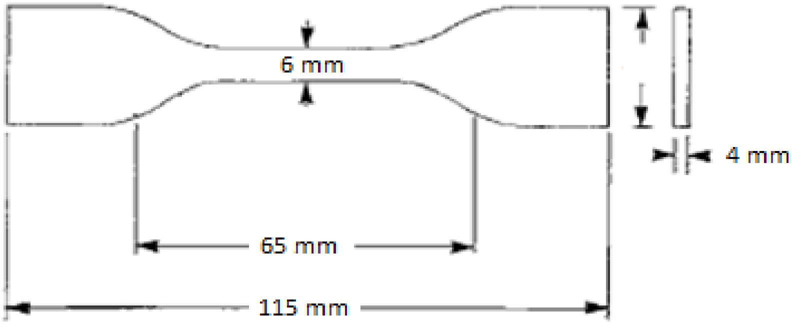

Figure 3.12 The shape and dimensions of the sample

3.3.5.2 Impact Test

In order to determine the impact properties of epoxy-based composites a Ceast Resil Impactor 6967 with 7.5 J pendulum was used. The impact testing instrument is shown in Figure 3.13. Impact test were performed according to ISO 179 standard. Dimensions of the specimens were 4×10×80 mm. Five specimens were tested for each formulation.

Figure 3.13 Impact testing instrument [71]

3.3.6 Accelerated Weathering Test

Accelerated weathering test was performed with a QUV Accelerated Weathering Tester Machine which is shown in Figure 3.14. The dimensions of the samples were $4 \times 10 \times 80$ mm^3. This test was carried out according to ASTM 6154 standard and Cycle 3 procedure. In the chamber, the sample of neat epoxy and epoxy-based composites were exposed to UV radiation at 70 ^{o}C for 8 hours followed by water condensation at 50 ^{o}C for 4 hours in repetitive cycle. The total exposure time was 300 hours. UVB 313 lamps with an irradiation level of 0.49 W/m^2 were used. In order to compare weatherability between weathered and unweathered samples, impact test was applied and also color change was observed using an 8 megapixel camera.

Figure 3.14 QUV Accelerated Weathering Tester Machine [72]

CHAPTER 4

RESULTS AND DISCUSSION

This section of the thesis consists of three parts. In the first part, preliminary works and their results are discussed. In the second part, final composites and their characterization results are discussed in detail. In the last part, accelerated weathering test results are given.

4.1 Characterization of Epoxy-Based Preliminary Composites

Preliminary composites were formed to find suitable type and sufficient amount of flame retardant additives. Therefore, they help to create the final compositions' formulations. In preliminary experiments, barium metaborate (BaM), zinc borate (ZnB), melamine phosphate (MP), melamine polyphosphate (MPP), red phosphorus (RP), pentaerythritol (PER), and dipentaerythritol (DPER) were used as flame retardant additives. Preliminary composites were characterized by their flammability and their mechanical behavior. The compositions of preliminary composites are given in previous section in Table 3.13.

4.1.1 Flammability Properties of Epoxy-Based Preliminary Composites

The LOI and UL-94 test results for preliminary composites are given in Table 4.1. In the first step of the preliminary composites, barium metaborate (BaM) was used at different ratios (5%, 10% and 20%). LOI value of neat epoxy was 19%. Adding 5%

BaM to neat epoxy increased the LOI value up to 25.75%. Also, LOI value increased up to 25.90% and 26.25% with the addition of 10% and 20% BaM, respectively. The increase of BaM concentration did not change the LOI value too much. Thus, BaM was used at lower concentration in final composites. The reason of the increase in the LOI value may be due to the formation of glassy layer on the polymer surface at high temperatures. Adding 1% zinc borate (ZnB) increased to the LOI value from 19% to 24.5%. This was due to the formation of protective glassy layer which protects the unburnt polymer from the flame. Furthermore, ZnB loses its crystalline water during combustion which dilutes the flammable gases and also released water act as a heat sink which decreases the temperature at the burning zone. Although adding BaM and ZnB into the epoxy matrix increased the LOI value when compared to that of neat epoxy, they failed to pass the UL-94 vertical burning test. The LOI results showed that BaM and ZnB are effective flame retardants for epoxy-based composites.

10% melamine polyphosphate (MPP) loading increased the LOI value to 26.5% and also reached V-1 in UL-94 result which indicates that material was self-extinguished between 10 and 30 seconds, without dripping. However, MPP was not used in final composites; the reason for this will be explained in next section.

Table 4.1 The LOI and UL-94 Results of Preliminary Composites

Sample (wt%)	**LOI (%O_2)**	**UL-94**
EP	19.00	No Rating
EP/5BaM	25.75	No Rating
EP/10BaM	25.90	No Rating
EP/20BaM	26.25	No Rating
EP/1ZnB	24.50	No Rating
EP/10MPP	26.50	V-1
EP/1BaM/1ZnB	24.25	No Rating
EP/10MP/1ZnB	26.00	V-1
EP/10MP/5RP	29.50	V-0
EP/10MP/5RP/1BaM	30.00	V-0
EP/5RP/3ZnB	27.50	V-1
EP/15MP/5PER	27.50	V-0
EP/15MP/5DPER	27.50	V-0

Then, binary and ternary composites were produced. In order to investigate the synergistic effect between BaM and ZnB, EP/1BaM/1ZnB composite was produced. Using BaM together with ZnB was not change the LOI value compared to EP/1ZnB composite. Therefore, they did not synergist to each other. Also, 10% MP were used together with 1% ZnB and the LOI value increased to 26.0% and UL-94 test showed V-1 rating.

When 5% red phosphorus (RP) together with 10% melamine phosphate (MP) was used instead of 1% ZnB and the LOI value reached 29.5% and V-0 rating in UL-94 test which indicates that material was self-extinguished in less than 10 seconds, without dripping. Also, with the addition of 1% BaM to the EP/10MP/5RP, the LOI value increased to 30% and V-0 rating in UL-94 test. The flammability test results showed that addition of red phosphorus combined with MP and BaM was effective in flame retardancy for epoxy resin. Under thermal stress, RP break down to form P_2 molecules which are active species in the gas phase [73]. Even though RP gave the good result in the flammability test, phosphine gas was formed during combustion, and it is a toxic gas and could be a threat to the health. Therefore, encapsulated RP generally are used as flame retardant additives. However, there was a similar study in the literature about flame retardant effect of boron compounds on epoxy containing red phosphorus; therefore red phosphorus was not used in the formulation of final composites [74-76].

Although barium metaborate increased the LOI value of epoxy-based composites, it did not show any improvement in UL-94 test. Therefore, intumescent effect of flame retardant addition on the prepared of epoxy-based composites, containing melamine phosphate, pentaerythritol (PER) and dipentaerythritol (DPER) was also investigated. MP was used as acid source and blowing agent. PER and DPER were used as a carbon source. Although EP/15MP/5PER and EP/15MP/5DPER were showed the same results of 27.5% LOI value and V-0 rating in UL-94 test, DPER was used in final composition as a flame retardant additive. This is due to a few studies about this addition are available in the literature to our knowledge.

4.1.2 Mechanical Behaviors of Epoxy-Based Preliminary Composites

The tensile test results of preliminary composites and discussion on these results are given below. Five specimens were tested to evaluate the average values of test results except for EP/10MPP, EP/1BaM/1ZnB, EP/10MP/5RP/1BaM and EP/15MP/5PER. Three or four specimens were tested for these composites which have similar values with the different samples.

The tensile strength of preliminary composites is shown in Figure 4.1 and the detail tensile strength data is tabulated in Table A.1 of Appendix A. It can be observed that the tensile strength of BaM containing epoxy-based composites decreased slightly from 50 MPa to 44.1 MPa with the increase of BaM concentrations from 0 to 20% by weight. The decrease can also be considered to be within the limiting standard deviation. This can be a result of non-homogeneous distribution at high loadings of BaM. So, BaM particles can form agglomerates and create stress concentrated areas. According to Figure 4.1, 10% MPP loading decrease the tensile strength value significantly. This can be related to poor adhesion between epoxy and MPP which can cause the low load transfer. The tensile strength values of the EP/10MP/1ZnB, EP/10MP/5RP, EP/10MP/5RP/1BaM, EP/5RP/3ZnB composites did not change significantly. However, the tensile strength of the EP/15MP/5PER and EP/15MP/5DPER composites decreased significantly. This is the result of poor compatibility of MP and PER/DPER with the epoxy matrix, and due to presence of high amounts of flame retardant additives in the composites [77].

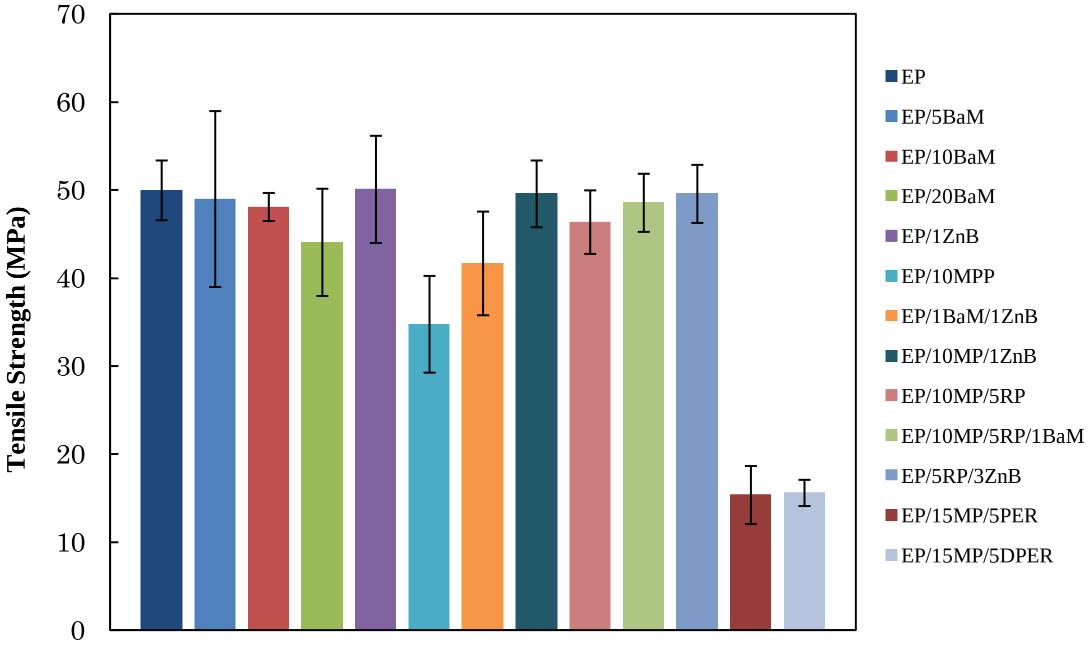

Figure 4.1 Tensile Strength of Preliminary Composites

Tensile moduli of the preliminary composites are given in Figure 4.2 and the detail tensile modulus data are tabulated in Table A.2 of Appendix A. In general, flame retardant additives increase the tensile modulus of composites. It is related to higher moduli of the additives. Tensile modulus of neat epoxy was 2761 MPa. According to the Figure 4.2, all composites had higher tensile modulus than neat epoxy except for EP/15MP/5PER and EP/15MP/5DPER. These composites were lower tensile modulus than neat epoxy which can be due to the PER and DPER structures. They are not flame retardant additives; but these additives are only used for carbon source as mentioned in the previous section. Therefore, they presumably showed plasticizing effect in the epoxy matrix. The highest tensile modulus was obtained for EP/10MP/5RP/1BaM composite. Tensile modulus increased from 2761 MPa to 3529.4 MPa. This can be related to high loading of additives which have higher moduli than that of the neat epoxy.

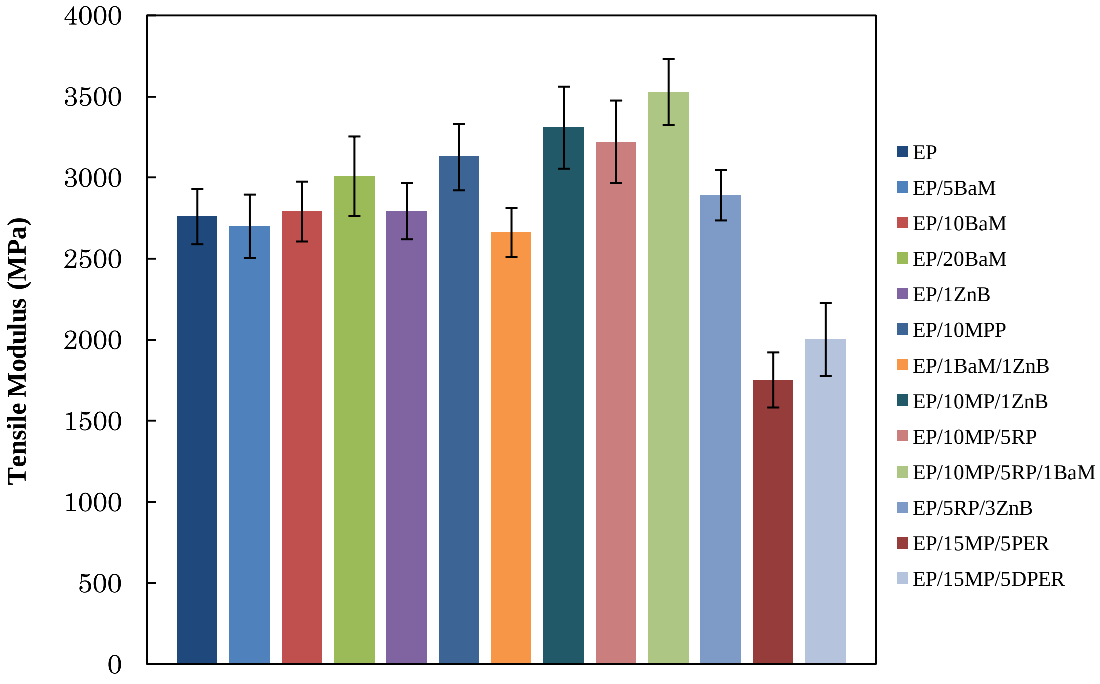

Figure 4.2 Tensile Modulus of Preliminary Composites

Elongation at break results of preliminary composites are shown in Figure 4.3 and the detail elongation at break data are tabulated in Table A.3 of Appendix A. In general, addition of flame retardant additives decreases the elongation at break value of neat epoxy. This can be a result of the restricted the mobility of polymer chain. When EP, EP/5BaM, EP/10BaM, and EP/20BaM were compared with each other, it was seen that increasing BaM percent decreased the elongation at break values. That may be related to the increasing concentration of this additive. Especially at high concentrations, BaM particles begin to agglomerate and form stress concentrated regions which as a result decreasing the elongation at break. On the other hand, when compared to other preliminary composites, loading of 10% MPP decreased the elongation at break value of neat epoxy much more than the others. Also, the most noticeable decrease was observed in the composites of EP/15MP/5PER and EP/15MP/5DPER just like the behavior observed in the tensile strength. This could be related to the presence of high amounts of flame retardant additives, which can cause irregular stress distribution in the epoxy-based composite, and also this can be resulted from the poor compatibility between MP and PER/DPER.

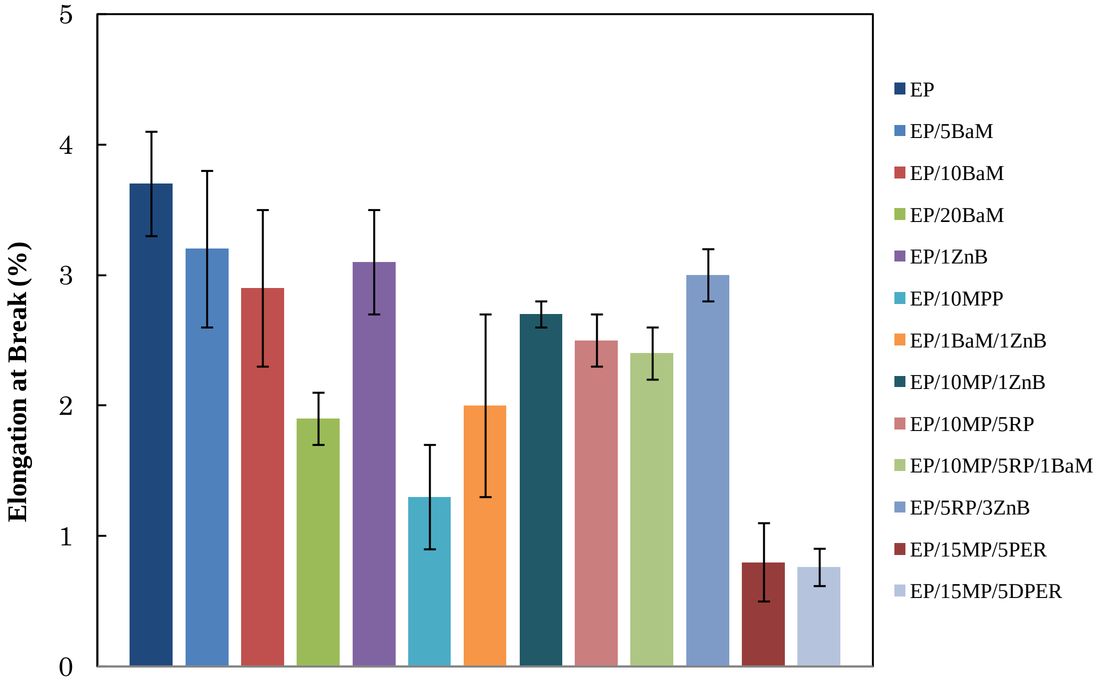

Figure 4.3 Elongation at Break of Preliminary Composites

According to the findings for the preliminary composites, the following can be summarized. Barium metaborate is an efficient flame retardant additive for the epoxy-based composites. Due to the low tensile properties of epoxy/MPP composite, it can be said that MPP is not suitable for epoxy and was not used in the final composites. Considering the mechanical test result, 20% of total loading can be considered excessively high for EP/MP/PER and EP/MP/DPER composites. Consequently, the concentration of additives should be lower than 20 wt % in the final composites. According to the result of flammability and mechanical tests, EP/15MP/5PER and EP/15MP/5DPER indicated the similar trends. Based on PER/DPER use, a few studies are available in the literature based to our knowledge, therefore, DPER was used as a carbon source in the final composites.

4.2 Characterization of Epoxy-Based Final Composites

Formulations of the final composites were prepared on the basis of the results from the preliminary experiments. Final composites were characterized by their morphology, flame retardation, thermal, and mechanical properties. Characterization of morphology was analyzed by SEM. Flame retardancy was evaluated by limiting oxygen index (LOI) and UL-94 vertical burning tests. Thermal stability and thermal degradation of compounds were studied by thermogravimetric analysis. Mechanical properties were investigated by tensile and impact tests.

4.2.1 Effects of Barium Metaborate on the Properties of Epoxy

The aim of this part is to investigate effects of lower amount of barium metaborate (BaM) on flame retardancy, and thermal and mechanical properties on the epoxy-based composites. As the higher amount of BaM did not change flammability of epoxy significantly, the addition of BaM into the epoxy was kept in small amounts. The formulations of the produced samples are given in Table 4.2.

Table 4.2 The Compositions of Neat Epoxy and EP/BaM Composites

Sample (wt%)	**EP**	**MP**	**DPER**	**MEC**	**BaM**	**ZnB**	**CaB**
EP	100	-	-	-	-	-	-
EP/0.5BaM	99.5	-	-	-	0.5	-	-
EP/1BaM	99	-	-	-	1	-	-
EP/3BaM	97	-	-	-	3	-	-

4.2.1.1 Morphological Analysis of Neat Epoxy and EP/BaM Composites

The scanning electron microscopy images of tensile fractured neat epoxy (EP) and impact fractured EP/3BaM are given in Figure 4.4 at 5000 and 10000 magnifications.

According to the Figure 4.4, smooth and glassy surfaces were observed for neat epoxy which indicates the brittle fracture. In the images, the white points, which are shown in white circles, indicate the barium metaborate particles. Surface roughness increased for the epoxy-based composite by adding 3% BaM into the epoxy matrix. A reduction in brittleness was expected by adding BaM to the polymer, due to the smooth fracture surface, which turns into a roughness in the structure according to Figure 4.4. There are some but few agglomerations of the particles. This result, which will be discussed in Section 4.2.1.5, can prove that EP/3BaM composite had lower mechanical properties with respect to the neat epoxy. Also, the distribution of BaM was observed to be homogeneous, but still not enough to improve the mechanical properties significantly.

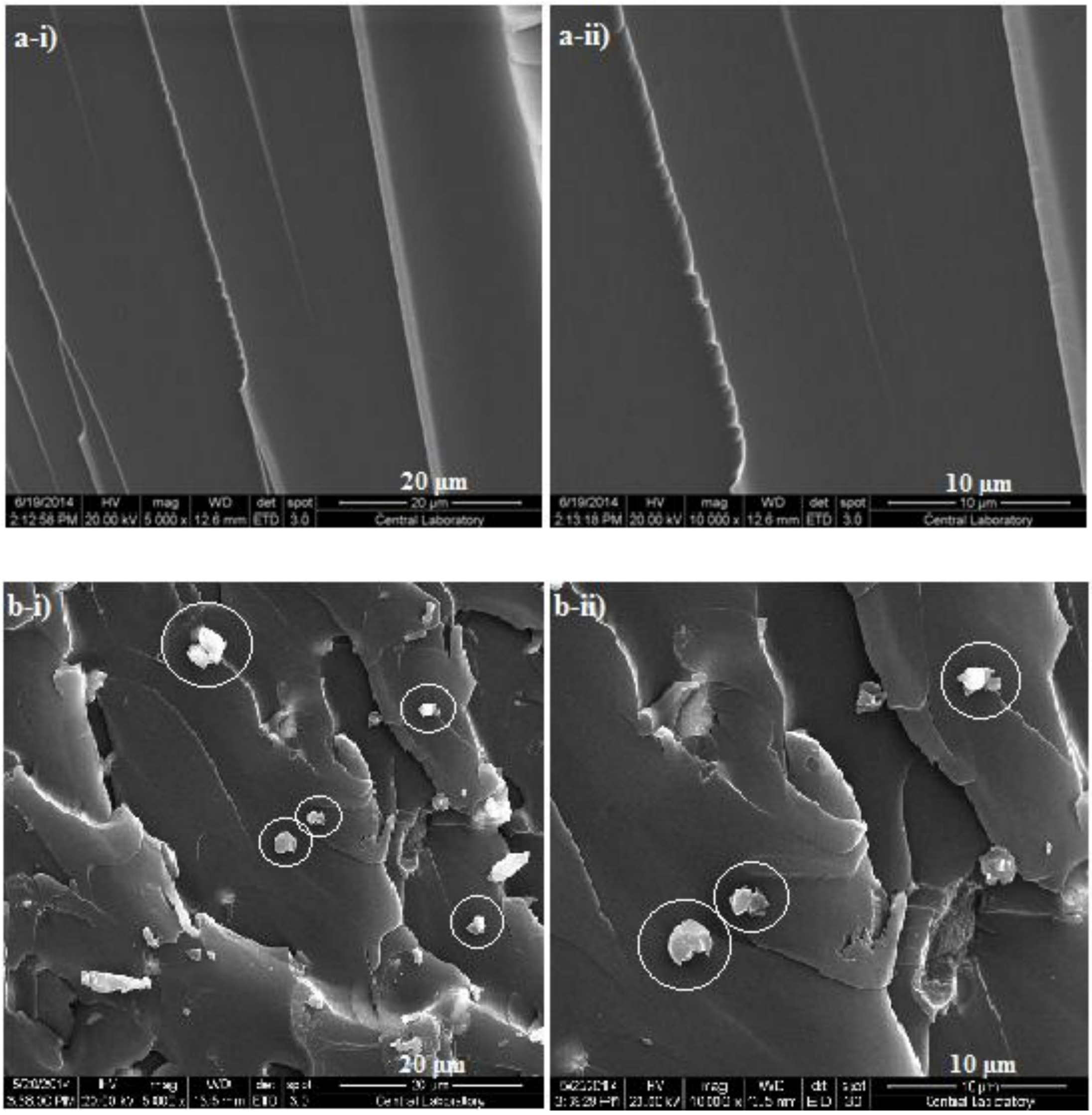

Figure 4.4 SEM images of a-i) Neat Epoxy at ×5000 magnification a-ii) Neat Epoxy at ×10000 magnification b-i) EP/3BaM at ×5000 magnification b-ii) EP/3BaM at ×10000 magnification

4.2.1.2 Flammability Properties of Neat Epoxy and EP/BaM Composites

The results of LOI and UL-94 vertical burning tests for neat epoxy and EP/BaM composites are given in Table 4.3.

Table 4.3 The Flammability Test Results of Neat Epoxy and EP/BaM Composites

Composites	**LOI (%O_2)**	**UL-94**
EP	19.00	No Rating
EP/0.5BaM	24.50	No Rating
EP/1BaM	25.00	No Rating
EP/3BaM	25.50	No Rating

The LOI and UL-94 flammability tests indicated that neat epoxy is a flammable polymer. Adding 0.5 % BaM into epoxy increased the LOI value of neat epoxy by 5.5 % from 19.0 % to 24.5 %. This result clearly shows that lower amount of BaM into epoxy matrix are effective in flame retardation for epoxy. When the concentration of BaM was increased from 0.5 % to 3 %, The LOI value increased from 24.5 % to 25.5 %. The reason of this increment in LOI value can be due to glassy layer formed on the polymer surface at high temperature. This layer insulates the bulk of the polymer from heat source by the formation of released B_2O_3. Also, barium metaborate decomposes endothermically, loses its hydration water at high temperature which dilutes the flammable gases and also releases water which acts as a heat sink and decreases the temperature. For this reason, the increase in LOI value was obtained for the epoxy-based composites containing BaM.

4.2.1.3 FTIR Results of Neat Epoxy and EP/BaM Composites

Chemical structures of produced composites were also characterized through FTIR analyses. FTIR results of the neat epoxy and the epoxy-based composites are given in Figure 4.5.

Barium metaborate includes B_3-O and B_4-O bonds with characteristic peaks at 852, 960, 1049 and 1446 cm^{-1}. The 852 cm^{-1} absorption peak showed symmetric vibration of B_4-O bond and the 960 cm^{-1} absorption peak showed symmetric vibration of B_3-O bond. The characteristic absorption peak for the asymmetric vibration of B_4-O and B_3-O bands were seen in 1049 cm^{-1} and 1446 cm^{-1}, respectively [78].

Epoxy consists of C-C, C-H, C-O, C-O-C and phenyl rings and curing agent includes C-H, N-H and C-N bonds. According to Figure 4.5, the characteristic absorption peak for the C-H stretching of all the samples was between 2800 and 3000 cm^{-1} absorption range which belongs to the methylene group. The C=C stretching aromatic ring band and the C-C stretching of aromatic band were seen in 1600 cm^{-1} and 1508 cm^{-1} absorption ranges, respectively. The characteristic absorption peak for the C-O-C stretching of ethers was at a wavenumber of 1036 cm^{-1}. Absorption peak at 830 cm^{-1} belonged to C-O-C bonds for oxirane groups. The peak at 1180 cm^{-1} was the absorption peak for C-N bonds coming from cycloaliphatic amines [79].

EP/BaM composites showed the same characteristic absorption peaks with respect to neat epoxy in the FTIR analysis. Therefore, no change was observed in the chemical structure with the addition of BaM into the epoxy.

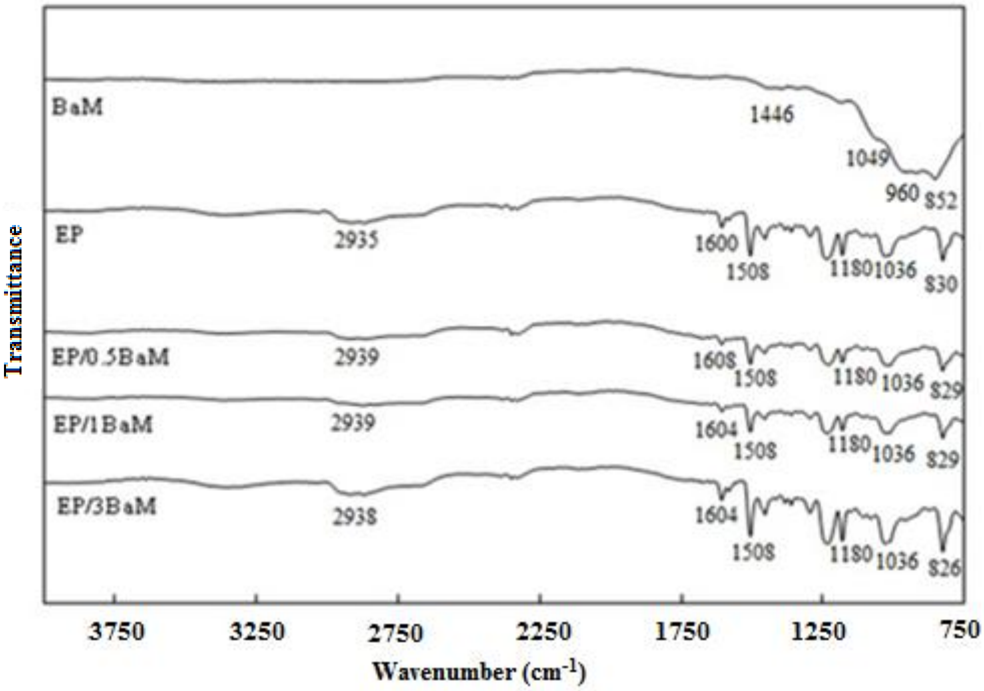

Figure 4.5 FTIR Results of Neat Epoxy and EP/BaM Composites

4.2.1.4 Thermal Analysis of Neat Epoxy and EP/BaM Composites

Results of thermogravimetric analysis for neat epoxy and EP/BaM composites are given in Figure 4.6. Onset of degradation temperature ($T_{10wt\%}$), half-way degradation temperature ($T_{50wt\%}$), maximum degradation temperatures and char yields at 900 ^{o}C are given in Table 4.4 and TG/DTA thermogram of samples is given in Appendix B, Figures B.1-B.4. Thermal decomposition temperature is a significant parameter for flame retardancy because the flame propagation and further free radical reactions take place at that temperature. Char yield is also important as char itself act as a heat insulator between flame and polymer surface, and prevents the further decomposition and further production of free radicals.

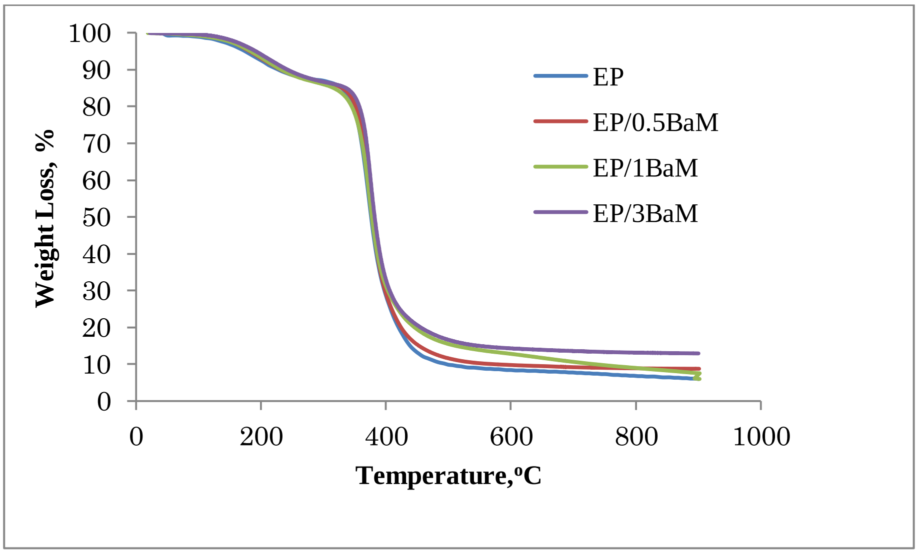

Figure 4.6 The TGA Curves of Neat Epoxy and EP/BaM Composites

Table 4.4 Thermal Degradation Temperatures and Char Yields of Neat Epoxy and EP/BaM Composites

Composites	**T_{Peak-1} (^{o}C)**	**T_{Peak-2} (^{o}C)**	**$T_{10wt\%}$ (^{o}C)**	**$T_{50wt\%}$ (^{o}C)**	**Char yield at 900^{o}C (%)**
BaM	214.8	-	677.7	-	89.99
EP	199.1	371.2	226.7	376.1	6.08
EP/0.5BaM	195.5	373.7	232.1	378.5	8.71
EP/1BaM	207.4	372.9	233.3	377.5	7.63
EP/3BaM	203.4	376.9	243.3	382.4	12.87

A two step decomposition is seen for neat epoxy with a maximum rate at 199.12 ^{o}C and 371.15 ^{o}C. Initial decomposition of neat epoxy was occurred due to the formation of C-C unsaturations via water elimination and the second decomposition was occurred because of the volatilization of small fragments [76].

It was clearly seen in Figure 4.6 that neat epoxy and EP/BaM composites decomposed similarly at the same temperature range. However, the amount of char formation increased with BaM loading as can be seen from Table 4.4. Char yield of neat epoxy was 6.08%, and EP/3BaM represented the highest char yield with respect to the neat epoxy and the other EP/BaM composites. Because BaM was more thermally stable than epoxy.

4.2.1.5 Mechanical Behaviors of Neat Epoxy and EP/BaM Composites

The general objective of this study was to improve flame retardant properties without sacrificing the mechanical properties of the composites. In order to investigate the effects of flame retardants on the mechanical properties of the epoxy-based composites, tensile and impact tests were applied. The detailed results of tensile and impact tests for the composites are given in Appendix A.

The tensile strength results of neat epoxy and EP/BaM composites are shown in Figure 4.7 and the detailed tensile strength data are tabulated in Table A.4 of Appendix A. Tensile strength value of neat epoxy was 50.0 MPa. Addition of 0.5% and 1% barium metaborate increased the tensile strength slightly, compared to the neat epoxy. When 3% BaM was added to epoxy, a small decrease in the tensile strength value was observed, which could be the result of agglomeration of the additive due to its relatively higher concentration. Agglomeration which acts as stress concentrated areas in the composite results in decrease in tensile strength.

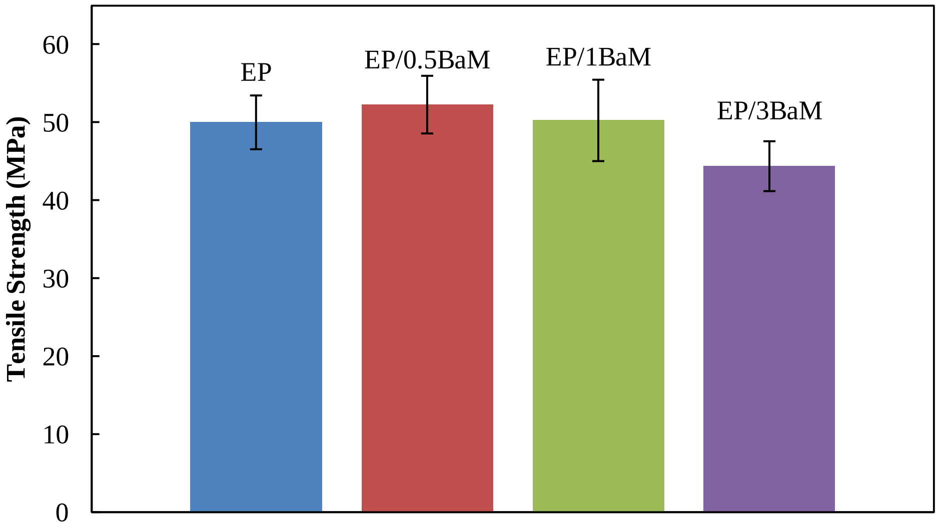

Figure 4.7 Tensile Strength of Neat Epoxy and EP/BaM Composites

Tensile modulus of neat epoxy and EP/BaM composites are given in Figure 4.8, and the detailed tensile modulus data is tabulated in Table A.5 of Appendix A, The tensile modulus of neat epoxy was 2761 MPa. Adding BaM to neat epoxy did not change the tensile modulus value significantly. This can be results of the low concentrations of BaM. In Section 4.1.2, adding 20% BaM into epoxy matrix increased tensile modulus from 2761 MPa to 3009 MPa due to much higher concentration of this additive.

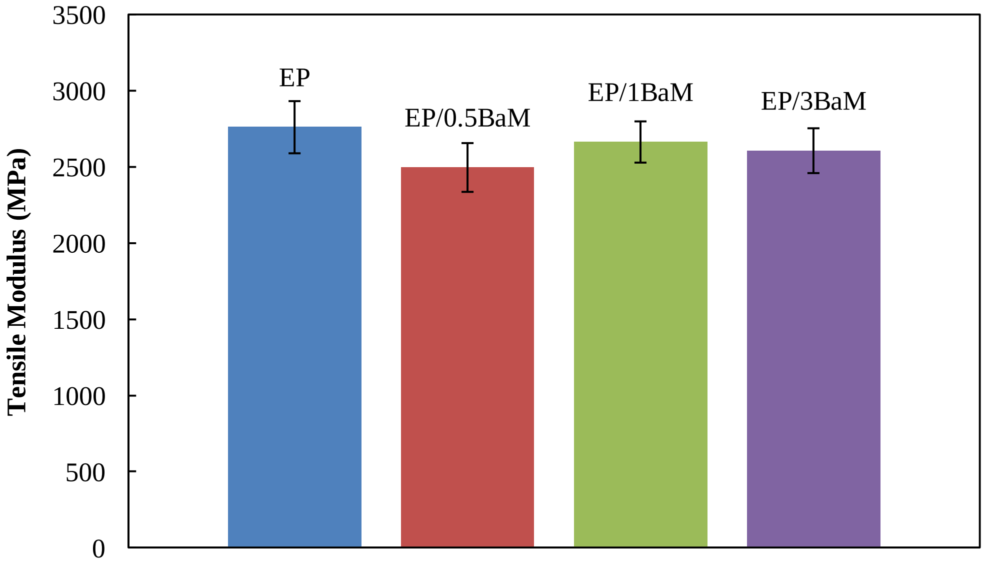

Figure 4.8 Tensile Modulus of Neat Epoxy and EP/BaM Composites

Elongation at break data of the neat epoxy and EP/BaM composites are given in Figure 4.9, and the detailed elongation at break data are tabulated in Table A.6 of Appendix A. Elongation at break value of neat epoxy was 3.7%. The elongation at break values of EP/0.5BaM and EP/1BaM did not change when compared to the neat epoxy. However, adding 3% BaM decreased the elongation at break value from 3.7% to 3.3%. This can be due to the same reason given in the explanation for decrease in tensile strength with 3% BaM addition to the epoxy. At high concentrations of BaM particles agglomerates form, and they create weak points and this results in an easy breakage of the material.

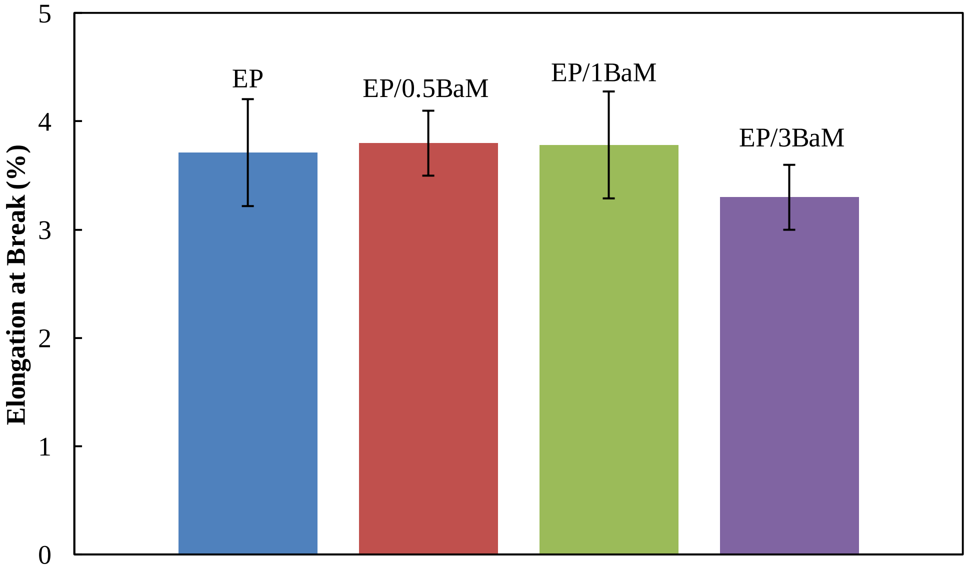

Figure 4.9 Elongation at Break Values of Neat Epoxy and EP/BaM Composites

Impact strength value of neat epoxy and EP/BaM composites are illustrated in Figure 4.10, and the detailed impact strength data are tabulated in Table A.7 of Appendix A. The results showed that adding BaM into the epoxy matrix reduced the impact strength. 0.5% BaM decreased the impact strength of neat epoxy from 11.4 kJ/m^2 to 3.9 kJ/m^2. Addition of 1% and 3% BaM to the neat epoxy increased the impact strength slightly when compared to the EP/0.5BaM. The reason of decrease in impact strength of neat epoxy could be due to the agglomerations of the barium metaborate. Because BaM is an inorganic additive and it could not react with epoxy matrix as can be obtained from FTIR analyses. As a result, it may create stress concentration areas, and this should reduce the impact strength value of the composites.

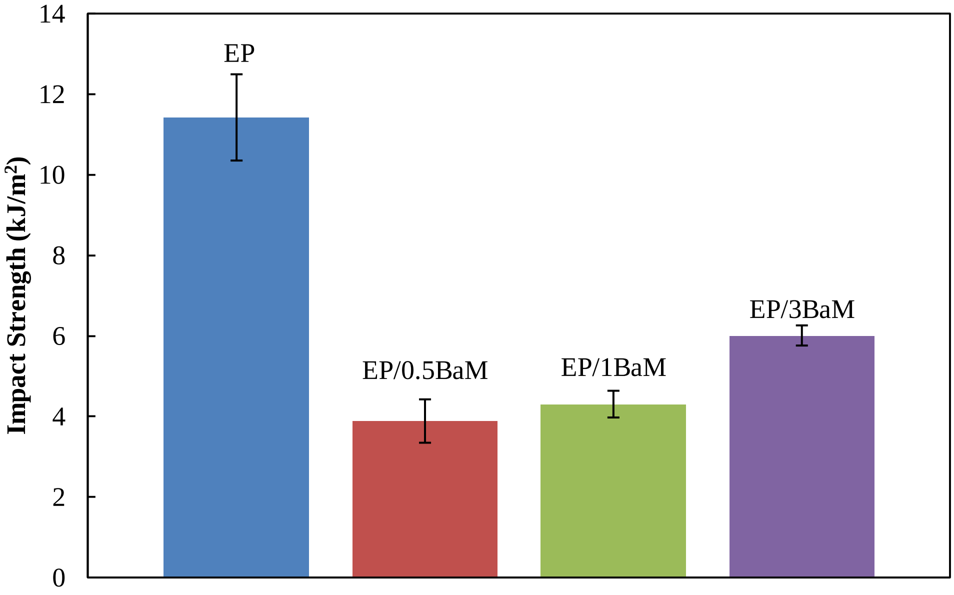

Figure 4.10 Impact Strength of Neat Epoxy and EP/BaM Composites

When all the test result of EP/BaM composites were assessed together, 1% BaM loading was chosen as the optimum concentration for the epoxy-based composite in the rest of the studies.

4.2.2 Effects of Methacrylate Epoxy Cyclosiloxane on the Properties of Epoxy

The aim of this part is to investigate the flame retardancy, thermal and mechanical effects of methacrylate epoxy cyclosiloxane (MEC) on properties of epoxy-based composites at various concentrations (0.5%, 1%, 3%) [21]. MEC structure was similar to epoxy, but the only difference between epoxy and MEC was Si atoms in the polymer backbone of MEC. The compositions of the samples are given in Table 4.5.

Table 4.5 The Compositions of Neat Epoxy and EP/MEC Composites

Sample (wt%)	EP	MP	DPER	MEC	BaM	ZnB	CaB
EP	100	-	-	-	-	-	-
EP/0.5MEC	99.5	-	-	0.5	-	-	-
EP/1MEC	99	-	-	1	-	-	-
EP/3MEC	97	-	-	3	-	-	-

4.2.2.1 Morphological Analysis of EP/MEC Composites

The SEM images of fracture surface which were taken from impact test samples of EP/1MEC composite is given in Figure 4.11 at different magnitudes. As discussed in Section 4.2.1.1, the fractured surface of neat epoxy was very smooth, which was a sign of brittle fracture. By adding 1% MEC into the neat epoxy, similar surface fracture was observed because of the similar structures of epoxy and MEC. Therefore, mechanical properties of them are expected to be similar.

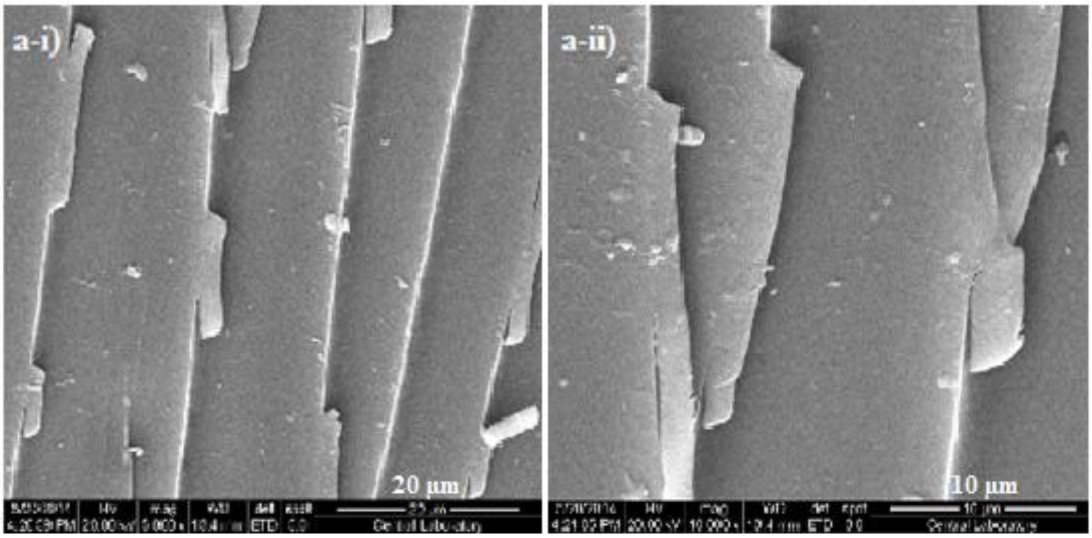

Figure 4.11 SEM images of a-i) EP/1MEC at ×5000 magnification a-ii) EP/1MEC at ×10000 magnification

4.2.2.2 Flammability Properties of Neat Epoxy and EP/MEC Composites

LOI values and UL-94 vertical burning test results for neat epoxy and EP/MEC composites are given in Table 4.6.

Table 4.6 The Flammability Test Results Neat Epoxy and EP/MEC Composites

Composites	**LOI (%O_2)**	**UL-94**
EP	19.0	No Rating
EP/0.5MEC	23.5	No Rating
EP/1MEC	24.0	No Rating
EP/3MEC	24.0	No Rating

According to the neat epoxy, there was a 4.5 % increase in the LOI value of EP/0.5 BaM composite. This increase can stems from the substance of silicon in the structure of methacrylate epoxy cyclosiloxane. Silicon-based additives were decomposed during the thermal decomposition and formed silicon oxide (SiO_2), which provides an insulating layer and prevent further decomposition of the material [76, 80]. Adding 1% MEC increased the LOI value up to 24% but 3% MEC addition did not change the LOI value. Also, epoxy-based composites failed to pass the UL-94 test and results showed 'no rating'.

4.2.2.3 FTIR Results of Neat Epoxy and EP/MEC Composites

Chemical structure of produced composites was also characterized by FTIR analyses. FTIR results of the neat epoxy and EP/MEC composites are given in Figure 4.12.

FTIR spectra of neat epoxy and EP/MEC composites resemble to each other due to nearly having same chemical structure of epoxy and MEC. The characteristic absorption peak for the C-H stretching of all of the samples was between 2800 and 3000 cm^{-1} absorption range. The C=C stretching aromatic ring band and the C-C stretching of aromatic band were seen at 1600 cm^{-1} and 1508 cm^{-1} wavenumbers, respectively. The characteristic absorption peak for the C-O-C stretching of ethers was at 1036 cm^{-1}. Absorption peak 830 cm^{-1} show C-O-C bonds for oxirane groups. The peak at 1180 cm^{-1} was the absorption peak for C-N bonds coming from cycloaliphatic amines.

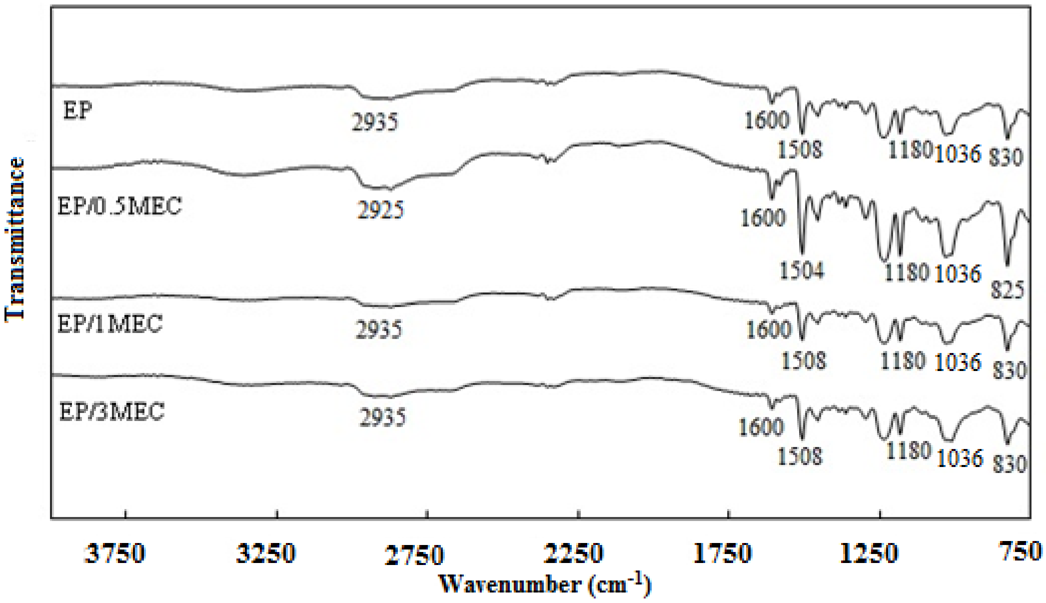

Figure 4.12 FTIR Results of Neat Epoxy and EP/MEC Composites

4.2.2.4 Thermal Analysis of Neat Epoxy and EP/MEC Composites

Results of thermogravimetric analysis for neat epoxy and EP/MEC composites are shown in Figure 4.13. Onset of degradation temperature ($T_{10wt\%}$), half-way degradation temperature ($T_{50wt\%}$), maximum degradation temperatures and char yields at 900 °C are given in Table 4.8, and TG/DTA thermograms of the samples are given in Appendix B.

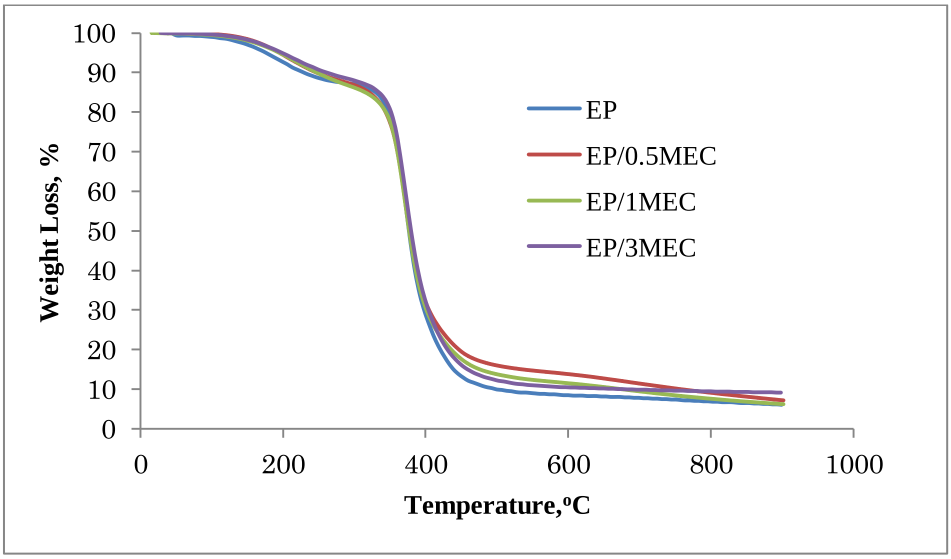

Figure 4.13 The TGA Curves of Neat Epoxy and EP/MEC Composites

Table 4.7 Thermal Degradation Temperatures and Char Yields of Neat Epoxy and EP/MEC Composites

Composites	**T_{Peak-1} (°C)**	**T_{Peak-2} (°C)**	**$T_{10wt\%}$ (°C)**	**$T_{50wt\%}$ (°C)**	**Char yield at 900°C (%)**
EP	199.1	371.2	226.7	376.1	6.08
EP/0.5MEC	207.2	371.6	246.4	376.8	7.20
EP/1MEC	218.1	371.6	246.9	376.6	6.32
EP/3MEC	223.8	373.7	255.4	379.6	9.11

According to Table 4.7, degradation temperature of epoxy resin was improved by the addition of MEC up to 3%. The first decomposition temperature of neat epoxy increased from 199.1 ^{o}C to 223.8 ^{o}C with 3% MEC loading. Methacrylate epoxy cyclosiloxane contain Si atoms in its structure. When it was decomposed, SiO_2 was formed, which raised the decomposition temperature of polymer, and resulted in a higher char yield [81]. It can be seen from Table 4.7 that the amount of char yield increased with MEC loading.

4.2.2.5 Mechanical Behaviors of Neat Epoxy and EP/MEC Composites

The tensile strength of neat epoxy and EP/MEC composites are given in Figure 4.14, and the detailed tensile strength data are tabulated in Table A.4 of Appendix A. When compared to the neat epoxy, tensile strength of EP/MEC composites decreased at all MEC concentrations. This can be related to MEC acted as a diluent in polymer blend and it may decrease the crosslink density of epoxy. Thus, tensile strength values of epoxy-based composites reduced with the addition of MEC to the neat epoxy.

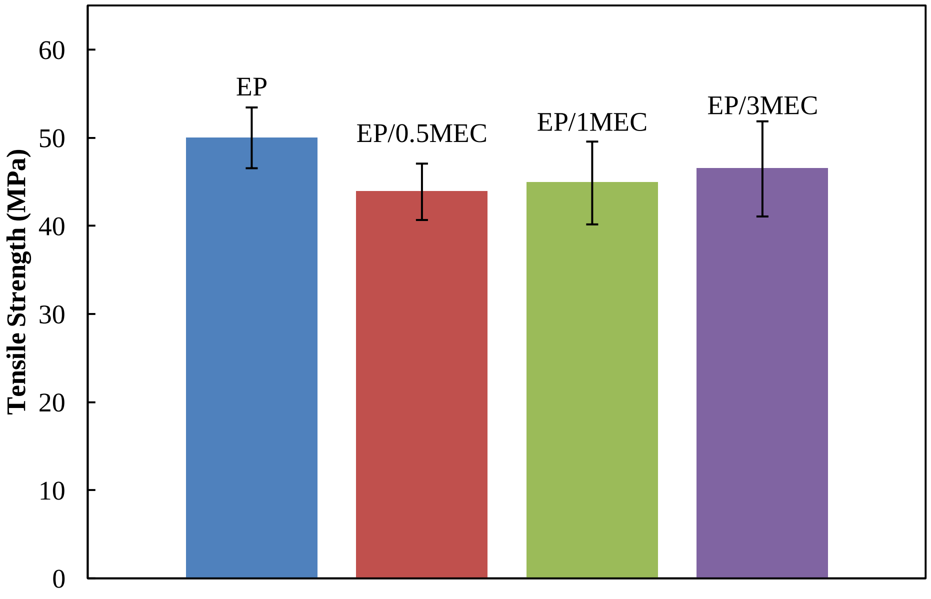

Figure 4.14 Tensile Strength of Neat Epoxy and EP/MEC Composites

The tensile modulus results of neat epoxy and EP/MEC composites are illustrated in Figure 4.15, and the detailed tensile modulus data are tabulated in Table A.5 of Appendix A. Neat epoxy had tensile modulus value of 2761 MPa. Tensile modulus of the EP/MEC composite decreased with the addition of MEC to 2267 MPa at 3% MEC concentration. This decrease can be related to the same reason, which was explained for the decrease of tensile strength as it was caused by diluent effect of MEC on the polymer composites.

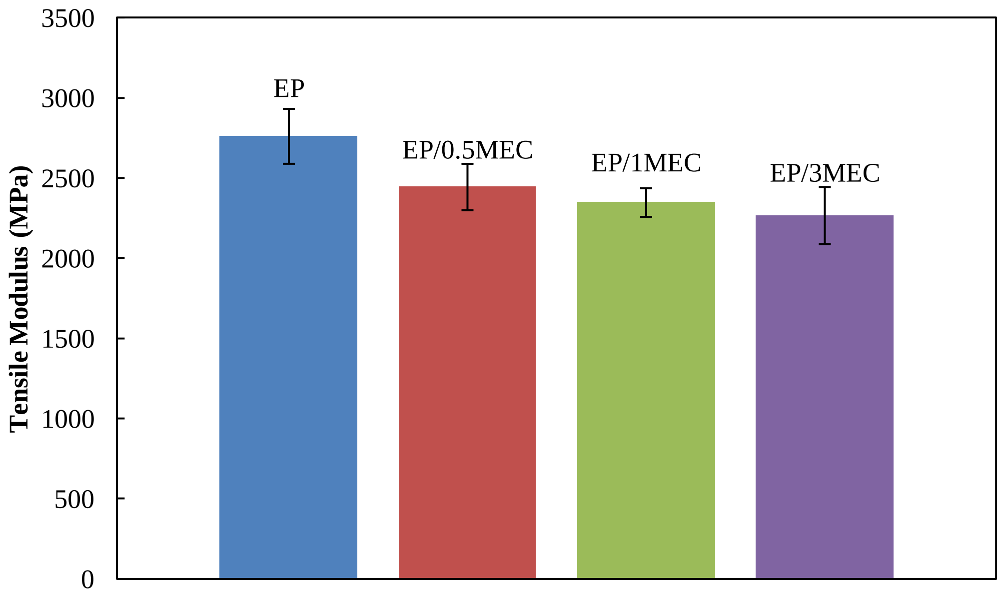

Figure 4.15 Tensile Modulus of Neat Epoxy and EP/MEC Composites

The elongation at break results of neat epoxy and EP/MEC composites are given in Figure 4.16, and the detailed elongation at break data are tabulated in Table A.6 of Appendix A. Addition of MEC had a positive impact on the elongation at the break. While elongation at break value of neat epoxy was 3.7%, 0.5% MEC loading was increased the elongation at break value to 4.3%. This can be due to the liquid structure of MEC which makes diluent effect on the polymer blends, and decreased crosslink density of epoxy and eventually increased the elongation at break value.

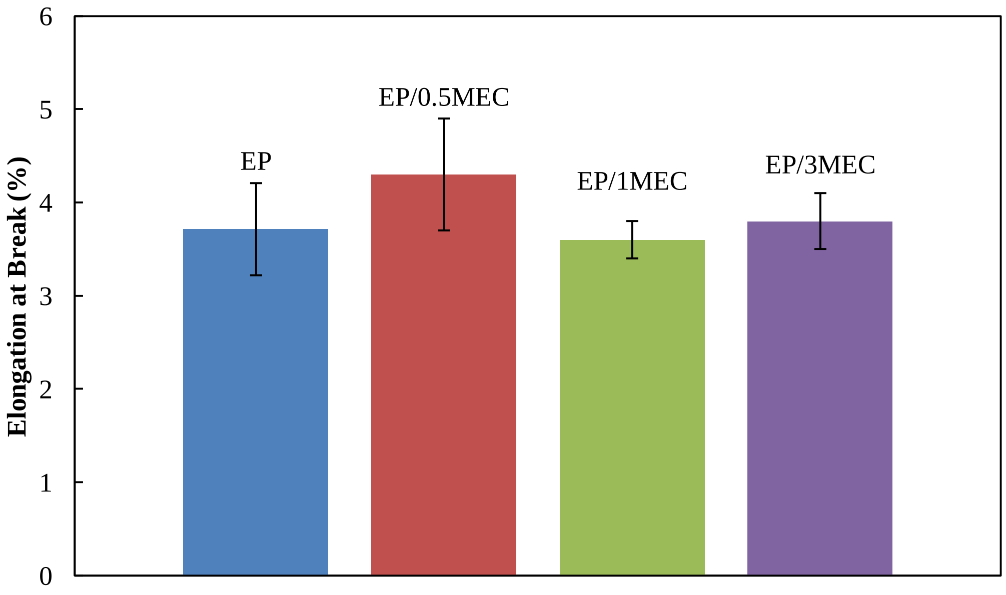

Figure 4.16 Elongation at Break of Neat Epoxy and EP/MEC Composites

The impact strength results of neat epoxy and EP/MEC composites are given in Figure 4.17, and the detailed impact strength data are tabulated in Table A.7 of Appendix A. The impact strength was decreased with the addition of MEC. It may be related to non-homogeneous distribution of MEC in the epoxy matrix or diluent effect of MEC on the polymer blends which caused to decrease crosslink density of epoxy. As shown in Figure 4.17, increase of the MEC concentration decreased the impact strength values of the epoxy-based composites.

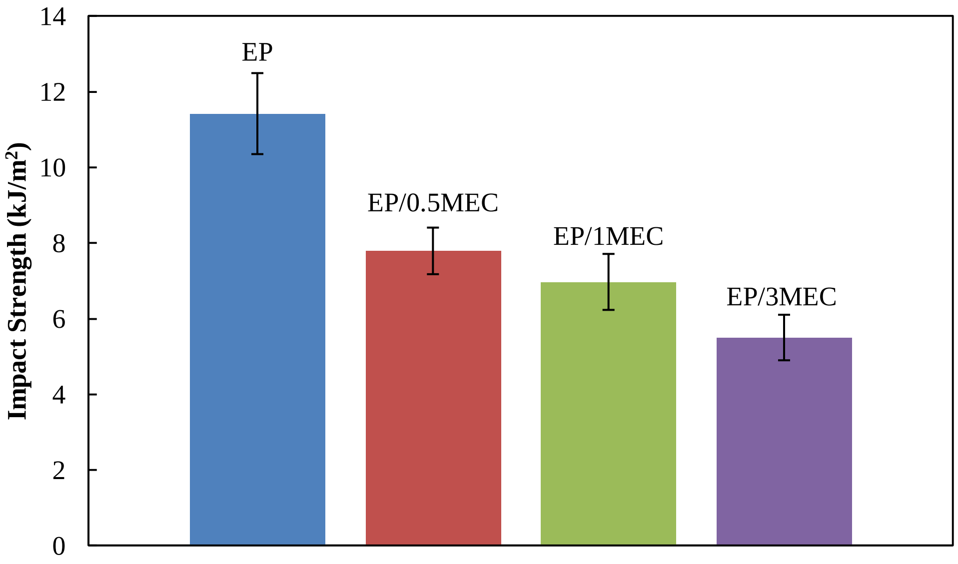

Figure 4.17 Impact Strength of Neat Epoxy and EP/MEC Composites

When the entire test results of EP/MEC composites, especially the LOI test results, were assessed together, 1% MEC was chosen as the optimum concentration for epoxy-based composites to be used in further related parts of the thesis.

4.2.3 Effects of Melamine Phosphate with Dipentaerythritol on the Properties of Epoxy

In this part of the thesis, the effects of the intumescent additives on the flame retardancy and the thermal and mechanical properties of the epoxy-based composites will be summarized. For the analyses, melamine phosphate (MP), dipentaerythritol (DPER), and their combinations at different ratios of 3:1, 1:1, and 1:3 were added into epoxy and the results were investigated. The compositions of samples are given in Table 4.8.

Table 4.8 The Compositions of Neat Epoxy and Composite Containing MP and/or DPER

Sample (wt%)	**EP**	**MP**	**DPER**	**MEC**	**BaM**	**ZnB**	**CaB**
EP	100	-	-	-	-	-	-
EP/10MP	90	10	-	-	-	-	-
EP/7.5MP/2.5DPER	90	7.5	2.5	-	-	-	-
EP/5MP/5DPER	90	5.0	5.0	-	-	-	-
EP/2.5MP/7.5DPER	90	2.5	7.5	-	-	-	-
EP/10DPER	90	-	10	-	-	-	-

4.2.3.1 Morphological Analysis of Composite Containing MP and/or DPER

The SEM images of impact fractured samples of EP/10MP and EP/5MP/5DPER composites at different magnitudes are given in Figure 4.18.

The fracture surface of the EP/10MP composite showed considerably different structure from the fracture surface of the neat epoxy (Figure 4.4). A much rougher surface of EP/10MP composite was obtained due to the MP addition.

Figure 4.18.b-i and 4.18.b-ii showed the SEM images of EP/5MP/5DPER composites at 5000 and 10000 magnifications, respectively. The images seem similar to the SEM photographs of EP/10MP composite (Figure 4.18.a-i and 4.18.a-ii).

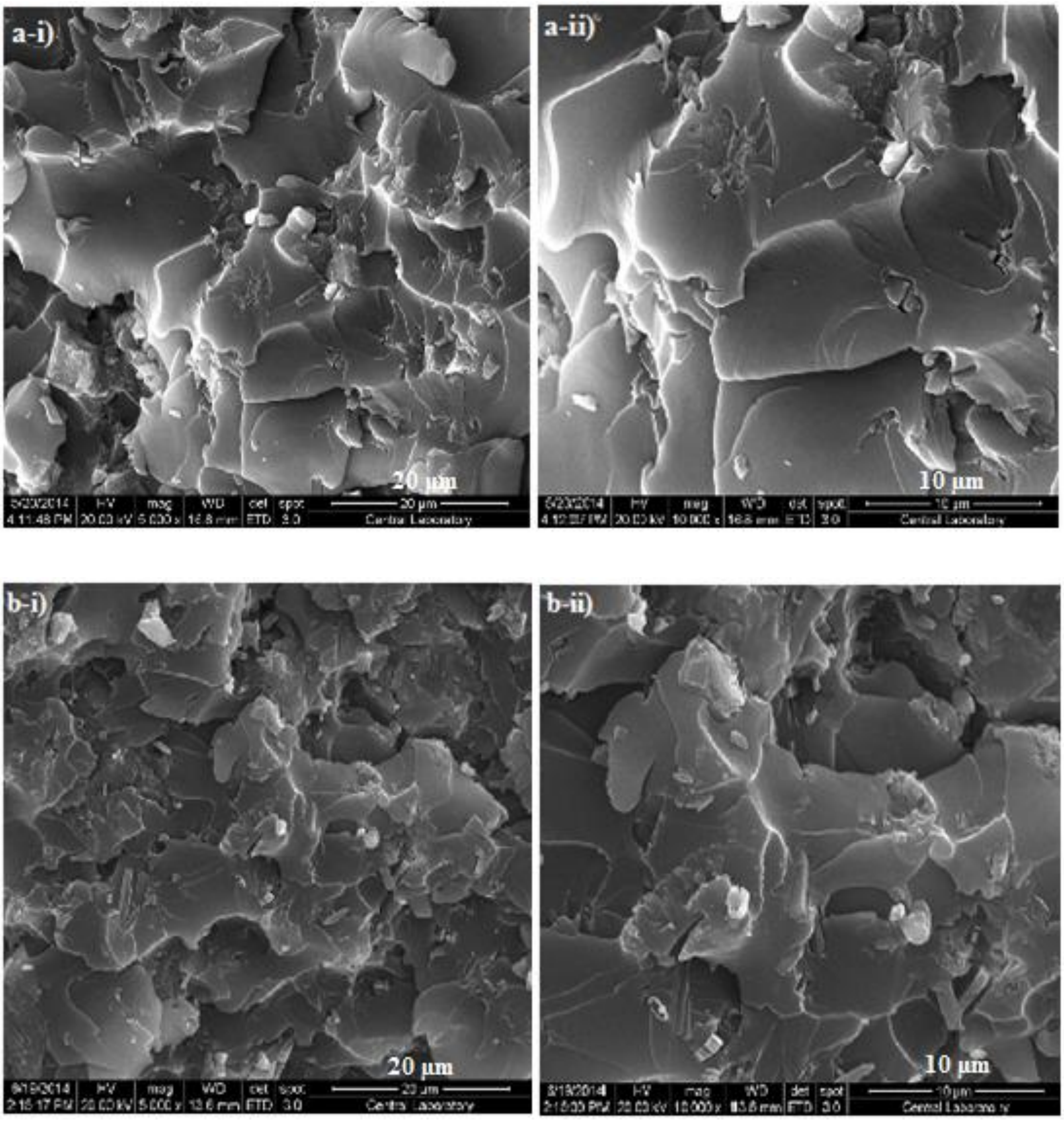

Figure 4.18 SEM images of a-i) EP/10MP at ×5000 magnification a-ii) EP/10MP at ×10000 magnification b-i) EP/5MP/5DPER at ×5000 magnification b-ii) EP/5MP/5DPER at ×10000 magnification

4.2.3.2 Flammability Properties of Neat Epoxy and Composite Containing MP and/or DPER

In order to investigate the effects of melamine phosphate, dipentaerythritol and their combinations with different ratios of 3:1, 1:1 and 1:3 on the flammability of the epoxy-based composites, LOI and UL-94 vertical burning tests were done, and their results are given in Table 4.9.

Table 4.9 The Flammability Test Results of Neat Epoxy and Composite Containing MP and/or DPER

Composites	**LOI (%O_2)**	**UL-94**
EP	19.0	No Rating
EP/10MP	27.0	No Rating
EP/7.5MP/2.5DPER	25.0	No Rating
EP/5MP/5DPER	24.5	No Rating
EP/2.5MP/7.5DPER	24.5	No Rating
EP/10DPER	24.0	No Rating

In intumescent systems, generally three main components are required as mentioned in Section 2.2.3.1. These are the acid source, the carbon source and the blowing agent. According to Table 4.9, melamine phosphate was used as an acid source and blowing agent and dipentaerythritol were used as the carbon sources [55, 77].

As it can be seen from Table 4.9 that adding 10% melamine phosphate to neat epoxy, increase the LOI value from 19% to 27%. The flame retardancy was provided by the elements of phosphorus and nitrogen, in MP. Melamine, which comes from thermal decomposition of melamine phosphate, can swell, leading to expansion of polymer and the formation of the swollen char [1, 12]. When melamine concentration was decreased, swelling effect of the composites also decreased and it can be seen in Figure 4.19. This swollen char can hinder the propagation of heat and oxygen into the inner polymer surface. In this way, it prevents the polymer from further burning. Also, inert volatile products, such as NH_3 and CO_2, dilute the oxygen and flammable gases in the gas phase.

According to Table 4.9, when melamine phosphate concentration decreased, the LOI value also decreased. DPER was used as a carbon source in this system but epoxy itself was also acted as a carbon source due to existing carbon in its structure [82]. Hence, it can be said that, DPER was not effective and not necessary for this system because of already available carbon content in the structure of epoxy.

The EP/10MP was found to be the best composite among the studied ones of this section with LOI value of 27 % due to its char-promoting mechanism, which enhance the protection of fire. However, EP/10MP composite still failed to pass the UL-94 test.

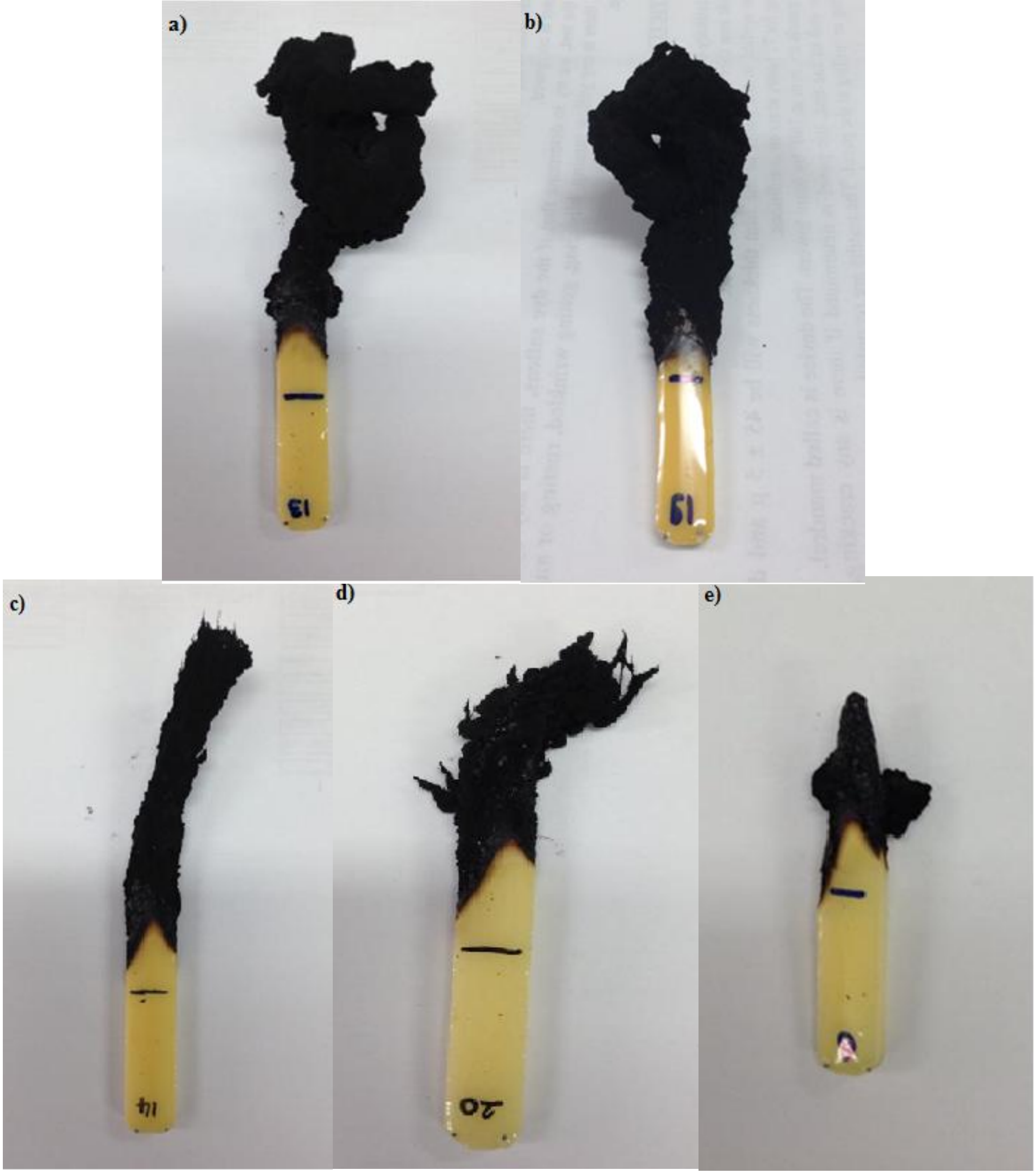

Figure 4.19 Photo of the Samples a) EP/10MP, b) EP/7.5MP/2.5DPER, c) EP/5MP/5DPER, d) EP/2.5MP/7.5DPER, e) EP/10DPER

4.2.1.3 FTIR Results of Neat Epoxy and Composite Containing MP and/or DPER

Chemical nature of MP and DPER filled epoxy-based composites were characterized using FTIR analysis. The FTIR results of the samples are given in Figure 4.20.

All of the composites showed similar results in FTIR analysis with respect to neat epoxy except for EP/10MP. Certain difference was observed in EP/10MP composites at 1670 cm^{-1} peak which can be attributed to the C=O stretching of amide group resulting from melamine phosphate. Because of the low concentration of melamine phosphate for the other composites, this peak was not observed for them. The characteristic absorption peak for the C-H stretching of all of the samples was between 2800 and 3000 cm^{-1} absorption range. The C=C and C-C stretchings of aromatic ring band were seen at 1600 cm^{-1} and 1508 cm^{-1} wavenumbers, respectively. The characteristic absorption peak for the C-O-C stretching of ethers was at 1036 cm^{-1} and the peak at 830 cm^{-1} show C-O-C bonds for oxirane groups. The peak at 1180 cm^{-1} was the absorption peak for C-N bonds from cycloaliphatic amines.

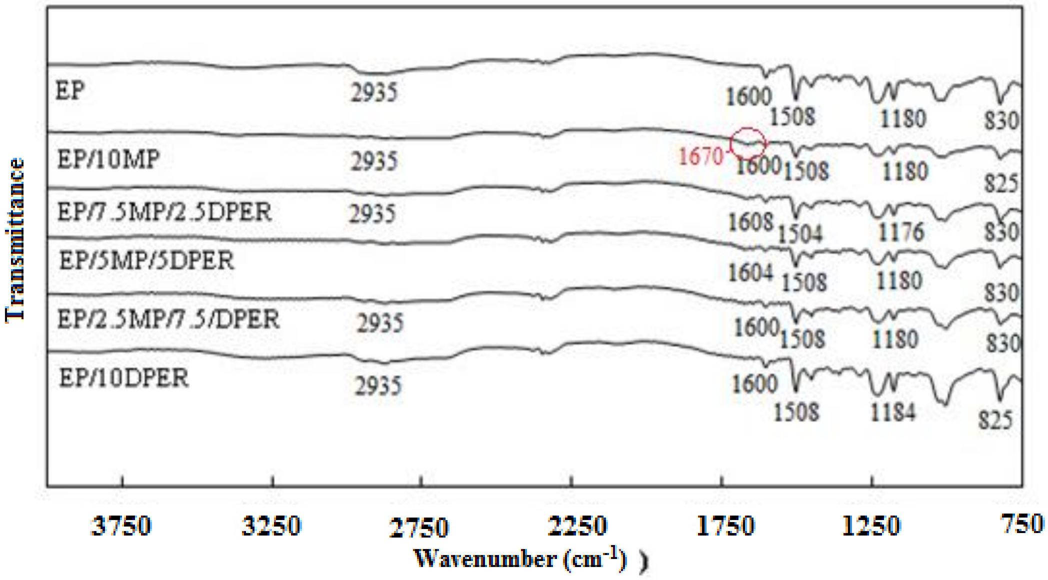

Figure 4.20 FTIR Results of Neat Epoxy and Composite Containing MP and/or DPER

4.2.3.4 Thermal Analysis of Neat Epoxy and Composite Containing MP and/or DPER

Results of thermogravimetric analyses for neat epoxy and containing MP and/or DPER composites are given in Figure 4.21. Onset of degradation temperature ($T_{10wt\%}$), half-way degradation temperature ($T_{50wt\%}$), maximum degradation temperatures and char yields at 900 ^{o}C are given in Table 4.10, and TG/DTA thermogram of samples are given in Appendix B.

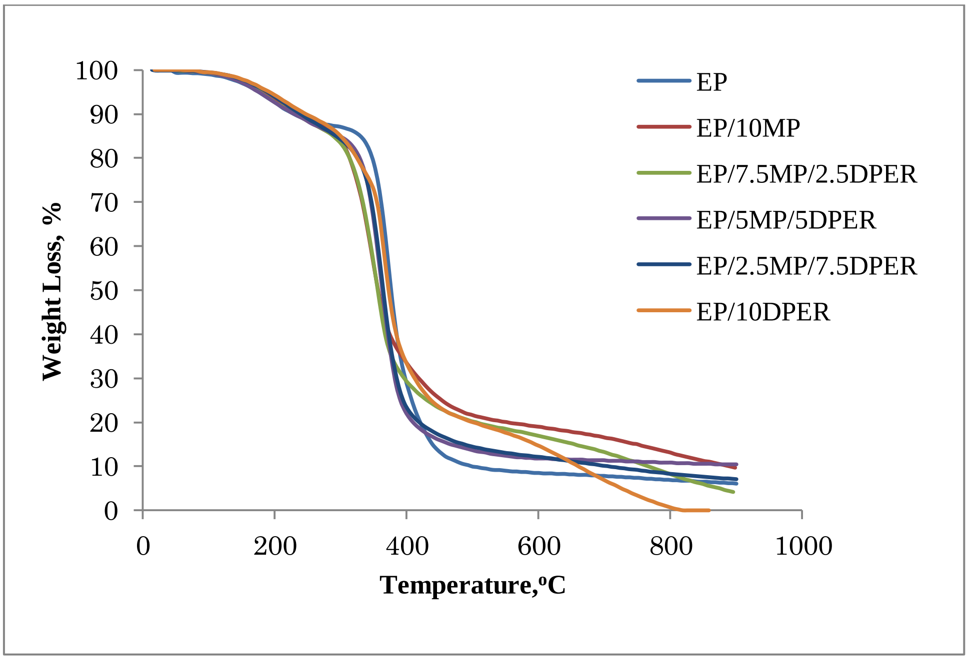

Figure 4.21 The TGA Curves of Neat Epoxy and Composite Containing MP and/or DPER

Table 4.10 Thermal Degradation Temperatures and Char Yields of Neat Epoxy and Composite Containing MP and/or DPER

Composites	**T_{Peak-1} (^oC)**	**T_{Peak-2} (^oC)**	**$T_{10wt\%}$ (^oC)**	**$T_{50wt\%}$ (^oC)**	**Char yield at 900^{o}C (%)**
MP	258.6	397.8	326.3	537.4	25.48
DPER	98.8	-	246.0	291.0	0
EP	199.1	371.2	226.7	376.1	6.08
EP/10MP	188.3	350.3	229.6	356.0	9.67
EP/7.5MP/2.5DPER	189.3	356.1	224.5	355.9	4.10
EP/5MP/5DPER	190.9	362.2	225.3	364.0	10.46
EP/2.5MP/7.5DPER	191.9	362.9	237.0	364.4	7.04
EP/10DPER	192.3	365.4	240.5	372.4	0

According to Table 4.10, the thermal stability of the composites decreased with the addition of additives. The most noticeable decrease was observed at 10% MP loading. The first and second decomposition temperatures decreased from 199.1 ^oC to 188.3 ^oC and from 371.2 ^oC to 350.3 ^oC, respectively. It may be due to the phosphate group in MP, which decomposes at lower temperature to generate heat-resistant char and it can retard the decomposition rate of epoxy [83]. While MP concentration decreased, the decomposition temperatures increased. Adding 10% DPER also decreased the decomposition temperature but not as much as MP.

The noticeable result of TGA test is that loading 10% MP to neat epoxy increased the char formation from 6.08% to 9.67%. This is because of the phosphorus-rich residue by phosphorous group of MP, which is able to protect and retard the epoxy matrix from further decomposition. On the other hand, it can be seen that EP/10DPER decomposes with no residue formation. This proves that DPER was acted as carbon source.

4.2.3.5 Mechanical Behaviors of Neat Epoxy and Composite Containing MP and/or DPER

Tensile strength values of epoxy-based composites are given in Figure 4.22, and the detailed tensile strength data are tabulated in Table A.4 of Appendix A. Tensile strength value of neat epoxy was 50.0 MPa. The tensile strength value of EP/10MP did not change significantly with the addition of melamine phosphate when compared to neat epoxy. It can be observed from Figure 4.22 that the tensile strength value decreased with the increase of the DPER concentration. The reason of that can be due to poor compatibility of MP and DPER with epoxy and also moisture sensitivity of DPER. DPER was a hydrophilic compound, and it was easily attacked by water (moisture). When DPER was blended with epoxy, the exudation of the additive might lead to a decrease in the mechanical properties of the epoxy-based composites [55].

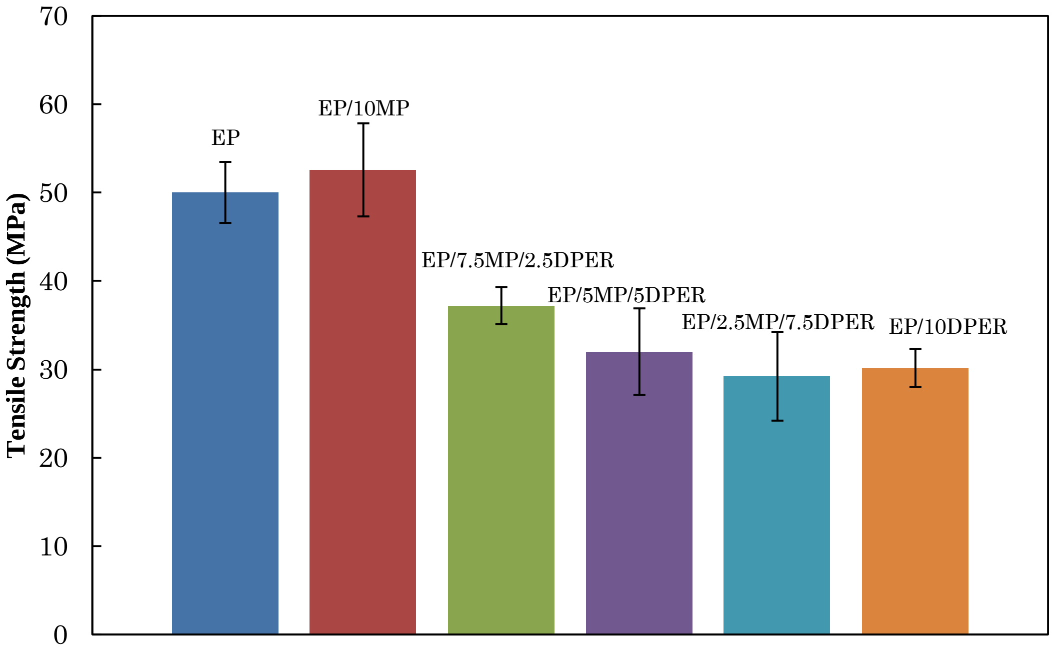

Figure 4.22 Tensile Strength of Neat Epoxy and Composite Containing MP and/or DPER

Tensile modulus of the composites is given in Figure 4.23, and the detailed tensile modulus data are tabulated in Table A.5 of Appendix A. Tensile modulus was slightly increased when 10% MP was added to neat epoxy from 2761 MPa to 2868 MPa. Because MP introduced stiffness to the epoxy matrix. Correspondingly, it can be observed that the tensile moduli of the composites decreased with increasing concentration of DPER due to diluent effect of DPER.

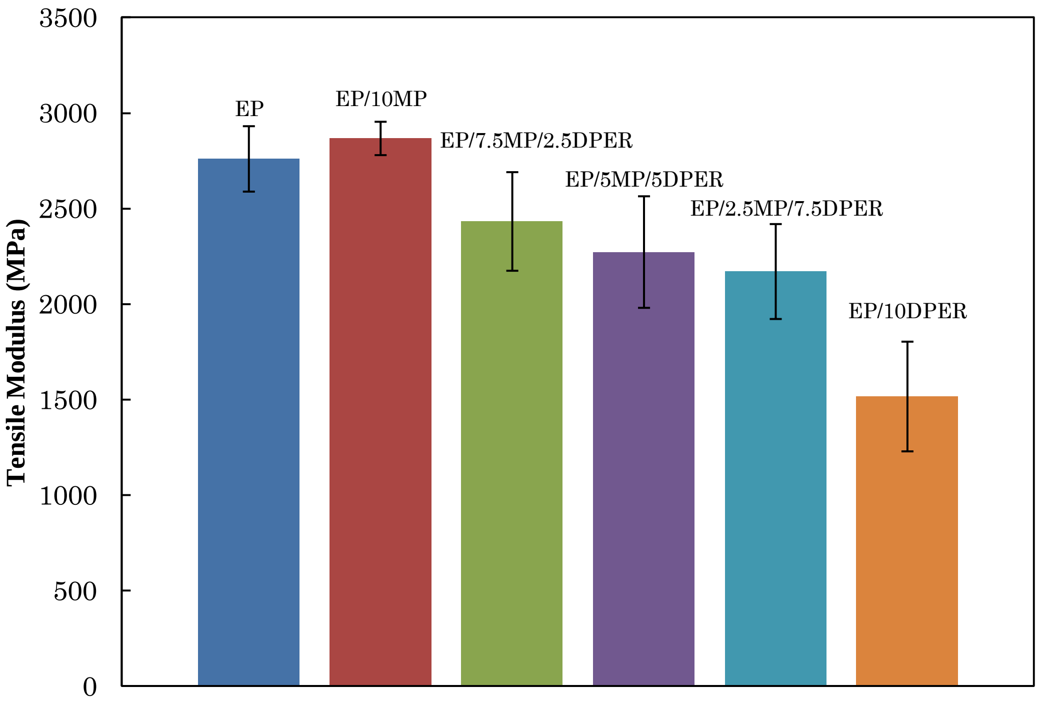

Figure 4.23 Tensile Modulus of Neat Epoxy and Composite Containing MP and/or DPER

Elongation at break value of the composites is given in Figure 4.24 and the detailed elongation at break data are tabulated in Table A.6 of Appendix A. Adding 10% MP to neat epoxy decreased the elongation at break value from 3.7% to 2.8%. This decrease may be due to the agglomerations of MP additives. Similarly, elongation at break value of the composites which include MP together with DPER considerably decreased because of the poor compatibility of the additives with epoxy [55]. The elongation at break value of the EP/10DPER composites was slightly higher than the EP/MP/DPER composites.

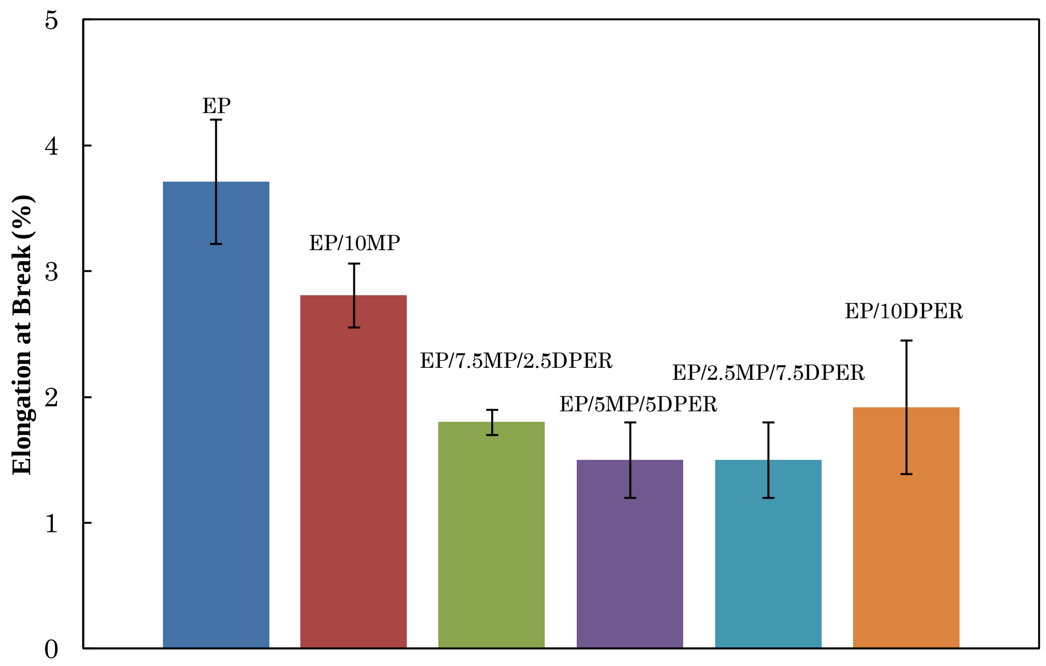

Figure 4.24 Elongation at Break Values of Neat Epoxy and Composite Containing MP and/or DPER

Impact strength of the composites is given in Figure 4.25 and the detailed impact strength data are tabulated in Table A.7 of Appendix A. Prepared composites had lower impact strength values than neat epoxy. For instance, loading 10% MP decreased the impact strength value considerably from 11.4 kJ/m^2 to 3.1 kJ/m^2. This can be due to agglomerations which create stress concentrated areas in the epoxy matrix due to poor compatibility between the polymer matrix and the additives.

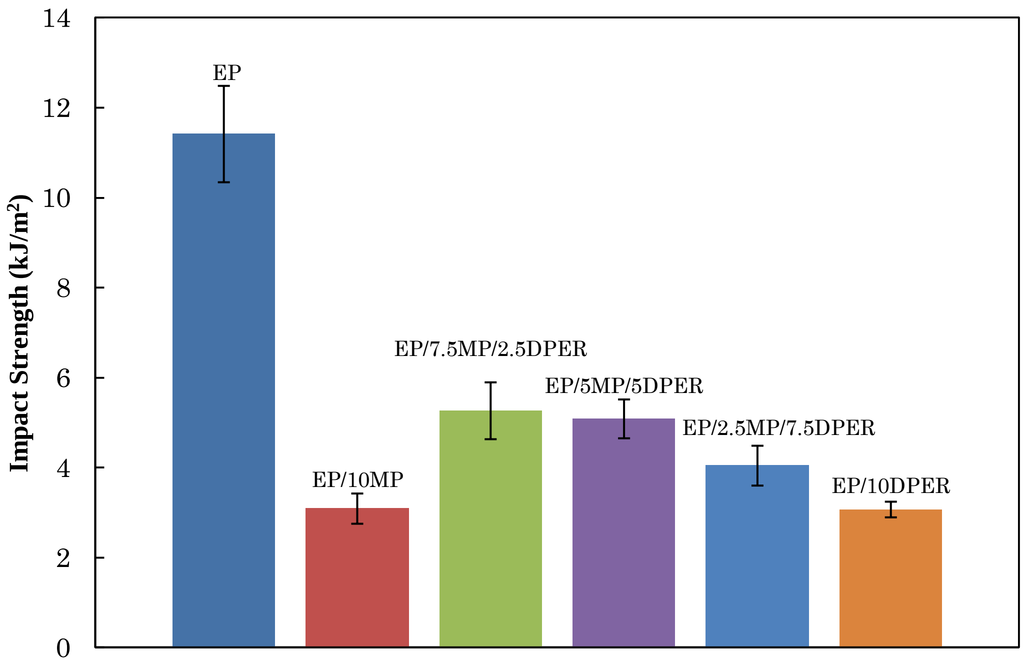

Figure 4.25 Impact Strength of Neat Epoxy and Composite Containing MP and/or DPER

4.2.4 Effects of Melamine Phosphate with Barium Metaborate on the Properties of Epoxy

In this part of the study, effects of melamine phosphate (MP) when used together with barium metaborate (BaM) were investigated on the flame retardant and other properties of epoxy. Formulations and compositions of the samples are given in Table 4.11.

Table 4.11 The Compositions Results of Neat Epoxy and Composite Containing MP and/or BaM

Sample (wt%)	EP	MP	DPER	MEC	BaM	ZnB	CaB
EP	100	-	-	-	-	-	-
EP/10MP	90	10	-	-	-	-	-
EP/10MP/0.5BaM	89.5	10	-	-	0.5	-	-
EP/10MP/1BaM	89	10	-	-	1	-	-
EP/10MP/3BaM	87	10	-	-	3	-	-

4.2.4.1 Morphological Analysis of Composite Containing MP and/or BaM

Figure 4.26 represents the fracture surfaces of the EP/10MP/1BaM composites at 5000 and 10000 magnifications. The fracture surface of the composites became rough when compare to the fracture surface of neat epoxy. It was observed as bright spots, corresponding to agglomerates. These agglomerates may be resulted from poor compatibility between the epoxy and the additives.

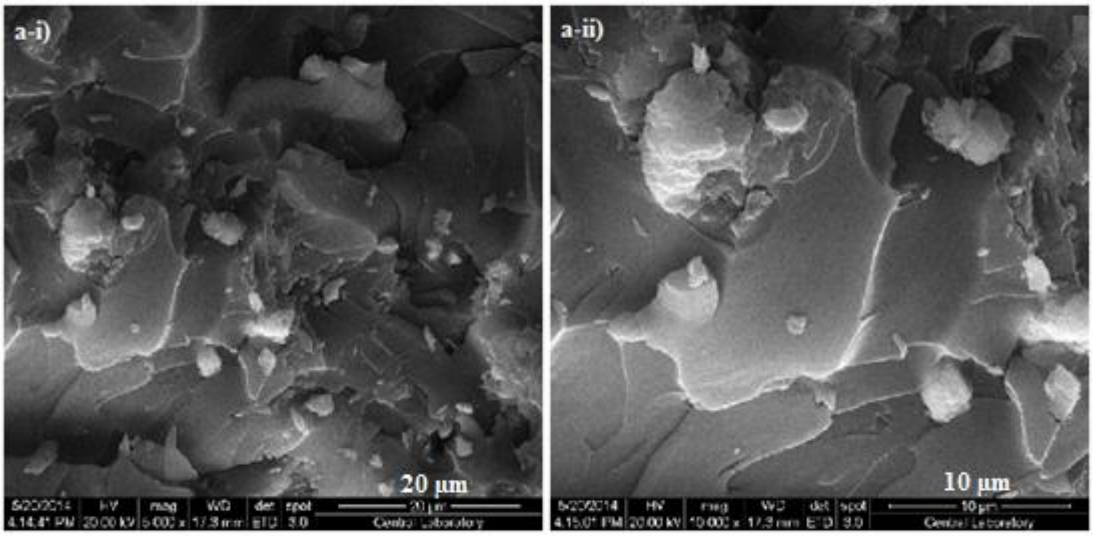

Figure 4.26 SEM images of a-i) EP/10MP/1BaM at ×5000 magnification a-ii) EP/10MP/1BaM at ×10000 magnification

4.2.4.2 Flammability Properties of Neat Epoxy and Composite Containing MP and/or BaM

Although there were improvements in the LOI value of epoxy when BaM was added only, there was no progress in the UL-94 test. Therefore, BaM was used together with melamine phosphate with the percentage of 10% in this part of the thesis. The results of LOI and UL-94 vertical burning test are given in Table 4.12.

Table 4.12 The Flammability Test Results of Neat Epoxy and Composite Containing MP and/or BaM

Composites	**LOI (%O_2)**	**UL-94**
EP	19.0	No Rating
EP/10MP	27.0	No Rating
EP/10MP/0.5BaM	27.0	V-1
EP/10MP/1BaM	27.0	V-0
EP/10MP/3BaM	27.0	V-0

It was seen that LOI value of neat epoxy was 19%. Adding 10% MP to epoxy increased the LOI value to 27%, but did not change the UL-94 result. Although adding 10% melamine phosphate together with barium metaborate at different concentrations (0.5%, 1%, 3%) did not change the LOI value of epoxy-based composites, there were improvements in the UL-94 results. 0.5% BaM loading increased the UL-94 results to V-1 rating. Adding 1% and 3% BaM to the EP/10MP was reached the best UL-94 results of "V-0". This can be related to barrier effect of BaM. Using BaM together with MP should enhance the flame retardant mechanism with barrier effect which form a protective layer and swelling effect.

In this way, the epoxy-based composites which containing melamine phosphate together with barium metaborate have been shown to be effective flame retarding for epoxy-based systems.

4.2.4.3 FTIR Results of Neat Epoxy and Composite Containing MP and/or BaM

Chemical structures of the produced composites were characterized by FTIR analyses. FTIR results of the neat epoxy and epoxy based composites are given in Figure 4.27.

FTIR spectra of neat epoxy and epoxy-based composites resemble to each other as seen in Figure 4.27. The only differences between neat epoxy and epoxy-based composites was the peak of C=O stretching of amide group resulting from melamine phosphate which was seen at 1670 cm^{-1}. The other characteristic absorption peaks for neat epoxy and epoxy-based composites was explained in Section 4.2.1.3.

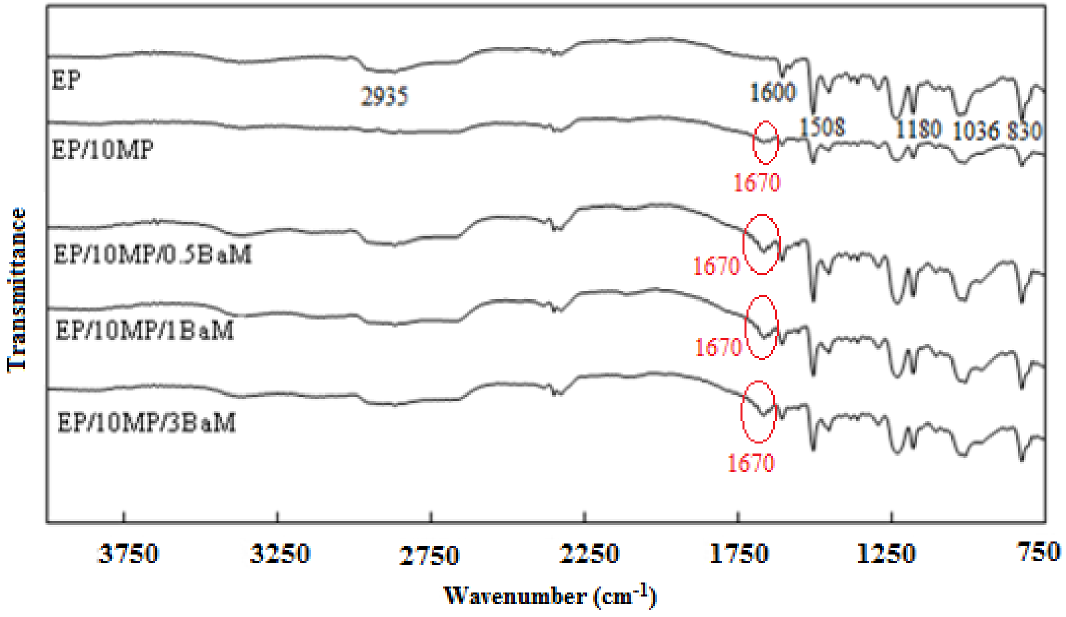

Figure 4.27 FTIR Results of Neat Epoxy and Composite Containing MP and/or BaM

4.2.4.4 Thermal Analysis of Neat Epoxy and Composite Containing MP and/or BaM

Results of thermogravimetric analysis for neat epoxy, EP/10MP and EP/10MP/BaM composites are given in Figure 4.28. Onset of degradation temperature ($T_{10wt\%}$), half-way degradation temperature ($T_{50wt\%}$), maximum degradation temperatures and char yields at 900 °C are given in Table 4.13, and TG/DTA thermograms of the samples are given in Appendix B.

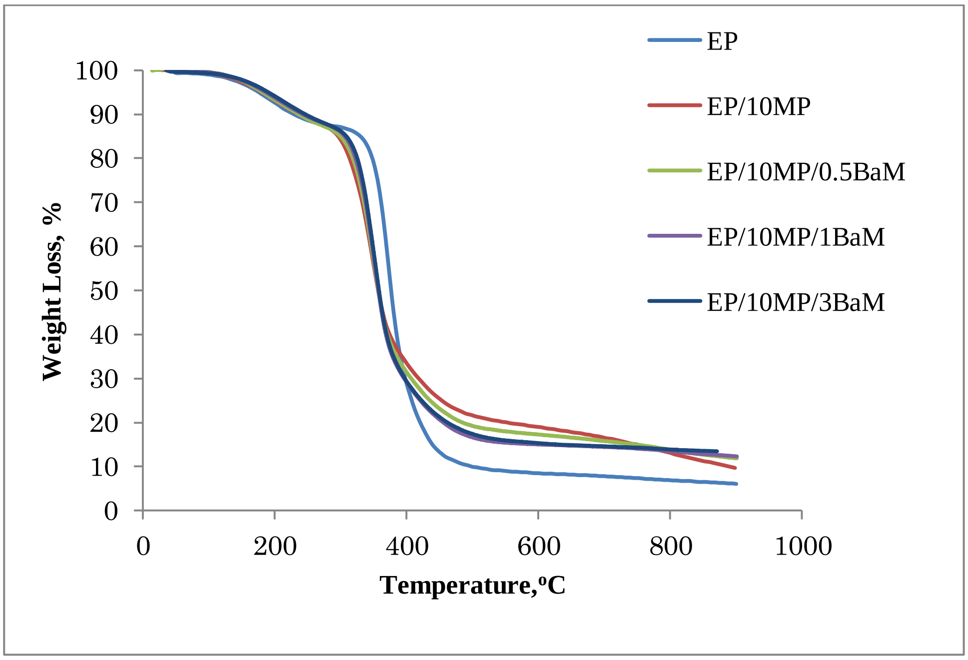

Figure 4.28 The TGA Curves of Neat Epoxy and Composite Containing MP and/or BaM

Table 4.13 Thermal Degradation Temperatures and Char Yields of Neat Epoxy and Composite Containing MP and/or BaM

Composites	**T_{Peak-1} (^{o}C)**	**T_{Peak-2} (^{o}C)**	**$T_{10wt\%}$ (^{o}C)**	**$T_{50wt\%}$ (^{o}C)**	**Char yield at 900^{o}C (%)**
EP	199.1	371.2	226.7	376.1	6.08
EP/10MP	188.3	350.3	229.6	356.0	9.67
EP/10MP/0.5BaM	193.0	350.7	237.4	356.9	11.81
EP/10MP/1BaM	193.4	354.3	242.4	357.2	12.26
EP/10MP/3BaM	195.5	354.9	246.3	358.3	13.44

The decomposition temperature of neat epoxy decreased with the addition of 10% MP. Adding MP together with BaM to neat epoxy significantly contributed to char formation. Addition of BaM slightly increased the decomposition temperatures. This can be due to the barrier effect of BaM. The most noticeable increase was observed in the char yield. Char yield of neat epoxy was increased from 6.08% to 13.44% with the loading of 3% BaM. Char acts as an insulator and improve the flame retardation of epoxy-based composites.

4.2.4.5 Mechanical Behaviors of Neat Epoxy and Composite Containing MP and/or BaM

The tensile strength of neat epoxy, EP/10MP and EP/10MP/BaM composites are given in Figure 4.29 and the detailed tensile strength data are tabulated in Table A.4 of Appendix A. When compared to neat epoxy, tensile strength of EP/10MP increased slightly. Although 10% MP loading increased the tensile strength, addition of the BaM into the EP/10MP composites decreased the tensile strength down to 33.5 MPa. This could be due to the poor adhesion between MP and BaM additives.

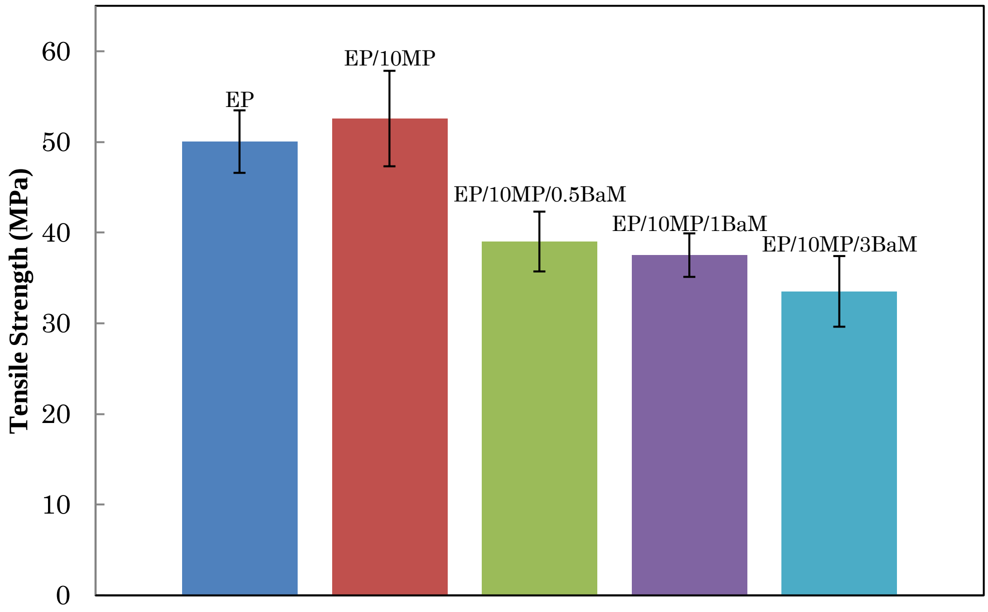

Figure 4.29 Tensile Strength of Neat Epoxy and Composite Containing MP and/or BaM

Tensile moduli of the samples are given in Figure 4.30, and the detailed tensile modulus data are tabulated in Table A.5 of Appendix A. Theoretically, addition of additives increased the tensile modulus of the epoxy because of the high modulus of the fillers. According to the Figure 4.30, addition of 10% MP into the epoxy increased the tensile modulus slightly. The other composites, on the other hand, had similar tensile modulus values with neat epoxy. This can be explained by the relatively poor dispersion of the additives in the epoxy matrix which would not increase the modulus values.

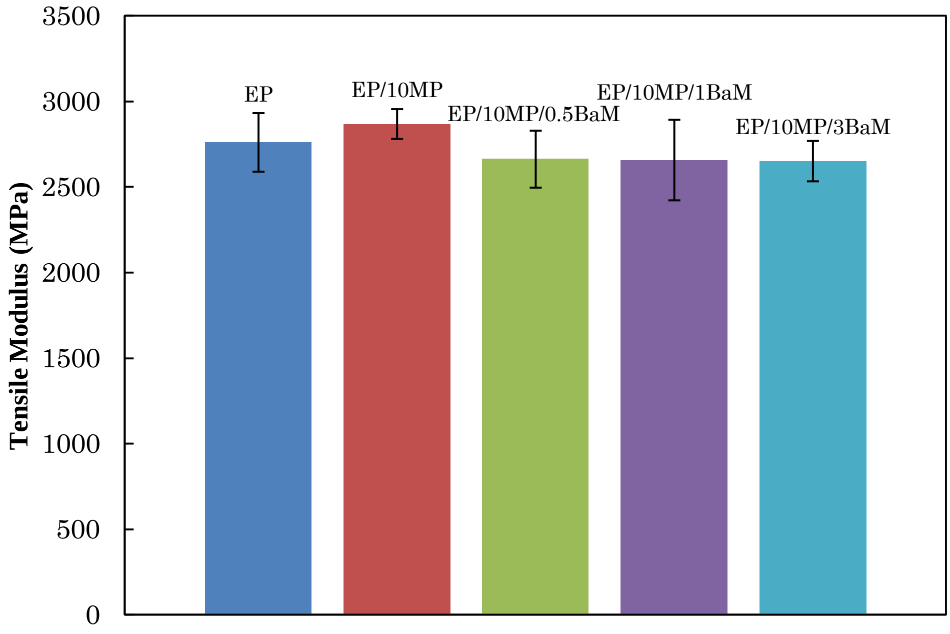

Figure 4.30 Tensile Modulus of Neat Epoxy and Composite Containing MP and/or BaM

Elongation at break values of the composites are given in Figure 4.31, and the detailed elongation at break data are tabulated in Table A.6 of Appendix A. As the concentration of additives in epoxy increased, elongation at break values decreased. This can be again related to poor dispersion and interaction between the epoxy matrix and MP and BaM additives.

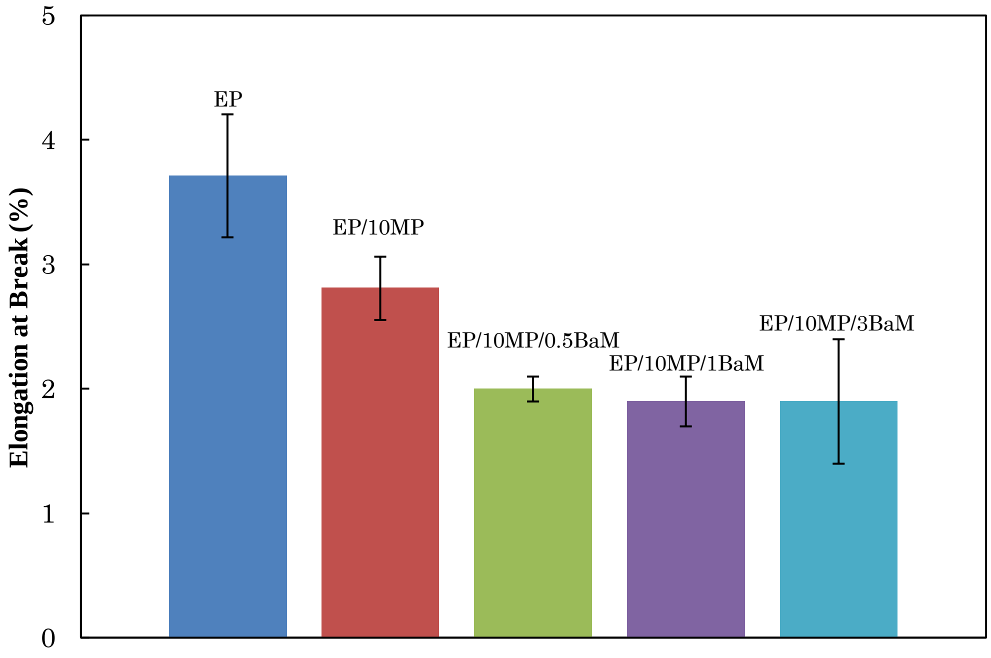

Figure 4.31 Elongation at Break Values of Neat Epoxy and Composite Containing MP and/or BaM

Impact strength of neat epoxy, EP/10MP and EP/10MP/BaM composites are given in Figure 4.32, and the detailed impact strength data are tabulated in Table A.7 of Appendix A. When compared to the EP/10MP and EP/10MP/BaM composites, impact strength value of neat epoxy considerably decreased. The reason of the decrease in impact strength can be due to the poor dispersion and interaction between the epoxy matrix and the additives. Also, the fillers were agglomerated, and this might create stress concentration areas, and decrease the impact strength of the composites.

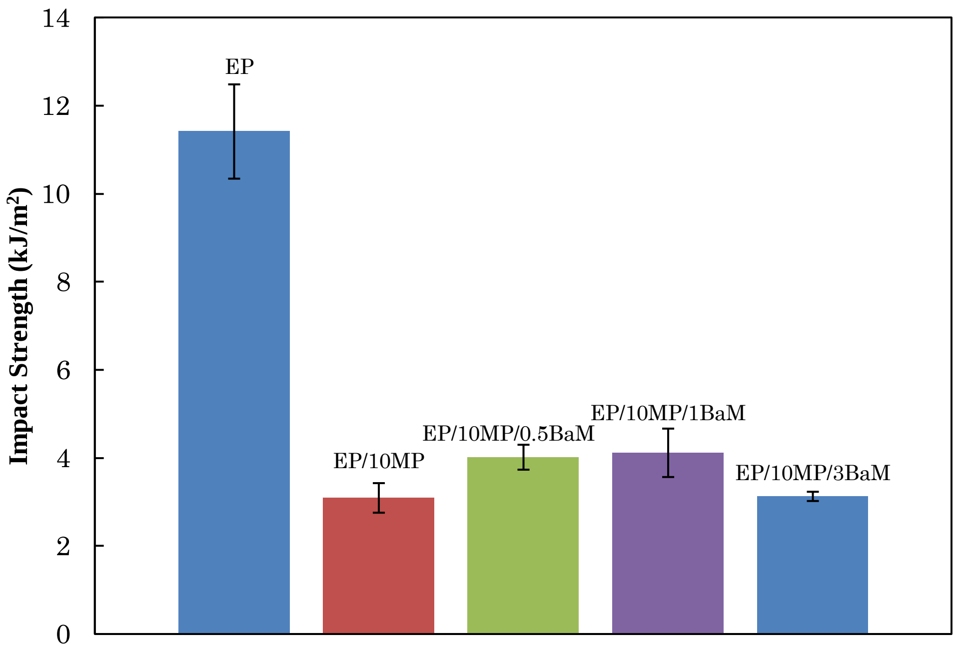

Figure 4.32 Impact Strength of Neat Epoxy and Composite Containing MP and/or BaM

According to the test results, the best composite among to MP and BaM containing composites was found as EP/10MP/1BaM due to its high LOI value, best UL-94 result, and reasonable mechanical properties with respect to the other composites.

4.2.5 Effects of MP-MEC with Types of Borates on the Properties of Epoxy

The potential synergistic effect of among melamine phosphate (MP) and/or methacrylate epoxy cyclosiloxane (MEC) on properties of epoxy composites containing borates such as barium metaborate (BaM), zinc borate (ZnB) and calcium borate (CaB) were investigated in this part of the thesis. Formulations and compositions are listed in Table 4.14.

Table 4.14 The Compositions of Neat Epoxy and Epoxy-Based Composites

Sample (wt%)	EP	MP	DPER	MEC	BaM	ZnB	CaB
EP	100	-	-	-	-	-	-
EP/1MEC/1BaM	98	-	-	1	1	-	-
EP/10MP/1MEC	89	10	-	1	-	-	-
EP/10MP/1MEC/1BaM	88	10	-	1	1	-	-
EP/10MP/1MEC/1ZnB	88	10	-	1	-	1	-
EP/10MP/1MEC/1CaB	88	10	-	1	-	-	1

4.2.5.1 Morphological Analysis of Epoxy-Based Composites

SEM micrographs of impact fractured test samples of EP/1MEC/1BaM, EP/10MP/1MEC and EP/10MP/1MEC/1BaM composites are given in Figure 4.33. The surfaces were examined from the SEM images with 2.000 and 5.000 magnifications.

The fracture surface of EP/1MEC/1BaM composite showed more compact and smooth structure than EP/10MP/1MEC and EP/10MP/1MEC/1BaM composites. Adding 1% MEC together with 1% BaM is expected to reveal better mechanical properties due to lower additives percentage than the other composites shown in Figure 4.33. Likewise, EP/1BaM/1MEC composite exhibited higher strength than the others which was discussed in the further section.

Figures 4.33.b and 4.33.c look similar to each other and smooth fractured surface turned into much rougher structure with respect to neat epoxy.

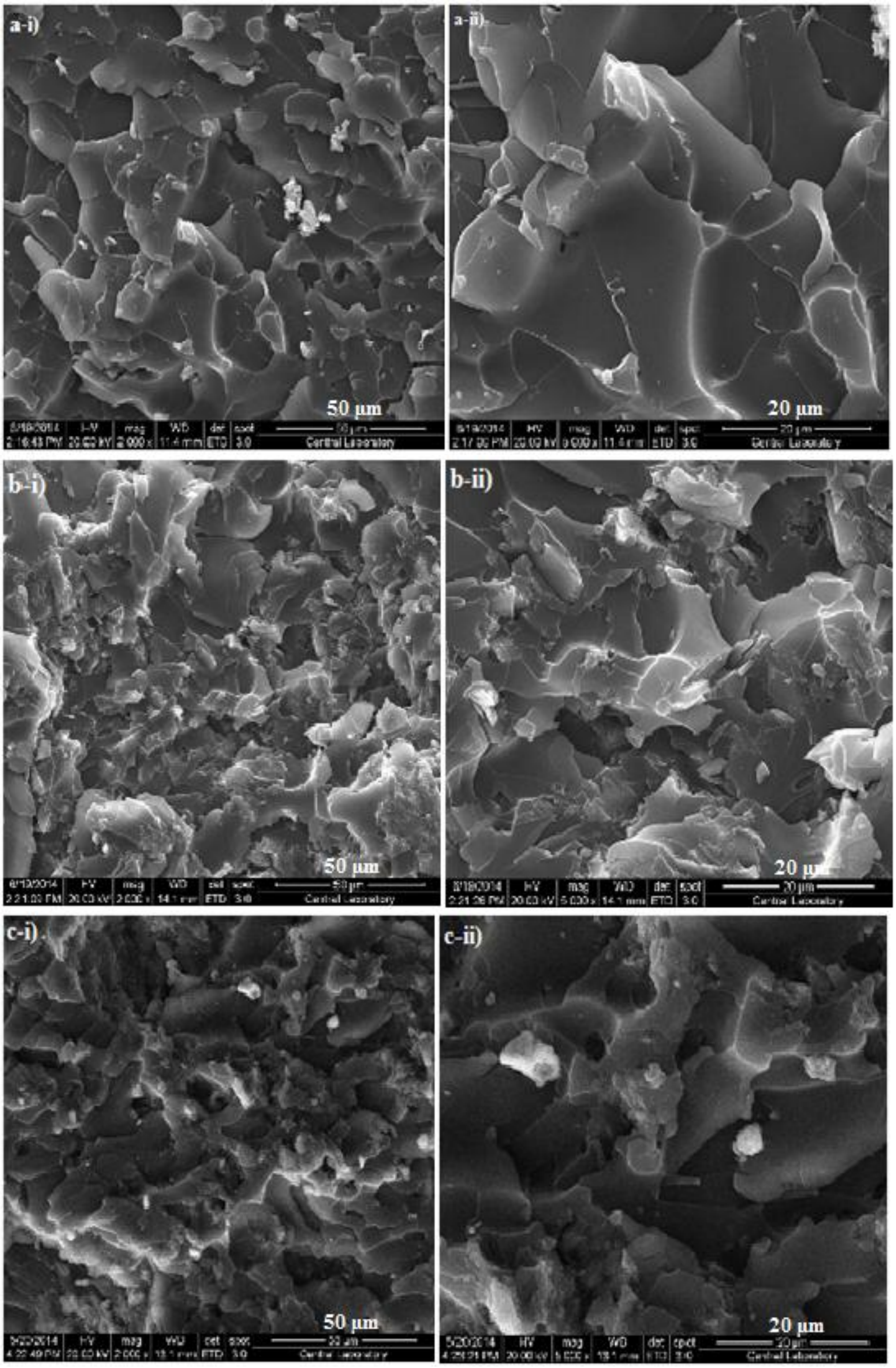

Figure 4.33 SEM images of a-i) EP/1MEC/1BaM at ×2000 magnification a-ii) EP/1BaM/1MEC at ×5000 magnification b-i) EP/10MP/1MEC at ×2000 magnification b-ii) EP/10MP/1MEC at ×5000 magnification c-i) EP/10MP/1MEC/1BaM at ×2000 magnification c-ii) EP/10MP/1MEC/1BaM at ×5000 magnification

4.2.5.2 Flammability Properties of Epoxy-Based Composites

In order to investigate synergistic effect among the additives and to examine zinc borate and calcium borate effects on flame retardant properties of epoxy-based systems, binary and ternary composites were prepared. LOI values and UL-94 vertical burning test results are given in Table 4.15.

Table 4.15 The Flammability Test Results of Neat Epoxy and Epoxy-Based Composites

Composites	**LOI (%O_2)**	**UL-94**
EP	19.0	No Rating
EP/1MEC/1BaM	24.5	No Rating
EP/10MP/1MEC	27.5	V-1
EP/10MP/1MEC/1BaM	27.5	V-1
EP/10MP/1MEC/1ZnB	27.5	V-1
EP/10MP/1MEC/1CaB	27.5	V-0

According to Table 4.15, the LOI values of EP/1MEC/1BaM and EP/10MP/1MEC composites were 24.5% and 27.5%, respectively. Using 10% MP together with 1% MEC slightly increased the LOI value up to 27.5%, and UL-94 result showed V-1 level which indicates that material was self-extinguished between 10 and 30 seconds without dripping, according to the EP/10MP composite (27.0%). Adding 1% BaM on EP/10MP/1MEC composites did not change the flammability test result. On the other hand, although EP/10MP/1BaM composite showed V-0 result at UL-94 test (Table 4.12) the UL-94 result of the EP/10MP/1MEC/1BaM composite showed V-1. This may be due to the addition of MEC, which suppressed the char formation of MP that caused a decrease in the UL-94 test result from V-0 to V-1.

Addition of 1% ZnB to the EP/10MP/1MEC composite did not change the flammability test results; on the other hand 1% CaB increased the UL-94 result from V-1 to V-0. Based on this result, it can be said that CaB was a more effective flame retardant than BaM and ZnB.

4.2.5.3 FTIR Results of Neat Epoxy and Epoxy-Based Composites

Chemical structure of the produced composites was also characterized by FTIR analyses. FTIR results of the neat epoxy and epoxy based composites are given in Figure 4.34.

Epoxy-based composites showed nearly the same characteristic absorption peaks in the FTIR analysis. According to Figure 4.34, composites which contained 10% MP showed the characteristic absorption peak for C=O stretching of amide group resulting from melamine phosphate. The other characteristic absorption peaks for neat epoxy and epoxy-based composites was explained in Section 4.2.1.3.

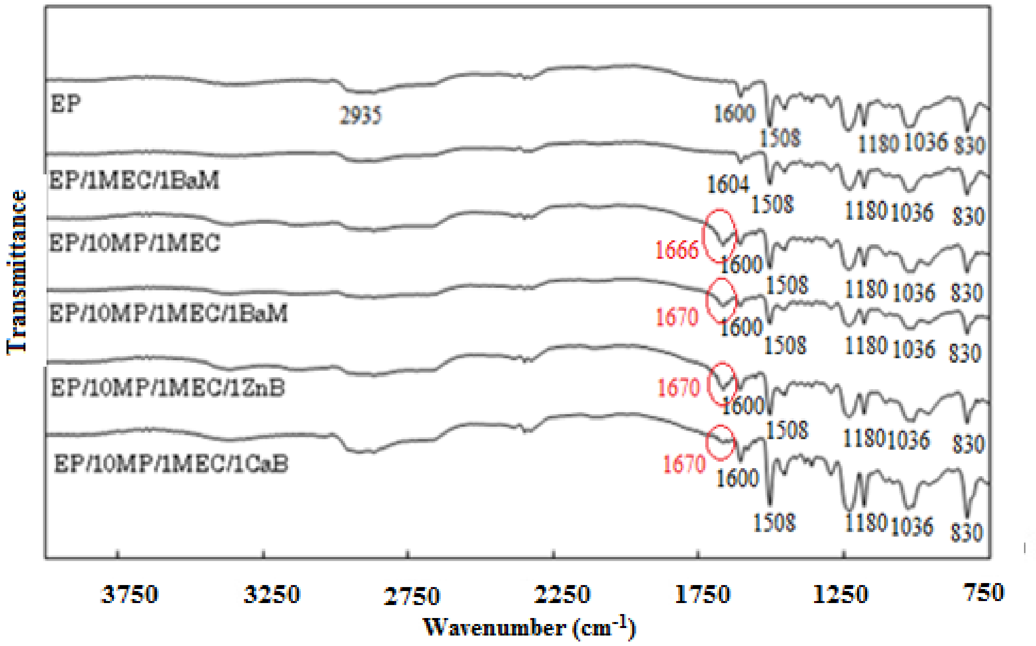

Figure 4.34 FTIR Results of Neat Epoxy and Epoxy-Based Composites

4.2.5.4 Thermal Analysis of Epoxy-Based Composites

Thermogravimetric analysis results of the composites are given in Figure 4.35. Onset of degradation temperature ($T_{10wt\%}$), half-way degradation temperature ($T_{50wt\%}$), maximum degradation temperatures and char yields at 900 ^{o}C are given in Table 4.16, and TG/DTA thermograms of samples are given in Appendix B.

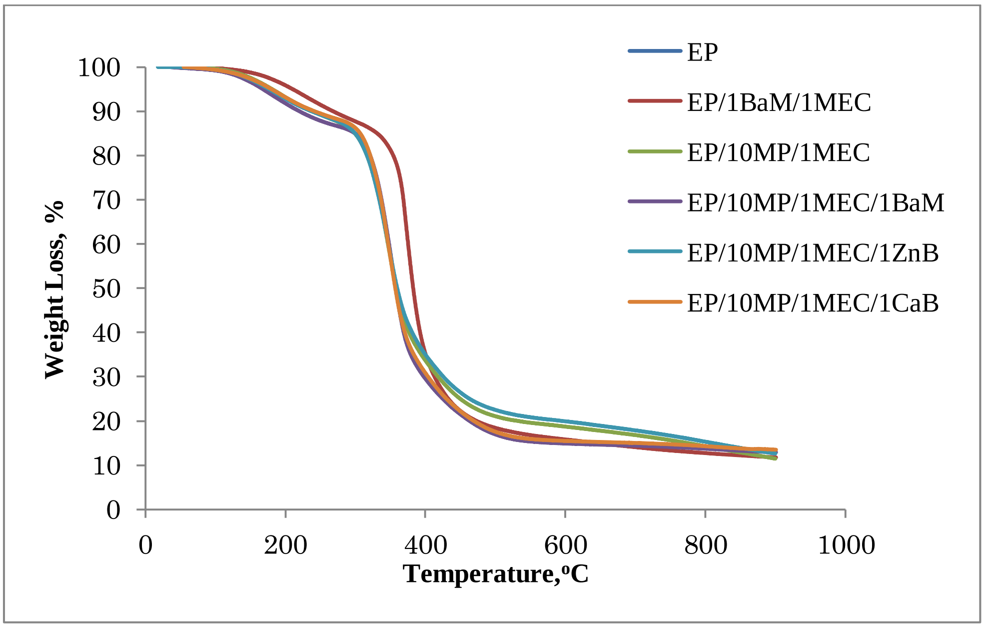

Figure 4.35 The TGA Curves of Neat Epoxy and Epoxy-Based Composites

Table 4.16 Thermal Degradation Temperatures and Char Yields of Neat Epoxy and Epoxy-Based Composites

Composites	**T_{Peak-1} (°C)**	**T_{Peak-2} (°C)**	**$T_{10wt\%}$ (°C)**	**$T_{50wt\%}$ (°C)**	**Char yield at 900°C (%)**
MP	258.6	397.8	326.3	537.4	25.48
BaM	214.8	-	677.7	-	89.99
ZnB	378.6	-	416.6	-	85.72
CaB	402.3	689.5	406.8	-	76.26
EP	199.1	371.2	226.7	376.1	6.08
EP/1MEC/1BaM	230.9	374.7	267.9	382.4	11.75
EP/10MP/1MEC	194.6	343.9	238.5	358.4	11.39
EP/10MP/1MEC/1BaM	186.2	355.5	219.8	357.6	12.88
EP/10MP/1MEC/1ZnB	187.9	346.2	237.2	360.0	12.60
EP/10MP/1MEC/1CaB	191.6	347.8	240.8	356.8	13.54

Using 1% MEC together with 1% BaM in the epoxy matrix showed improvements in initial decomposition temperature and char yield with respect to neat epoxy. This may be attributed to existence of Si atoms in the polymer backbone of MEC together with high thermal stability of BaM additive. When 1% BaM loading was replaced with 10% MP, it was observed that the decomposition temperatures decreased with respect to neat epoxy slightly. This is because of the MP being less stable inorganic compound than BaM. Also, this was proved by the TGA results of the MP and BaM which are given in Table 4.16. The composite containing boron compounds had lower the decomposition temperatures than neat epoxy. The largest percentage decrease was observed in the EP/10MP/1MEC/1BaM composite and the smallest percentage decrease was observed in the EP/10MP/1MEC/1CaB composite. Among the boron compounds; the less thermally stable compound was BaM and the most thermally stable compound was CaB.

The char yield of the composites was higher than neat epoxy. Thus, the composites had better flame retardant properties than neat epoxy. Char yield of composites containing BaM, ZnB and CaB was higher than neat epoxy, EP/1MEC/1BaM and EP/10MP/1MEC composites. It is because of the boron compounds being more thermally stable. Also, BaM, ZnB and CaB retained their weight about 89.99%, 85.72%, and 76.26% at 900 ^{o}C, respectively.

4.2.5.5 Mechanical Behaviors of Epoxy-Based Composites

Tensile strength of the composites is given in Figure 4.36, and the detailed tensile strength data are tabulated in Table A.4 of Appendix A. It was observed that increasing the concentration of additives caused a decrease in the tensile strength. This can be attributed to stress concentrated areas which were formed due to agglomeration of the particles at high concentrations.

When EP/10MP/1MEC/1BaM, EP/10MP/1MEC/1ZnB and EP/10MP/1MEC/1CaB were compared with one another to see the borate effect on tensile strength values; it was seen that almost similar tensile strength values were obtained for these composites. This may be owing to the particle size of BaM (3.5 µm) which is smaller than those of the others (ZnB: 5 µm and CaB: 4.3 µm) because of increasing particle size leads to the shape of agglomerated particles to become more irregular and the agglomerated irregular particles may be cracked easily when the load is applied [84].

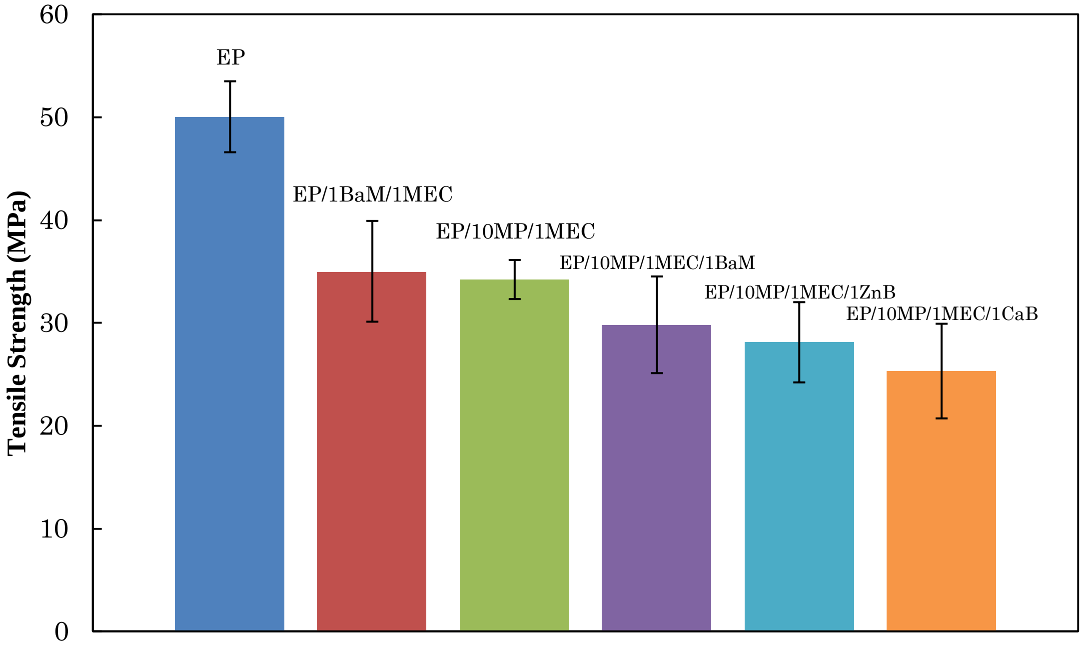

Figure 4.36 Tensile Strength of Epoxy-Based Composites

Tensile moduli of the composites are given in Figure 4.37, and the detailed tensile modulus data are tabulated in Table A.5 of Appendix A. Except for EP/10MP/1MEC/1BaM, the tensile modulus of the composites was similar to neat epoxy. The tensile modulus of the EP/10MP/1MEC/1BaM composite was lower than the other composites, and this may be due to the inefficient load transfer of the particles in the epoxy matrix. Hence, they decrease the tensile modulus of the composite.

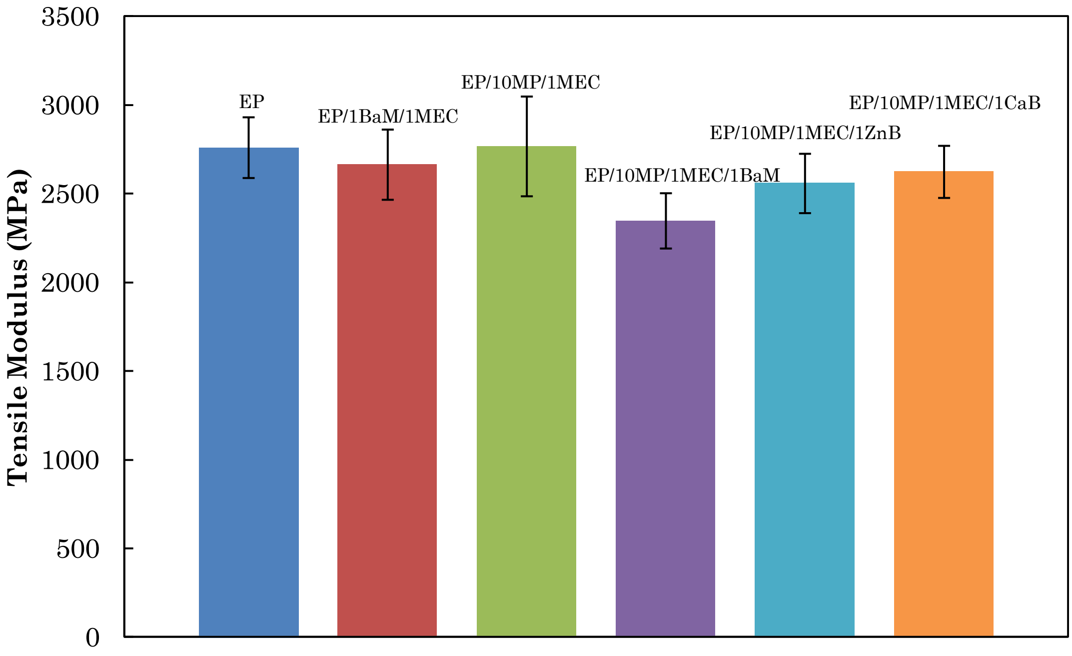

Figure 4.37 Tensile Modulus of Epoxy-Based Composites

Elongations at break values of the composites are given in Figure 4.38, and the detailed elongation at break data are tabulated in Table A.6 of Appendix A. The decrease at elongation at break value with the increase of additive concentration was due to the high loading level of the additives. Flame retardant additives restricted the mobility of polymer chain and decreased the elongation at break value.

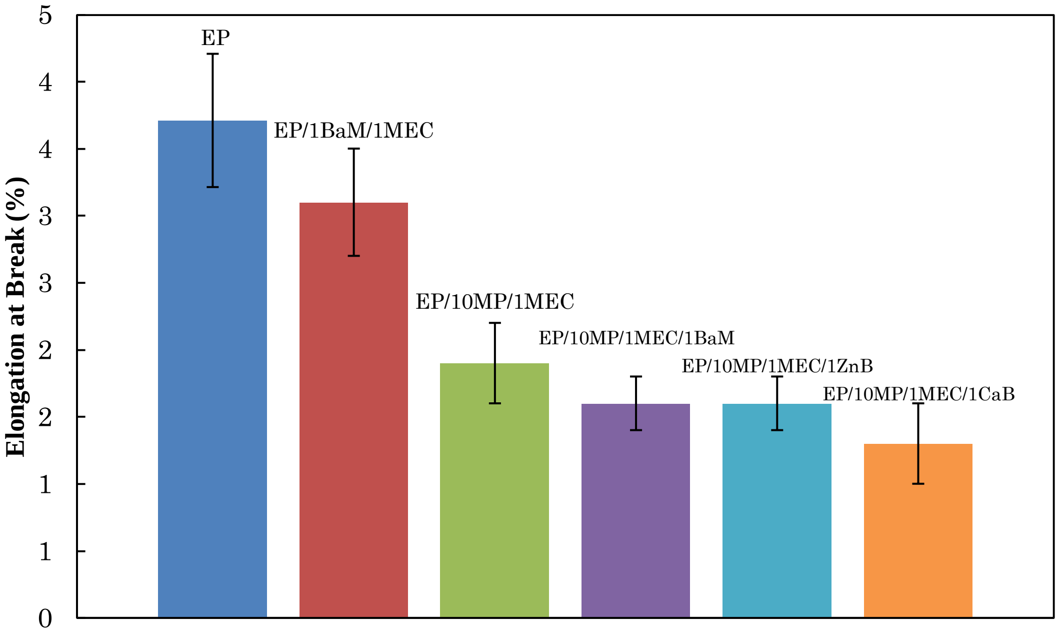

Figure 4.38 Elongation at Break of Epoxy-Based Composites

Impact strength value of neat epoxy and the epoxy-based composites are given in Figure 4.39, and the detailed impact strength data is tabulated in Table A.7 of Appendix A. Impact strength of the EP/1BaM/1MEC composite was close to the impact strength of neat epoxy and was significantly higher than the other composites. This can be due to the efficient load transfer and the low concentrations of the additives. The impact strength of the other composites was slightly close to each other and was lower than neat epoxy which could be the result of agglomeration of the additives due to loading at high concentrations.

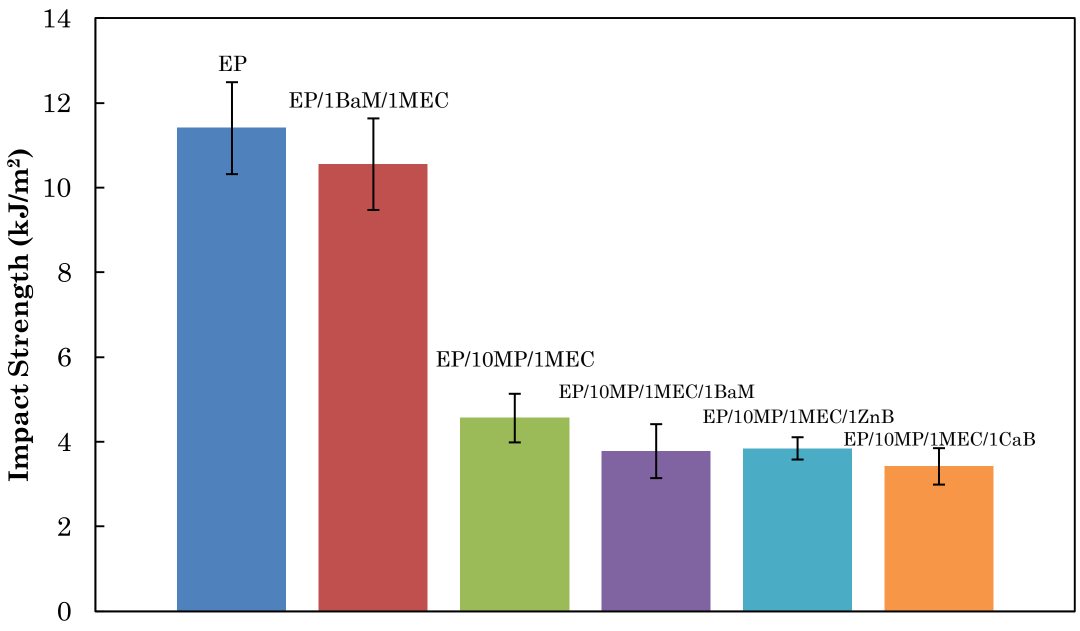

Figure 4.39 Impact Strength of Epoxy-Based Composites

4.3 Accelerated Weathering Test of Epoxy-Based Composites

In the third part of the thesis, the weatherability of neat epoxy and epoxy-based composites under certain conditions specified in Section 3.3.6 were examined. In order to determine the performance of weathered and unweathered samples, impact test was applied. Also, morphologies of the composites were investigated, and color change was observed using a camera.

For this purpose, neat epoxy and epoxy based composites containing barium metaborate, methacrylate epoxy cyclosiloxane (MEC) and melamine phosphate were exposed to UV radiation and moisture for 300 hours. Formulations and compositions of these samples are given in Table 4.17.

Table 4.17 The Compositions of the Composites Subjected to Accelerated Weathering Test

Sample (wt%)	EP	MP	DPER	MEC	BaM	ZnB	CaB
EP	100	-	-	-	-	-	-
EP/0.5BaM	99.5	-	-	-	0.5	-	-
EP/1BaM	99	-	-	-	1	-	-
EP/3BaM	97	-	-	-	3	-	-
EP/10MP	90	10	-	-	-	-	-
EP/10MP/1BaM	89	10	-	-	1	-	-
EP/10MP/1MEC	89	10	-	1	-	-	-
EP/10MP/1MEC/1BaM	88	10	-	1	1	-	-

4.3.1 Morphological Analysis of the Accelerated Weathering Test Composites

After exposure, surface of all the samples showed discoloration due to the photo-oxidation reactions by the effects of UV and moisture. Color in neat epoxy changed from colorless to yellow and the composites changed less discoloration than the neat epoxy. This indicates that discoloration of neat epoxy was greater than the filled composites. The color changes of the samples are given in Figure 4.40.

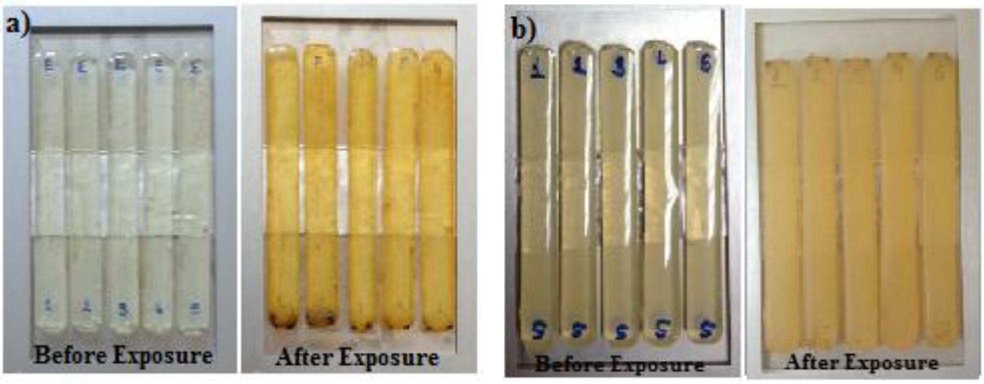

Figure 4.40 Photographs of weathered and unweathered samples a)EP b) EP/0.5BaM c) EP/1BaM d) EP/3BaM e) EP/10MP f) EP/10MP/1BaM g) EP/10MP/3BaM h) EP/10MP/1MEC ı) EP/10MP/1MEC/1BaM

Figure 4.40 – (Continued) Photographs of weathered and unweathered samples a)EP b) EP/0.5BaM c) EP/1BaM d) EP/3BaM e) EP/10MP f) EP/10MP/1BaM g) EP/10MP/3BaM h) EP/10MP/1MEC ı) EP/10MP/1MEC/1BaM

The SEM images of neat epoxy, before and after exposure are given in Figure 4.41. Fracture surface was examined again in order to investigate the morphology of the samples

The SEM images of the neat epoxy before exposure showed smooth surface. According to Figure 4.41, microcracking on the surface of the specimen was observed after exposure. This was caused by the polymer matrix becoming extremely brittle due to the increased crosslinking resulting from UV radiation and moisture [32]. UV photons from radiation led to chain scission reactions on the surface of epoxy to form the polymer radicals. To give a branched molecule, the fragments can link to the main chain of neighboring molecule. Thus, the degree of crosslinking was increased which resulted in high brittleness.

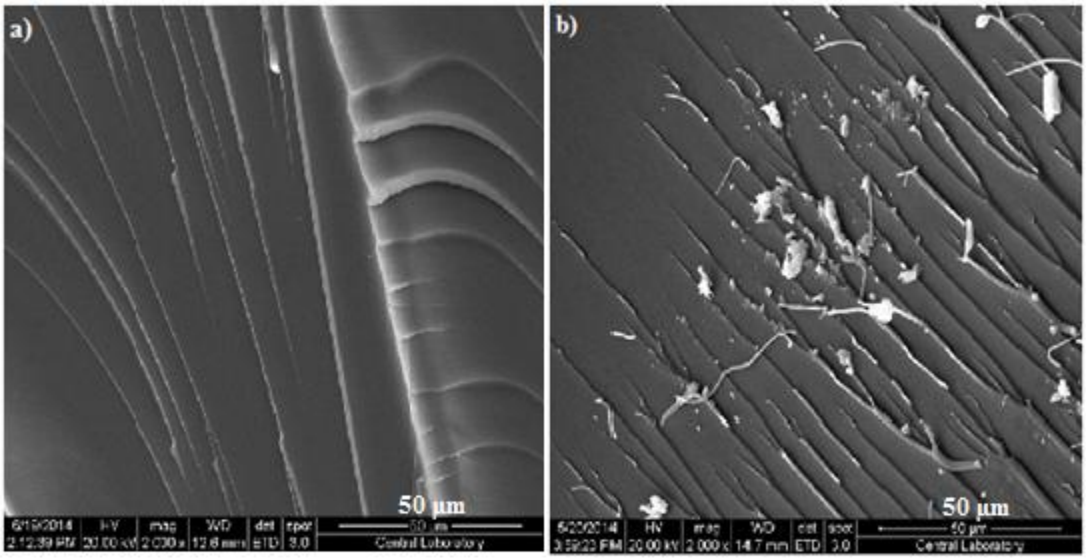

Figure 4.41 SEM images of Neat Epoxy a) No Exposure at ×2000 b) 300 h Exposure at ×2000 magnification

Figure 4.42.a image was taken from the fracture surface of neat epoxy at 5000 and 10000 magnifications. Figure 4.42.b and Figure 4.42.c image show the fracture surface of the neat epoxy and EP/3BaM before and after being exposed to the accelerated weathering test. Neat epoxy with no exposure exhibited very smooth and featureless surface. However, after UV radiation and moisture exposure, microcracking formed on the fracture surface due to molecular chain scissions.

When neat epoxy and EP/3BaM were compared with each other after exposure, it was resulted that fracture surface of the neat epoxy had more microcracks than the

EP/3BaM composite. It can be related to barrier property effect of BaM which might impede moisture uptake and delay the penetration of free radicals and oxygen into the composite [85].

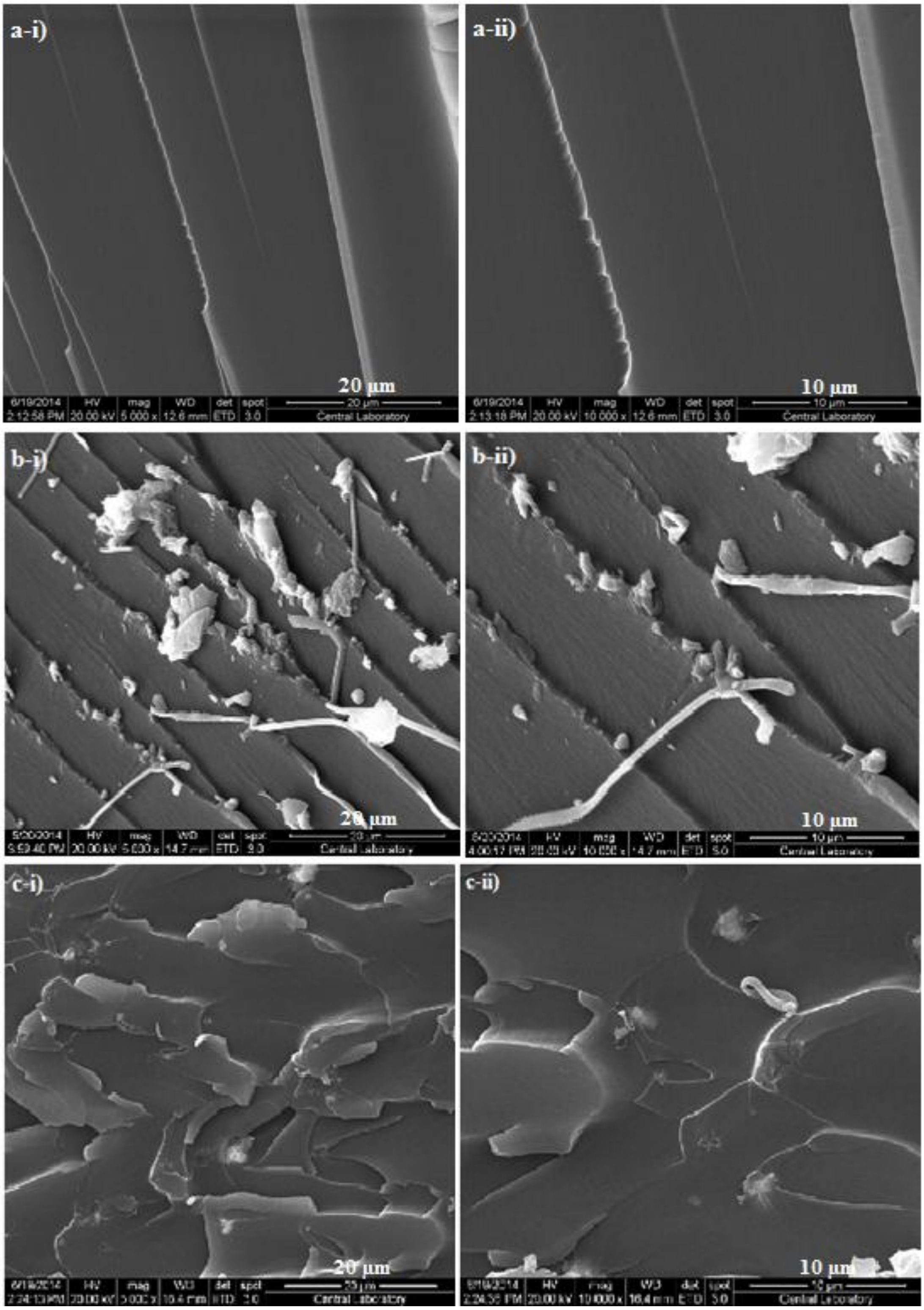

Figure 4.42 SEM images of a-i) EP No Exposure at ×5000 magnification a-ii) EP No Exposure at ×10000 magnification b-i) EP 300 h Exposure at ×5000 magnification b-ii) EP 300 h Exposure at ×10000 magnification c-i) EP/3BaM 300 h Exposure at ×5000 magnification c-ii) EP/3BaM 300 h Exposure at ×10000 magnification

4.3.2 FTIR Results of the Composites Subjected to Accelerated Weathering Test

FTIR results for the accelerated weathering test samples are given in Figure 4.43. The blue lines show the FTIR analyses of the samples before accelerated weathering test and the red lines indicate the FTIR analyses of the samples after accelerated weathering test.

FTIR results of the samples, before accelerated weathering test, resemble to each other. After accelerated weathering test, except for EP/10MP/1MEC and EP/10MP/1MEC/1BaM composites, all the composites showed the same characteristic absorption peaks with respect to in the FTIR analysis before exposure.

It was observed that intensity of some peaks in the EP/10MP/1MEC and EP/10MP/1MEC/1BaM composites increased after accelerated weathering test. Certain differences were observed for the peaks at 1600 cm^{-1} and 1670 cm^{-1} wavenumbers. These peaks may be attributed to C=C stretching aromatic ring of epoxy and C=O stretching of amide group. The C=O stretching band at 1670 cm^{-1} due to formation of amide groups increased for these composites suggesting that the greater extent of degradation takes place [86].

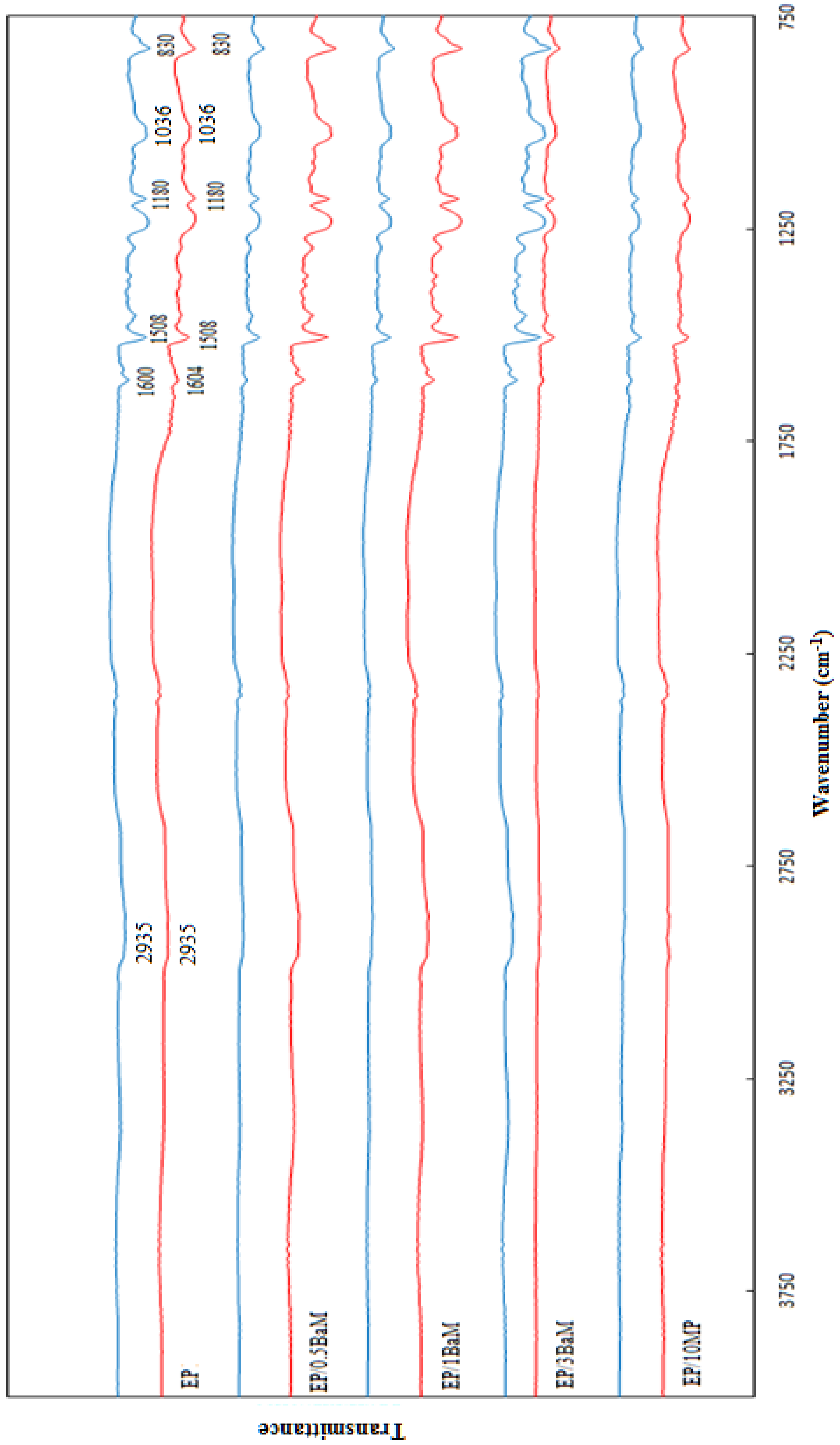

Figure 4.43 FTIR Results of the Composites Subjected to Accelerated Weathering Test

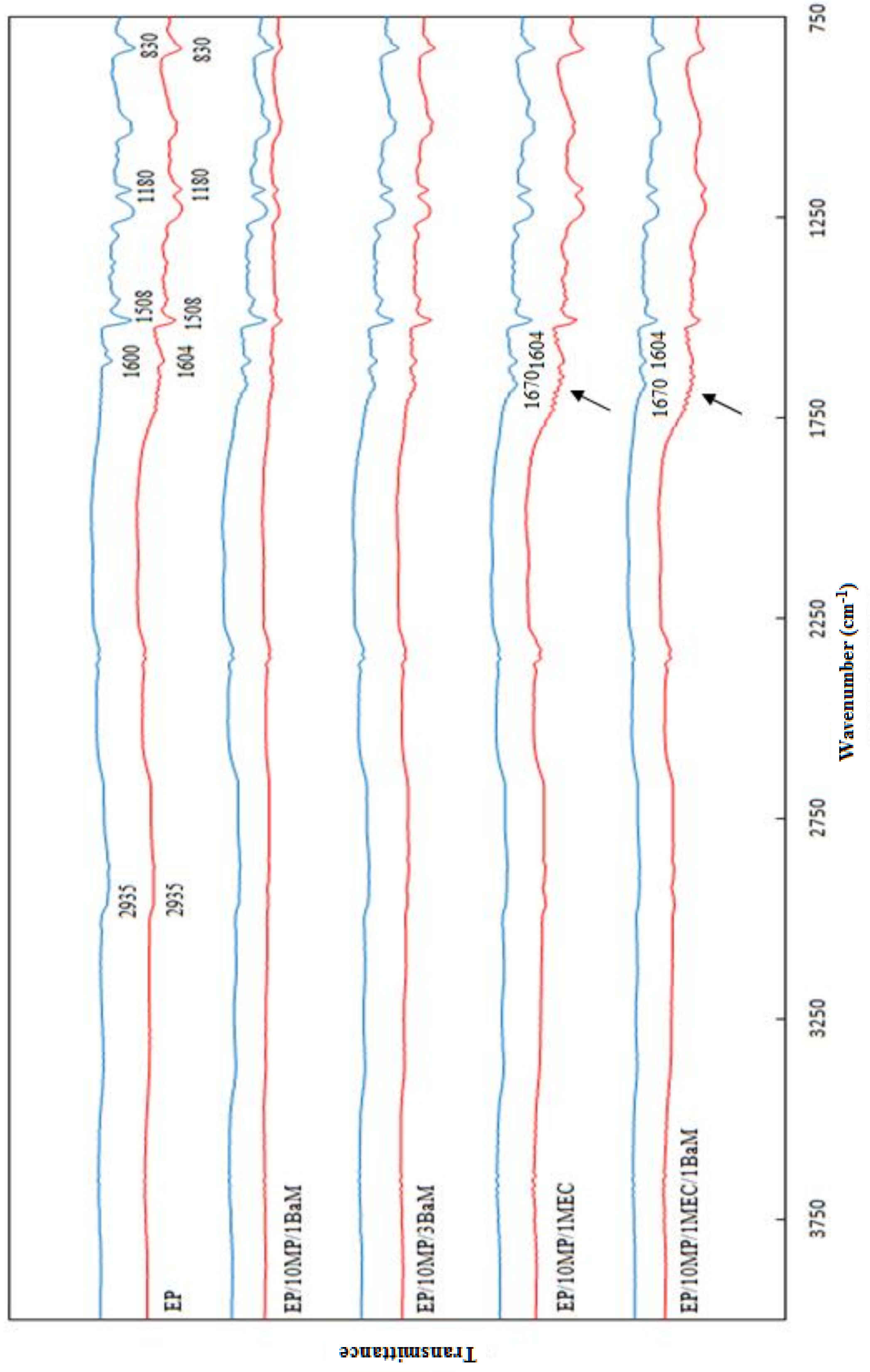

Figure 4.43 – (Continued) FTIR Results of the Composites Subjected to Accelerated Weathering Test

4.3.3 Mechanical Behaviors of the Composites Subjected to Accelerated Weathering Test

The impact test results of unweathered and weathered composites are given in Figure 4.44, and the detailed impact strength data are tabulated in Table 8 of Appendix A. Also, decrease in percentage of impact results of the composites were showed in parentheses in Figure 4.44.

According to Figure 4.44, the impact strength of the weathered composites for all additives loadings decreased compared to unweathered composites. The effects of photo-oxidative degradation process which was initiated by UV radiation in the presence of oxygen and moisture were the main causes for the decrease in impact strength of weathered filled composites [87].

Impact strength of neat epoxy before accelerated weathering test was 11.4 kJ/m^2 as shown in Figure 4.44. After exposure the UV radiation and moisture for 300 hours, the impact strength of the neat epoxy was determined 2.7 kJ/m^2. This decrease corresponds to 76.1%. The impact strength reduction can be due to the formation of microcracks on the surface of epoxy which were caused by UV radiation and moisture. UV photons from radiation led to chain scission reactions on the surface of epoxy to form the polymer radicals. To give a branched molecule, the fragments may link to the main chain of neighboring molecule. Thus, the degree of crosslinking was increased which resulted in high brittleness. Additionally, the existence of microcracking may lead to increase the ingress of moisture [33, 58].

Although there was an important decrease in impact strength of neat epoxy, the reduction of impact strength for EP/BaM composites was not as much as neat epoxy. While the reduction for EP/0.5BaM was 50.9%, the decrease for EP/1BaM composites was 39.8%. Consequently, the increased amount of barium metaborate, have a positive effect on the impact strength of the material. This could be due to the barrier property of the BaM which prevents the moisture uptake that leads to deteriation in the polymer, and also it has broad transparency range [88]. However, decrease of impact strength value was more significant than EP/1BaM when the concentration of BaM was increased to up 3%. So, the optimum concentration of BaM can be considered as 1% in the epoxy-based composites for accelerated weathering test.

While impact strength of EP/10MP was 3.1 kJ/m^2 before the accelerated weathering test, it decreased to 1.7 kJ/m^2 after subjected to the test conditions. This decrease corresponds to 45.2%. Adding 1% BaM to EP/10MP composites decreased the impact strength value slightly after exposure from 4.1 kJ/m^2 to 3.5 kJ/m^2. As shown in Figure 4.44, impact strength of EP/10MP/3BaM composites showed reduction from 3.1 kJ/m^2 to 2.8 kJ/m^2 after accelerated weathering test. According to this result using BaM together with MP cause an increase in the UV radiation and moisture stability of the epoxy-based composites.

Impact strength value of EP/10MP/1MEC composites decreased from 4.6 kJ/m^2 to 2.6 kJ/m^2 and impact strength value of EP/10MP/1MEC/1BaM composite decreased from 3.8 kJ/m^2 to 2.5 kJ/m^2 after accelerated weathering test. These reductions correspond to 42.8% and 34.3%, respectively. This indicates that adding 1% BaM to EP/10MP/1MEC composites increase the UV radiation and the moisture stability of epoxy-based composites and this can be related to barrier effect of BaM.

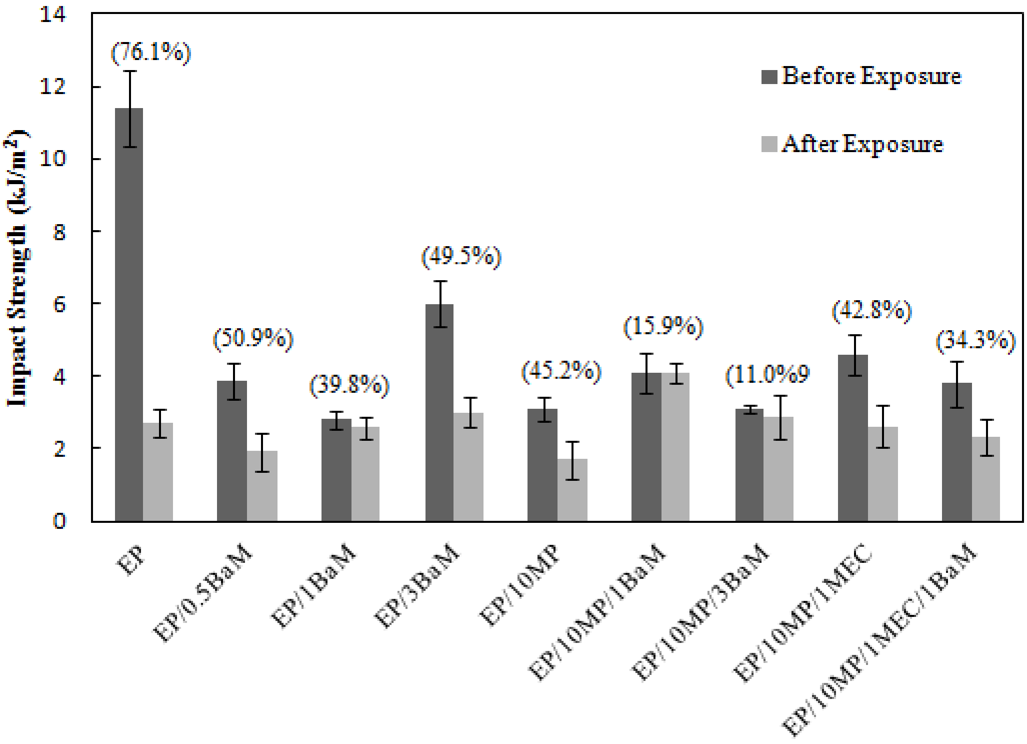

Figure 4.44 Impact Strength of the Samples Before and After Exposure of the Accelerated Weathering Test

CHAPTER 5

CONCLUSIONS

Epoxy resin is one of the most important thermosetting polymers, widely used in various fields of industry. However, like most of the polymeric materials, epoxy resins are flammable and this restricts their application areas. This study aimed to develop the flame retardant property of epoxy. In order to increase the flame retardancy of epoxy, epoxy-based composites were produced with various additives. Epoxy was synthesized by using EPIKOTE 828 as an epoxy resin and EPIKURE F205 as a hardener. Neat epoxy had a LOI value 19% and “no rating” level in the UL-94 results. Moreover, neat epoxy had a tensile strength of 50 MPa, elongation at break of 3.8%, tensile modulus of 2771 MPa and impact strength of 11.4 kJ/m^2.

In the first section of this thesis, preliminary composites were prepared to find suitable type and sufficient amount of flame retardant additives for creating the formulations of final composites. Barium metaborate (BaM), zinc borate (ZnB), melamine phosphate (MP), melamine polyphosphate (MPP), red phosphorus (RP), pentaerythritol (PER), and dipentaerythritol (DPER) were used as flame retardant additives. The LOI value of the composite increased when compared to neat epoxy. 20% BaM increased the LOI value from 19.0% to 26.25%. EP/10MP/1ZnB had 26.0% LOI value and V-1 rating in UL-94 result. The highest LOI value was obtained in EP/10MP/5RP/1BaM which was 30.0% and V-0 rating. Although the best flame retardancy property was obtained with red phosphorus, it was not used in the formulations of final compositions due to the release of phosphine gas during combustion. Overall, in preliminary composites, when concentration of the additives increased in the epoxy matrix, tensile strength and elongation at break value decreased and tensile moduli of the composited increased except for EP/15MP/5PER and EP/15MP/5DPER composites. Because of PER and DPER structure, they behaved like plasticizing agent in epoxy matrix and decreased tensile modulus.

In the second section of the thesis, final composites were prepared. BaM and MEC were added to epoxy matrix separately with 0.5%, 1% and 3% by weight ratios. According to flammability, thermal and mechanical properties, 1% was found the optimum concentration for both additives. 1% BaM increased the LOI value from 19% to 25% but decreased the impact strength from 11.4 kJ/m^2 to 4.3 kJ/m^2. Furthermore, adding 1% MEC increased the LOI value to up 24.0%. In order to investigate intumescent effect of epoxy, MP was used together with DPER. However, the main problem in intumescent system was that the decrease in mechanical properties of epoxy-based composites was too much. According to the flame retardancy and mechanical test results, DPER was not used in the further composites. 10% MP loading increased the LOI value from 19% to 27% but in the UL-94 test result showed “no rating”. Subsequently, BaM was used together with MP. BaM were added to the epoxy-based composite with 10% MP content of 0.5%, 1%, and 3% by weight ratios. UL-94 test results increased with the increase of BaM concentration. For example, EP/10MP/0.5BaM composite showed V-1 rating and EP/10MP/1BaM and EP/10MP/3BaM composites showed V-0 rating. Because the decrease in the mechanical properties of EP/10MP/3BaM composite was much more than EP/10MP/1BaM composite, EP/10MP/1BaM composite was selected as the composite with optimum MP and BaM concentrations with respect to its flame retardancy and mechanical properties. Also, ZnB and CaB were used as additives to compare effects of borates in flame retardancy properties of epoxy. Highest LOI value, UL-94 result, and char yield were obtained in the EP/10MP/1MEC/1CaB composite with 27.5%, V-0 rating and 13.54% char yield, respectively.

UV and moisture stability of the neat epoxy and epoxy-based composites were investigated in the last section of this thesis. In order to investigate the change of mechanical properties, the samples were tested with impact test before and after exposure. It can be observed that the impact strength of the composites decreased after exposure for all composites. Molecular chain scission occurred on the polymer surface to form the polymer radicals and to give a branched molecule; the fragments can link to the main chain of neighboring molecule. Thus, the degree of crosslinking was increased which resulted in high brittleness and this could be the main reason to lose the impact strength. The largest percentage decrease was seen in neat epoxy. Adding BaM only reduced the percentage decrease from 76.1% to 39.8% due to the barrier effect of BaM. According to the impact strength test results, the EP/1BaM composite gave the least decrease when compared to EP/0.5BaM and EP/3BaM. EP/10MP had a 3.1 kJ/m^2 impact strength value before exposure, after a 300 hours exposure this value decreased to 1.7 kJ/m^2. This decrease corresponds the 45.2%. On the other hand, adding BaM together with MP increased the moisture and UV radiation stability just like flame retardant properties of epoxy-based composites. EP/10MP/3BaM showed the least decrease in impact strength before and after exposure. This decrease corresponds to 11.0%. Additionally, color change was observed in the samples. The maximum change in color was seen in the neat epoxy from colorless to yellow. Besides this, the color of the composites changed from white to yellowish.

To conclude, the EP/10MP/1BaM composite showed successful flame retardant properties with 27% LOI value and V-0 rating in UL-94 test, among the studied materials. Also, UV and moisture stability of the composite was improved when compared with that of neat epoxy.

CHAPTER 6

RECOMMENDATIONS

It can be suggested that barium metaborate and methacrylate epoxy cyclosiloxane can be used as a flame retardant additives in different polymeric materials and through investigation of flame retardancy, thermal and mechanical properties of the composites in another studies. Additionally, in order to prevent agglomeration in epoxy-based composites, process parameters of composite production may be changed and/or surface modification can be done on the fillers. Furthermore, tensile test can also be applied for the accelerated weathering test samples to obtain more data about UV and moisture stability of epoxy-based composites. Also, change in mechanical and physical properties of the accelerated weathering test with respect to time can be examined.

REFERENCES

1. Laoutid, F., Bonnaud, L., Alexandre, M., Lopez-Cuesta, J.M., Dubois, P., “New Prospects in Flame Retardant Polymer Materials: From Fundamentals to Nanocomposites”, Materials Science and Engineering 63(3), 2009.
2. Horrocks, A.R., Price, D., Fire retardant materials, CRC Press, Boston, (2001).
3. Gerard, C., Fontaine, G., Bourbigot, S. New Trends in Reaction and Resistance to Fire of Fire-retardant Epoxies, materials, 3, 4476-4499, 2010.
4. Troitzsch, J.H., Overview of Flame Retardants, Chimica Oggi/Chemistry Today, 16, 1998.
5. Jain, P., Choudhary, V., Varma, I.K., Flame Retarding Epoxies With Phosphorus, Journal of Macromolecular Science, Part C: Polymer Reviews, 42(2), 139-183, 2002.
6. Lu, S.Y., Hamerton, I., Recent developments in the chemistry of halogen-free flame retardant polymers, Progress Polymer Science, 27, 1661-1712, 2002.
7. Koskiniemi, M.S., Calcium pyroborate as a microbicide for plastics, U.S. Patent, 5,482,989, 1996.
8. Stauffer, E., Nicdaeid, N., Chemistry of Fire, Encyclopedia of Forensic Sciences, 161-166, 2013.
9. Pal, G., Macskasy, H., Their behavior in fire, Elsevier, New York, 1991.
10. Chapple, S., Anandjiwala, R., Flammability of Natural Fiber-reinforced Composites and Strategies for Fire Retardancy: A Review, Journal of Thermoplastic Composite Materials, 23:871, 2010.

11. Gao, M., Wu, W., Yan, Y., Thermal Degradation and Flame Retardancy of Epoxy Resins Containing Intumescent Flame Retardant, Journal of Thermal Analysis and Calorimetry, 95, 605-608, China, 2009.
12. Wang, G., Yang, J., Thermal degradation study of fire resistive coating containing melamine polyphosphate and dipentaerythritol, Progress in Organic Coatings, 72, 605-611, China, 2011.
13. Lomakin S.M., Zaikov GE., Ecological aspects of polymer flame retardancy. Utrecht: VSP; 1999.
14. http://www.flameretardants-online.com/images/userdata/pdf/168_DE.pdf
15. Levchik, S., Flame Retardant Polymer Nanocomposites, Eds Wiley, Hoboken, 1, 2007.
16. Costa, L., Camino, G., Luda, D., Cortemiglia, P., Fire and Polymers, ACS Symposium, 425, 211, 1990.
17. Levchik, S.V., Costa, L., Camino, G., Mechanistic Study of Combustion Performance and Thermal Decomposition Behavior of Nylon-6 with Added Halogen-Free Fire Retardants, Polymer Degradation and Stability, 54, 217-222 1996.
18. Dibello, P.M., Manganaro, J.L., Aguinaldo, E.R., Mahmood, T., Lindahi, C.B., Barium Compounds, Kirk-Othmer Encyclopedia of Chemical Technology, 3, 351-375, 2003
19. Green, J., Katz, H.S., Milewski, J.V., Handbook of Fillers for Plastics, Van Nostrand Reinhold, New York, 1987.
20. Iji, M., Serizawa, S., Silicone Derivatives as New Flame Retardants for Aromatic Plastics Used in Electronic Devices, Polymers for Advanced Technologies, 9, 593-600, 1998.
21. http://www.designermoleculesinc.com/files/CS-783_(R1116)_-_Epoxy_and_Methacrylate_functional_cyclosiloxane.pdf, last accessible 12 August 2014
22. Hara, O., Curing Agents for Epoxy Resin, Three Bond Technical News, 1990
23. Miracle, D. B., Donaldsan, S.L., Introduction to Composites, ASM Handbook, Vol. 21, ASM International Online, 2003.
24. Bhatnagar, M.S., Epoxy Resins (Overview), The Polymeric Materials Encyclopedia, 1996.

25. Liu, J.Q., Chang, B., Jia, D.D., Liu, W.L., He, F.Y., Liu, Q.Z., Yao, J.S., Wang, X.Q., Wu, Y.Z., Design and fabrication of a novel superhydrophobic surface based on a copolymer of styrene and bisphenol A diglycidyl ether monoacylate, Royal Society of Chemistry, 4, 18025-18032, 2014.
26. http://web.mit.edu/3.082/www/team2_f01/chemistry.html, last accessible 12 August 2014.
27. Leisegang, E.C., Stephan, A.M., The Thermal Degradation In Vacuo of an Amine-Cured Epoxide Resin, Journal of Applied Polymer Science, 14, 1961-1981, 1970.
28. Bishop, D.P, Smith, D.A., Combined Pyrolysis and Radiochemicals Gas Chromatography for Studying the Thermal Degradation of Epoxy Resins and Polyimides, Journal of Applied Polymer Science, 14, 205-223, 1970.
29. Patterson-Jones, J.C., The mechanism of the thermal degradation of aromatic amine-cured glycidyl ether-type epoxide resins, Journal of Applied Polymer Science, 19, 1539-1547, 1975.
30. Lee, L.H., Mechanism of thermal degradation of phenolic condensation polymers. II. Thermal Stability and Degradation schemes of epoxy resin, Journal of Polymer Science Part A: Polymer Chemistry, 3, 859-882, 1965.
31. Vogt, J., Thermal analysis of epoxy-resins: Identification of decomposition products, Thermochimica Acta, 85, 411-414, 1985.
32. Kumar, B.G., Singh, R.P., Nakamura, T., Degradation of Carbon Fiber-reinforced Epoxy Composites by Ultraviolet Radiation and Condensation, Journal of Composite Materials, 36(24), 2713-2733, 2002.
33. Tipton, B., M. Sc. Dissertation, University of Central Florida, 2008.
34. Hoskin, B.C., Baker, A.A., Composite Materials for Aircraft Structures, New York, N.Y. : American Institute of Aeronautics and Astronautics, Inc., 1986.
35. Nakamura, T., Singh, R.P., Vaddadi, P., Effects of Environmental Degradation of Flexural Failure Strength of Fiber Reinforced Composites, Experimental Mechanics, 46, 257-268, 2006.

36. Mailhot, B., Ouahiuune, M.T., Gardette, J.L., Study of the Degradation of an Epoxy/Amine Resin, 1 Photo- and Thermo-Chemical Mechanism, Macromolecular Chemistry and Physics, 206, 575-584, 2005.
37. Strong, A.B., Composites Manufacturing Materials, Methods, and Applications, Deaborn, Michigan: Society of Manufacturing Engineers, 2008.
38. Leng, Y., "Materials Characterization: Introduction to Microscopic and Spectroscopic Methods", John Wiley&Sons, Asia, 2008.
39. Ersaraç, F.N., M.Sc. Dissertation, Middle East Technical University, 2012.
40. Fenimore, C. P., Martin, F. J., Flammabilty of Polymers, Combustion and Flame, 10(2), 135-139, 1966.
41. Camino, G., Costa, L., Casorati, E., Bertelli, G., Locatelli, R., The oxygen Index Method in Fire Retardance Studies of Polymeric Materials, Journal of Applied Polymer Science, 35, 1988.
42. ASTM D3801 – 10: Standard Test Method for Measuring the Comparative Burning Characteristics of Solid Plastics in a Vertical Position.
43. http://www.labservis.net/cihaz-periyodik-bakim/ft-ir/, last accessible 12 August 2014.
44. Coats, A.W., Redfern, J.P., "Thermogravimetric Analysis: A Review", Analyst 88, 906-924, 1963.
45. Özkan, N., PST 508 Characterization Techniques of Polymers, Lecture Notes: Mechanical Testing of Materials, Ankara, 2012.
46. http://archive.nrc-cnrc.gc.ca/eng/ibp/irc/cbd/building-digest-157.html, last accessible 12 August 2014
47. Meyers, M.A., Chawla, K.K., "Mechanical Behaviors of Materials", Cambridge University (1998).
48. http://www.twi-global.com/technical-knowledge/published-papers/the-evaluation-of-root-defects-in-fsw-by-through-hole-impact-testing-preliminary-studies-july-2005, last accessible 12 August 2014
49. http://en.wikipedia.org/wiki/Weather_testing_of_polymers#Accelerated_natural_weathering, last accessible 12 August 2014

50. http://www.q-lab.com/products/quv-weathering-tester/quv, last accessible 12 August 2014.

51. Cowan, J., Manley, T.R., The Effects of Inorganic on the Burning of PVC, The British Polymer Journal, 4, 44-47, 1976.

52. Baltacı, B., Çakal, G.Ö., Bayram, G., Eroğlu, İ., Özkar, S., Surfactant modified zinc borate synthesis and its effect on the properties of PET, Powder Technology, 244, 38-44, 2013.

53. Kılınç, M., Ph.D. Dissertation, Middle East Technical University, 2009.

54. Ishii, T., Kokaku, H., Nagai, A., Nishita, T., Kakimoto, M., Calcium Borate Flame Retardation System for Epoxy Molding Compounds, Polymer Engineering and Science, 46, 799-806, 2006.

55. Lv, P., Wang, Z., Hu, K., Fan, W., Flammability and thermal degradation of flame retarded polypropylene composites containing melamine phosphate and pentaerythritol derivatives, Polymer Degradation and Stability, 90, 523-534, 2005.

56. Chen, W.Y., Wang, Y.Z., Chang, F.C., Thermal and Flame Retardation of Melamine Phosphate-Modified Epoxy Resins, Journal of Polymer Research, 11, 109-117, 2004.

57. Jumahat, A., Soutis, C., Abdullah, S.A., Kasolang, S., Tensile properties of nanosilica/epoxy nanocomposites, Procedia Engineering, 1634-1640, 2012.

58. Chang, L.N., Chow, W.S., Accelerated Weathering on Glass Fiber/Epoxy/Organo-montmorillonite Nanocomposites, Journal of Composites Materials, 44, 1421-1434, 2010.

59. http://www.momentive.com/Products/TechnicalDataSheet.aspx?id=4364, last accessible 12 August 2014

60. http://www.momentive.com/Products/TechnicalDataSheet.aspx?id=8388, last accessible 12 August 2014

61. http://www.acros.be/DesktopModules/Acros_Search_Results/Acros_Search_Results.aspx?search_type=ProductNumber&SearchString=38196, last accessible 12 August 2014

62. http://aerospace.basf.com/common/pdfs/BASF_Melapur_Halogen-free_Flame_Retardants_DS_USL_sfs.pdf, last accessible 12 August 2014

63. http://www.sigmaaldrich.com/catalog/product/aldrich/236241?lang=en&region=TR, last accessible 12 August 2014
64. http://www.sigmaaldrich.com/catalog/product/aldrich/d203203?lang=en&region=TR, last accessible 12 August 2014
65. http://www.chempoint.com/products/catalog/great-lakes-solutions/great-lakes-solutions-antimony-flame-retardants/zinc-borate-antimony-flame-retardants, last accessible 12 August 2014
66. http://www.sigmaaldrich.com/catalog/product/aldrich/755818?lang=en&region=TR, last accessible 12 August 2014
67. http://tcychem.com/user/image/tds_red_phosphorus.pdf, last accessible 12 August 2014
68. http://www.sigmaaldrich.com/catalog/product/sial/24201?lang=en&region=TR, last accessible 12 August 2014.
69. Şengör, İ., M.Sc. Dissertation, Middle East Technical University, 2013.
70. http://www.aptifirst.com/dynisco/loi_limiting_oxygen_indexer.htm, last accessible 12 August 2014
71. http://www.ccsi-inc.com/p-impact-ceast-resil-impactor-6963.htm, last accessible 12 August 2014
72. http://www.q-lab.com/products/quv-weathering-tester/quv, last accessible 12 August 2014
73. Rakotomalala, M.,Wagner, S., Döring, M., Recent Developments in Halogen Free Flame Retardants for Epoxy Resins for Electrical and Electronic Applications, Materials, 3, 4300-4327, 2010.
74. Pecht, M., Deng, Y., Electronic device encaposulation using red phosphorus flame retardants, Microelectronics Reliability, 46, 53-62, 2006.
75. Laotid, F., Ferry, L., Lopez-Cuesta, J.M., Crespy, A., Red-phosphorus/aluminium oxide compositions as flame retardants in recycled poly(ethylene terephthalate), Polymer Degradation and Stability, 82, 357-363, 2003.
76. Doğan, M., Ünlü, S.M., Flame retardant effect of boron compounds on red phosphorus containing epoxy resins, Polymer Degradation and Stability, 99, 12-17, 2014.

77. Wang, G., Yang, J., Thermal degradation study of fire resistive coating containing melamine polyphosphate and dipentaerythritol, Progress in Organic Coatings, 72, 605-611, 2011.

78. Sun, H.Y., Sun, W., Huang, Y.X., Mi, J.X., Low Temperature Flux Synthesis and Characterizations of a New Layered Barium Borate $BaB_8O_{11}(OH)_4$, Journal of Inorganic and General Chemistry, 636, 977-981, 2010.

79. Gonzales, M.G., Cabanelas, J.C., Baselga, J., Applications of FTIR on Epoxy Resins-Identification, Monitoring the Curing Process, Phase Seperation and Water Uptake, Infrared Spectroscopy-Materials Science, Engineering and Technology, InTech, 2012.

80. Li, Q., Jiang, P., Wei, P., Studied on the properties of polypropylene with a new silicon-containing intumescent flame retardant, Journal of Polymer Science: Part B: Polymer Physics, 43, 2548-2556, 2005.

81. Hsiue, G.H., Wang, W.J., Chang, F.C., Synthesis, Characterization, Thermal and Flame-Retardant Properties of Silicon-Based Epoxy Resins, Journal of Applied Polymer Science, 73, 1231-1238, 1999.

82. Wang, Z., Lv, P., Hu, Y., Hu, K., Thermal degradation study of intumescent flame retardants by TG and FTIR: Melamine phosphate and its mixture with pentaerythritol, Journal of Analytical and Applied Pyrolysis, 86, 207-214, 2009.

83. Lim, W.K.P., Mariatti, M., Chow, W.S., Mar, K.T., Effect of intumescent ammonium polyphosphate (APP) and melamine cyanurate (MC) on the properties of epoxy/glass fiber composites, Composites: Part B, 43, 124-128, 2012.

84. Nakamura, Y., Yamaguchi, M., Okubo, M., Matsumoto, T., Effects of Particle Sizeon Mechanical and Impact Properties of Epoxy Resin Filled with Spherical Silica, Journal of Applied Polymer Science, 45, 1281-1289, 1992.

85. Woo R.S.C., Chen, Y., Zhu, H., Li, J.K.K., Leung, K.Y., Environmental degradation of epoxy-organoclay nanocomposites due to UV exposure. Part 1: Photo-degradation, Science and Technology, 67, 3448-3456, 2007.

86. Kim, H., Urban, M.W., Molecular Level Chain Scission Mechanisms of Epoxy and Urethane Polymeric Films Exposed to UV/H2O. Multidimensional Spectroscopic Studies, Langmuir, 16, 5382-5390, 2000.

87. Bakar, A.A., Hassan, A., Yusof, A.F.M., Effect of Accelerated Weathering on the Mechanical Properties of Oil Palm Empty Fruit Bunch Filled UPVC Composites, Iranian Polymer Journal, 14(7), 627-635, 2005.

88. Eimerl, D., Davis, L., Velsko, S., Graham, E.K., Zalkin, A., Optical, mechanical, and thermal properties of barium borate, Journal of Applied Physics, 62, 1968-1983, 1987.

APPENDIX A

MECHANICAL ANALYSIS

Table A.1 Tensile Strength of Preliminary Composites (MPa)

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	48.19	54.83	51.42	50.05	45.65	50.03	3.45
EP/5BaM	42.3	52.8	57.1	41.8	51.3	49.1	6.7
EP/10BaM	46.2	49.6	47.7	49.2	-	48.2	1.6
EP/20BaM	52.7	36.3	41.3	44.2	46.1	44.1	6.1
EP/1ZnB	56.4	56.2	47.2	48.5	42.2	50.1	6.1
EP/10MPP	32.1	34.1	30.2	42.7	-	34.8	5.5
EP/1BaM/1ZnB	37.6	50.4	39.6	39.1	-	41.7	5.9
EP/10MP/1ZnB	53.6	45.6	46.6	53.6	48.7	49.6	3.8
EP/5RP/3ZnB	54.6	54.0	44.5	47.7	47.0	49.6	4.5
EP/10MP/5RP	45.2	51.6	41.6	46.2	47.6	46.4	3.6
EP/10MP/5RP/1BaM	51.4	51.3	44.7	46.9	-	48.6	3.3
EP/15MP/5PER	17.4	17.4	11.6	-	-	15.4	3.3
EP/15MP/5DPER	17.0	13.9	15.2	14.7	17.4	15.6	1.5

Table A.2 Tensile Modulus (MPa) of Preliminary Composites

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	2659.8	3044.6	2599.0	2745.3	2757.4	2761.2	171.2
EP/5BaM	2461.9	2705.1	2904.7	2550.9	2880.4	2700.6	195.8
EP/10BaM	2662.4	2749.5	3063.4	2692.0	-	2791.8	184.6
EP/20BaM	3360.6	2791.7	2764.9	3023.0	3108.3	3009.7	245.2
EP/1ZnB	2870.1	2847.7	2819.5	2943.3	2494.0	2794.9	174.4
EP/10MPP	3336.4	3237.2	3066.0	2869.4	-	3127.3	204.9
EP/1BaM/1ZnB	2628.1	2597.4	2880.8	2541.3	-	2661.9	150.3
EP/10MP/1ZnB	3526.8	2874.7	3344.8	3431.1	3368.8	3309.2	252.9
EP/5RP/3ZnB	2780.1	3061.0	2683.8	2952.6	2982.8	2892.1	155.2
EP/10MP/5RP	3205.4	3272.9	2838.9	3553.6	3236.3	3221.4	254.9
EP/10MP/5RP/1BaM	3660.4	3659.5	3233.7	3564.1	-	3529.4	202.3
EP/15MP/5PER	1655.1	1655.6	1949.5	-	-	1753.4	169.8
EP/15MP/5DPER	2345.5	2028.7	1745.5	2031.9	1867.8	2003.9	225.5

Table A.3 Elongation at Break (%) of Preliminary Composites

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	4.4	3.6	3.1	3.9	3.6	3.7	0.5
EP/5BaM	3.5	2.6	4.0	3.5	2.7	3.2	0.6
EP/10BaM	3.0	3.6	2.1	3.0	-	2.9	0.6
EP/20BaM	1.9	1.8	2.1	2.1	1.7	1.9	0.2
EP/1ZnB	3.3	3.0	2.7	2.7	3.6	3.1	0.4
EP/10MPP	1.0	1.2	1.1	1.9	-	1.3	0.4
EP/1BaM/1ZnB	1.7	3.1	1.6	1.6	-	2.0	0.7
EP/10MP/1ZnB	2.8	2.8	2.5	2.7	2.7	2.7	0.1
EP/5RP/3ZnB	3.3	3.2	2.9	2.9	2.8	3.0	0.2
EP/10MP/5RP	2.5	2.8	2.3	2.4	2.7	2.5	0.2
EP/10MP/5RP/1BaM	2.4	2.4	2.2	2.7	-	2.4	0.2
EP/15MP/5PER	1.0	1.0	0.5	-	-	0.8	0.3
EP/15MP/5DPER	0.7	0.6	0.8	0.6	1.0	0.8	0.1

Table A.4 Tensile Strength of Final Composites (MPa)

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	48.19	54.83	51.42	50.05	45.65	50.03	3.45
EP/0.5BaM	55.0	53.4	50.7	46.7	55.8	52.3	3.7
EP/1BaM	45.5	46.6	53.7	57.7	47.9	50.3	5.2
EP/3BaM	39.4	44.9	45.6	48.1	43.9	44.4	3.2
EP/0.5MEC	45.7	47.1	38.9	42.7	45.3	43.9	3.2
EP/1MEC	49.2	50.8	42.0	41.9	40.7	44.9	4.7
EP/3MEC	52.9	44.5	50.9	44.8	39.4	46.5	5.4
EP/10MP	48.9	59.4	48.3	57.1	49.18	52.57	5.27
EP/7.5MP/2.5DPER	36.0	36.8	39.0	34.6	39.6	37.2	2.1
EP/5MP/5DPER	38.8	30.3	35.1	26.3	29.7	32.0	4.9
EP/2.5MP/7.5DPER	34.7	33.5	23.3	29.7	24.9	29.2	5.0
EP/10DPER	33.2	27.9	31.3	28.5	29.8	30.1	2.2
EP/10MP/0.5BaM	37.1	42.9	36.4	36.2	42.1	39.0	3.3
EP/10MP/1BaM	39.6	38.1	33.9	39.6	36.5	37.5	2.4
EP/10MP/3BaM	28.5	33.5	35.6	38.6	31.2	33.5	3.9
EP/1BaM/1MEC	42.8	35.8	30.7	31.1	34.7	35.0	4.9
EP/10MP/1MEC	32.2	34.5	32.8	34.3	37.1	34.2	1.9
EP/10MP/1MEC/1BaM	37.7	26.4	30.1	26.0	28.9	29.8	4.7
EP/10MP/1MEC/1ZnB	28.4	25.3	34.6	27.5	24.6	28.1	3.9
EP/10MP/1MEC/1CaB	19.4	31.7	26.3	26.3	22.8	25.3	4.6

Table A.5 Tensile Modulus (MPa) of Final Composites

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	2659.8	3044.6	2599.0	2745.3	2757.4	2761.2	171.2
EP/0.5BaM	2558.7	2492.4	2342.8	2358.4	2732.7	2497.0	160.0
EP/1BaM	2611.6	2679.7	2684.4	2859.2	2486.2	2664.2	135.3
EP/3BaM	2430.4	2607.8	2724.6	2493.8	2778.7	2607.1	147.7
EP/0.5MEC	2584.3	2417.3	2273.2	2602.3	2348.7	2445.2	144.7
EP/1MEC	2319.5	2465.0	2368.6	2219.3	2369.8	2348.4	89.4
EP/3MEC	2109.3	2293.6	2128.6	2252.5	2552.9	2267.4	178.0
EP/10MP	3008.8	2892.8	2838.8	2807.8	2793.4	2868.3	87.294
EP/7.5MP/2.5DPER	2288.0	2316.4	2696.2	2149.5	2719.5	2433.9	258.0
EP/5MP/5DPER	2387.3	2244.0	2406.4	2543.5	1786.9	2273.6	292.0
EP/2.5MP/7.5DPER	2367.2	2457.5	2052.6	1836.6	2144.7	2171.7	248.5
EP/10DPER	1264.0	1404.3	1276.3	1890.3	1752.9	1517.6	287.1
EP/10MP/0.5BaM	2877.3	2458.1	2617.9	2580.7	2781.1	2663.0	166.3
EP/10MP/1BaM	2511.2	3013.1	2743.0	2617.9	2403.1	2657.7	235.3
EP/10MP/3BaM	2675.0	2714.0	2443.4	2728.7	2696.0	2651.4	118.0
EP/1BaM/1MEC	2843.4	2666.0	2329.5	2743.9	2743.0	2665.2	197.9
EP/10MP/1MEC	2815.2	2306.3	2937.7	2834.3	3031.1	2784.9	281.2
EP/10MP/1MEC/1BaM	2306.7	2369.9	2259.9	2201.0	2604.1	2348.3	155.8
EP/10MP/1MEC/1ZnB	2462.7	2511.8	2854.0	2517.3	2450.1	2559.2	167.4
EP/10MP/1MEC/1CaB	2610.0	2737.6	2471.1	2807.1	2496.9	2624.6	146.9

Table A.6 Elongation at Break (%) of Final Composites

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	4.4	3.6	3.1	3.9	3.6	3.7	0.5
EP/0.5BaM	3.6	4.2	4.0	3.7	3.6	3.8	0.3
EP/1BaM	3.8	3.0	3.9	4.2	4.1	3.8	0.5
EP/3BaM	3.1	3.3	3.4	2.9	3.8	3.3	0.3
EP/0.5MEC	3.2	4.3	4.5	4.2	5.2	4.3	0.7
EP/1MEC	3.6	3.8	3.3	3.8	3.7	3.6	0.2
EP/3MEC	3.9	3.6	4.3	3.5	3.9	3.8	0.3
EP/10MP	2.8	2.8	3.1	2.9	2.4	2.8	0.3
EP/7.5MP/2.5DPER	1.6	1.8	1.8	1.9	1.8	1.8	0.1
EP/5MP/5DPER	1.8	1.3	1.2	1.3	2.0	1.5	0.3
EP/2.5MP/7.5DPER	1.6	1.4	1.0	2.0	1.4	1.5	0.3
EP/10DPER	2.6	1.6	2.4	1.5	1.5	1.9	0.5
EP/10MP/0.5BaM	1.9	2.1	2.0	2.1	1.9	2.0	0.1
EP/10MP/1BaM	2.0	1.7	1.9	2.1	2.0	1.9	0.2
EP/10MP/3BaM	1.2	1.8	2.7	1.9	1.8	1.9	0.5
EP/1BaM/1MEC	3.0	3.6	3.4	2.7	2.7	3.1	0.4
EP/10MP/1MEC	1.6	2.4	1.7	1.8	1.9	1.9	0.3
EP/10MP/1MEC/1BaM	1.9	1.4	1.8	1.7	1.4	1.6	0.2
EP/10MP/1MEC/1ZnB	1.6	1.5	1.9	1.5	1.4	1.6	0.2
EP/10MP/1MEC/1CaB	1.0	1.7	1.3	1.4	1.1	1.3	0.3

Table A.7 Impact Strength (kJ/m^2) of Final Composites

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	10.23	12.20	10.35	12.55	11.78	11.40	1.10
EP/0.5BaM	3.60	4.00	3.35	4.75	3.70	3.90	0.50
EP/1BaM	4.40	4.50	4.20	3.78	4.63	4.30	0.30
EP/3BaM	5.95	5.63	6.13	6.30	6.03	6.00	0.30
EP/0.5MEC	6.75	8.33	7.93	7.80	8.15	7.80	0.60
EP/1MEC	6.10	7.68	7.80	6.75	6.53	7.00	0.70
EP/3MEC	4.90	4.88	6.25	5.63	5.85	5.50	0.60
EP/10MP	2.85	3.25	2.78	3.60	3.00	3.10	0.30
EP/7.5MP/2.5DPER	5.78	4.95	6.10	4.90	4.63	5.30	0.60
EP/5MP/5DPER	4.88	5.60	4.48	5.18	5.33	5.10	0.40
EP/2.5MP/7.5DPER	4.35	4.40	3.40	4.33	3.78	4.10	0.40
EP/10DPER	3.25	3.13	2.83	3.20	2.90	3.10	0.20
EP/10MP/0.5BaM	3.70	4.03	3.80	4.40	4.18	4.00	0.30
EP/10MP/1BaM	4.50	3.60	4.23	4.75	3.70	4.10	0.60
EP/10MP/3BaM	3.10	2.98	3.13	3.20	3.25	3.10	0.10
EP/1BaM/1MEC	11.63	11.78	9.50	10.23	9.65	10.60	1.10
EP/10MP/1MEC	5.38	4.58	4.40	3.78	4.68	4.60	0.60
EP/10MP/1MEC/1BaM	3.30	3.93	3.13	4.75	3.80	3.80	0.60
EP/10MP/1MEC/1ZnB	4.00	3.78	4.10	3.93	3.43	3.80	0.30
EP/10MP/1MEC/1CaB	3.00	4.08	3.13	3.30	3.60	3.40	0.40

Table A.8 Impact Strength of Accelerated Weathering Test Samples after Exposure (kJ/m^2)

Samples	**1**	**2**	**3**	**4**	**5**	**Mean**	**Std. Dev.**
EP	2.60	2.75	3.35	2.48	2.48	2.73	0.37
EP/0.5BaM	2.18	2.45	1.20	1.60	2.15	1.92	0.51
EP/1BaM	2.90	2.43	2.88	2.38	2.38	2.59	0.27
EP/3BaM	3.00	3.13	3.20	3.38	2.45	3.03	0.35
EP/10MP	1.20	2.35	1.48	1.30	2.15	1.70	0.52
EP/10MP/1BaM	3.38	3.13	3.30	3.85	3.60	3.45	0.28
EP/10MP/3BaM	3.30	3.12	3.00	2.45	1.93	2.76	0.57
EP/10MP/1MEC	2.45	1.93	3.43	2.35	3.00	2.63	0.59
EP/10MP/1MEC/1BaM	2.05	2.45	2.33	3.30	2.35	2.50	0.47

APPENDIX B

TGA RESULTS OF THE SAMPLES

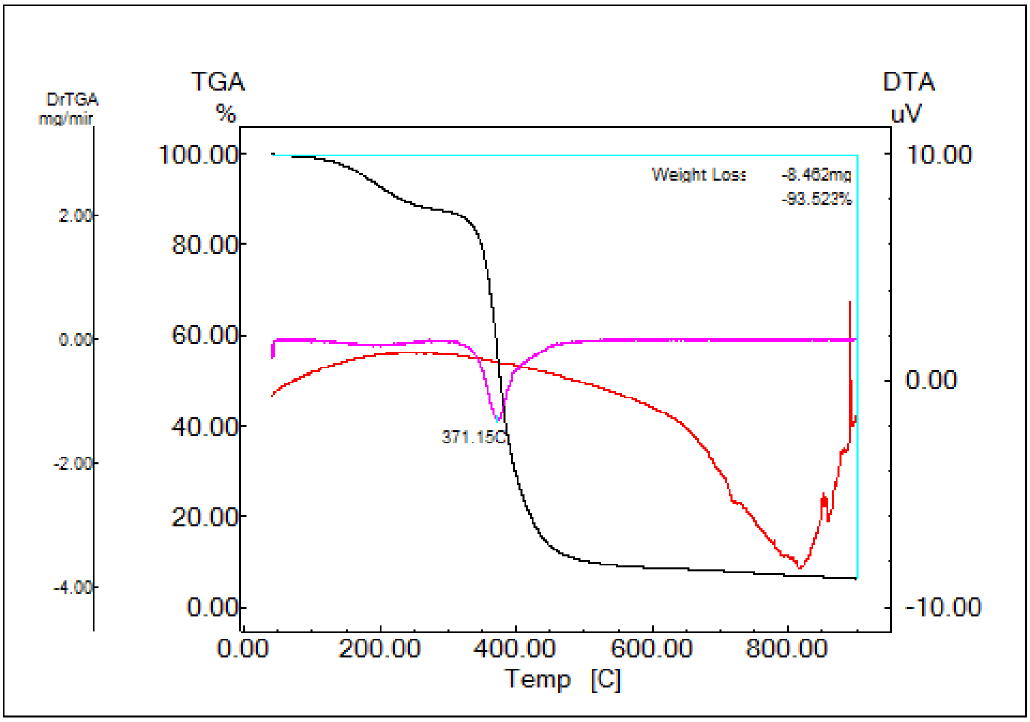

Figure B.1 TG/DTA Thermogram of Neat Epoxy

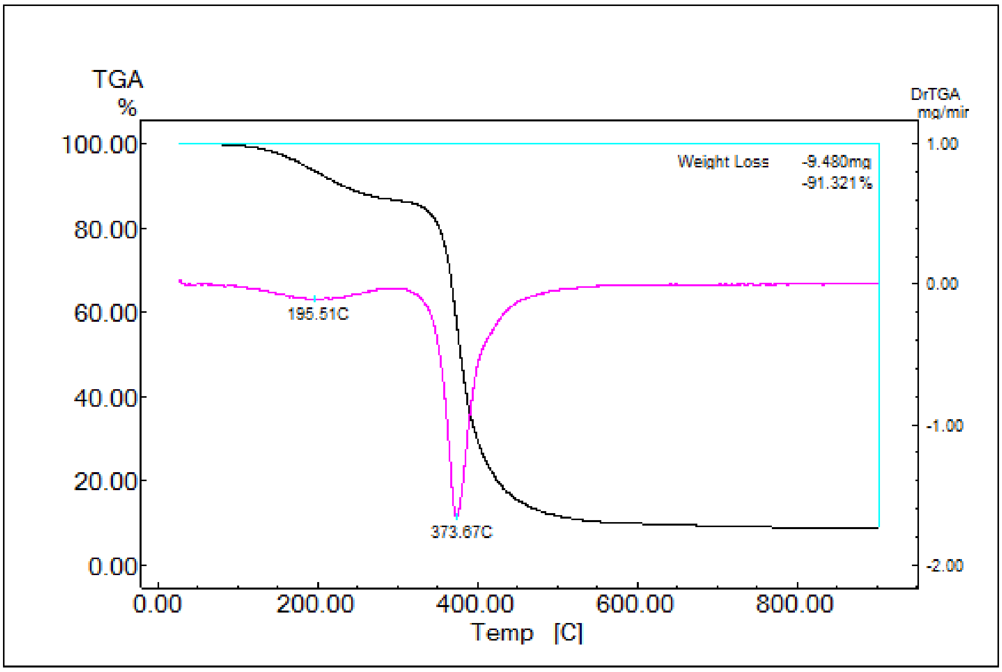

Figure B.2 TG/DTA Thermogram of EP/0.5BaM

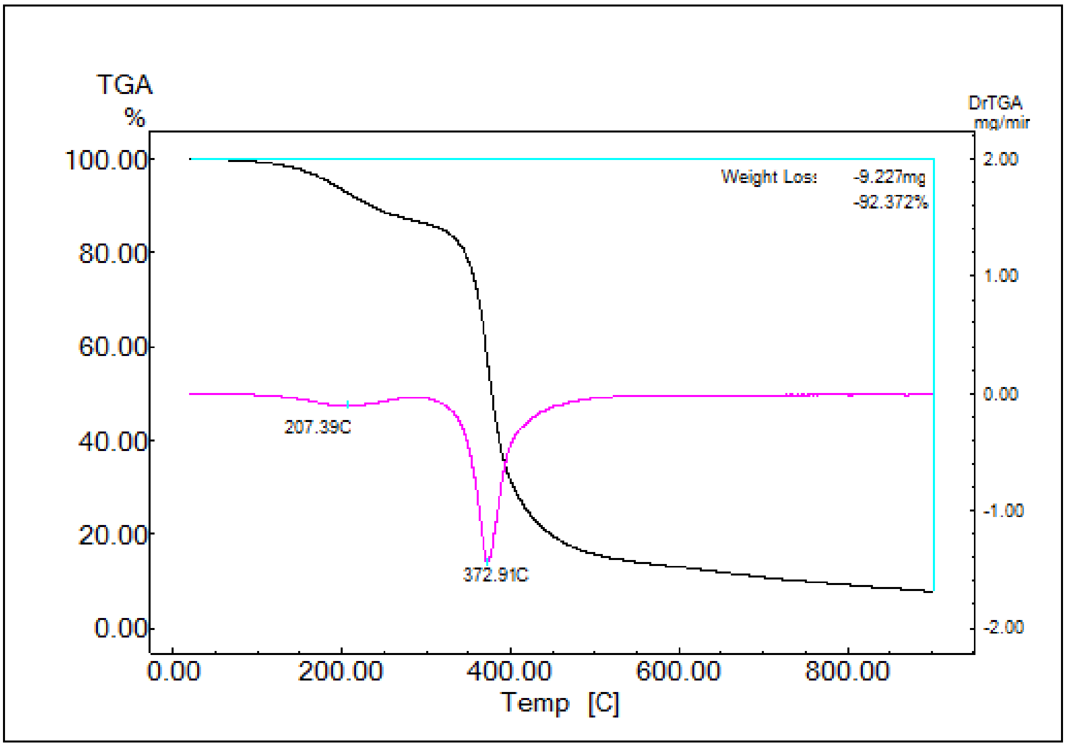

Figure B.3 TG/DTA Thermogram of EP/1BaM

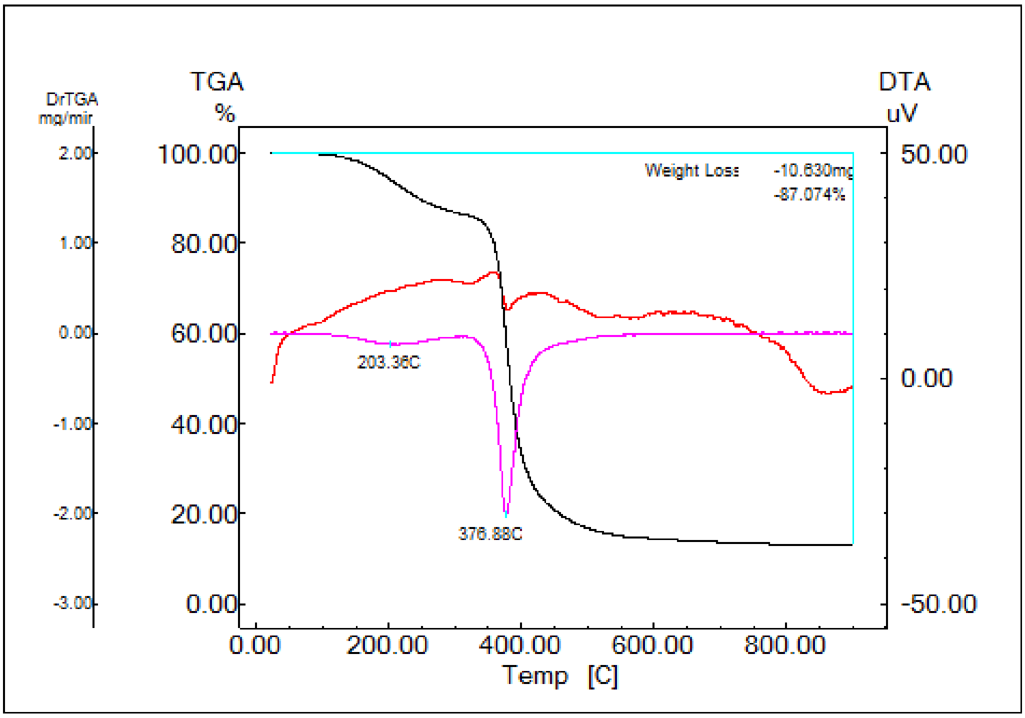

Figure B.4 TG/DTA Thermogram of EP/3BaM

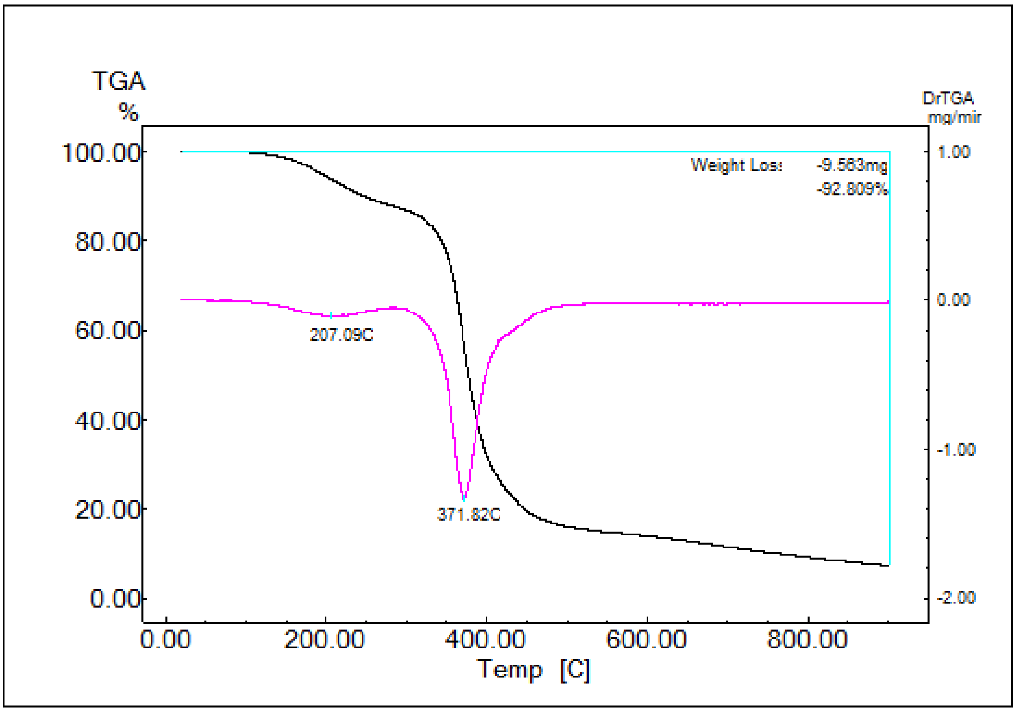

Figure B.5 TG/DTA Thermogram of EP/0.5MEC

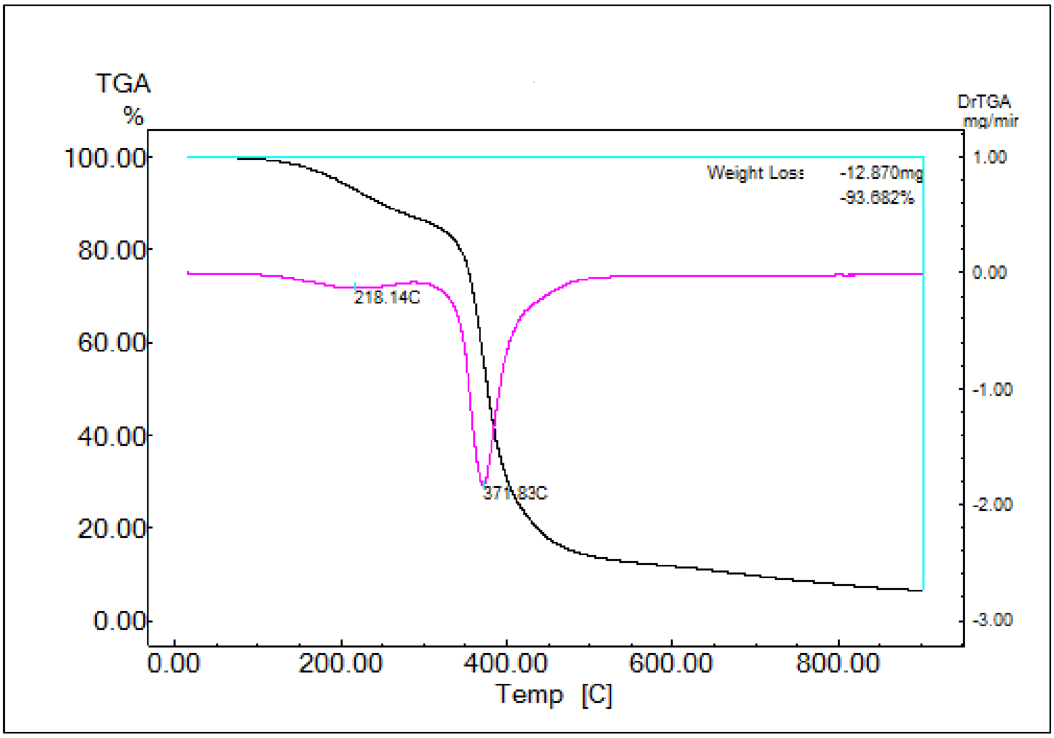

Figure B.6 TG/DTA Thermogram of EP/1MEC

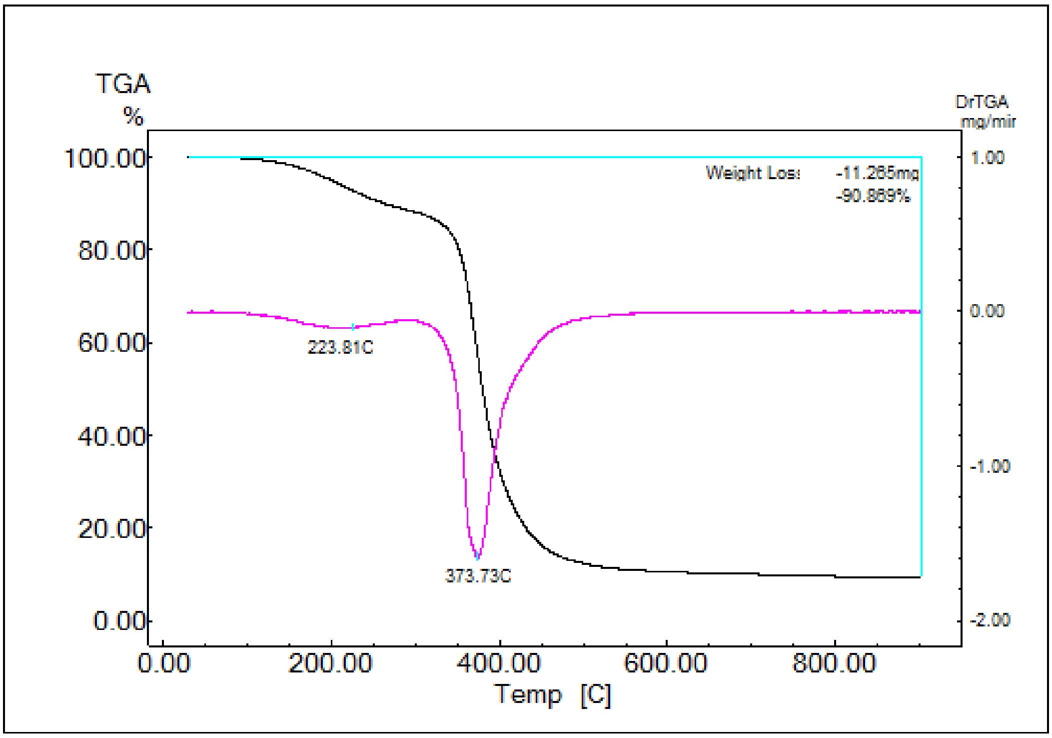

Figure B.7 TG/DTA Thermogram of EP/3MEC

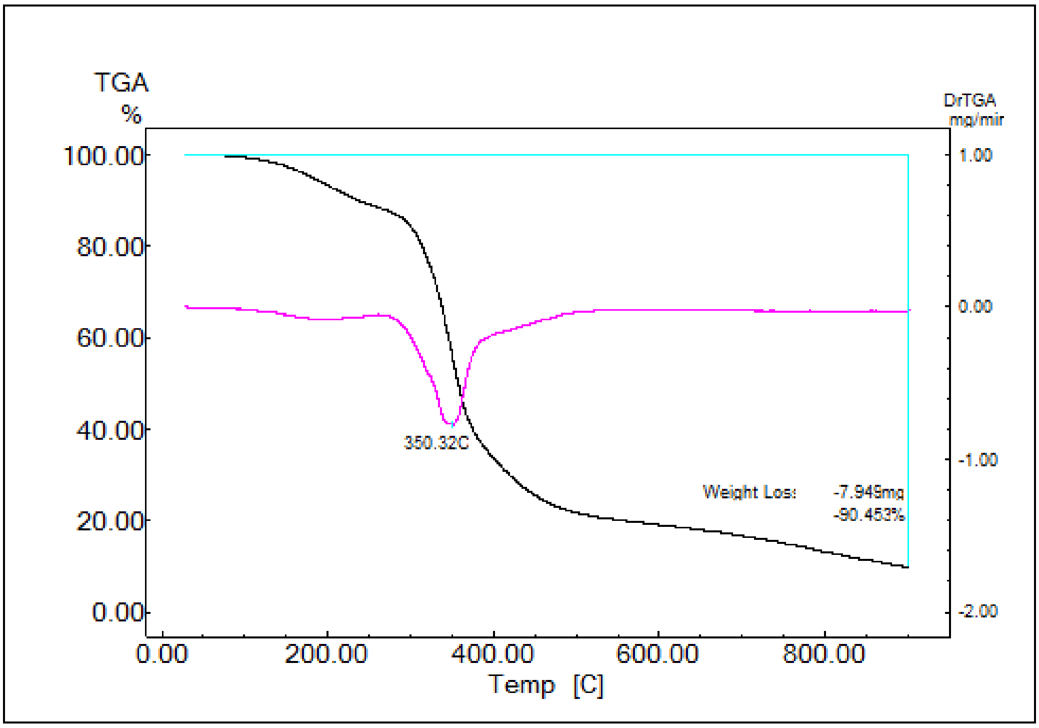

Figure B.8 TG/DTA Thermogram of EP/10MP

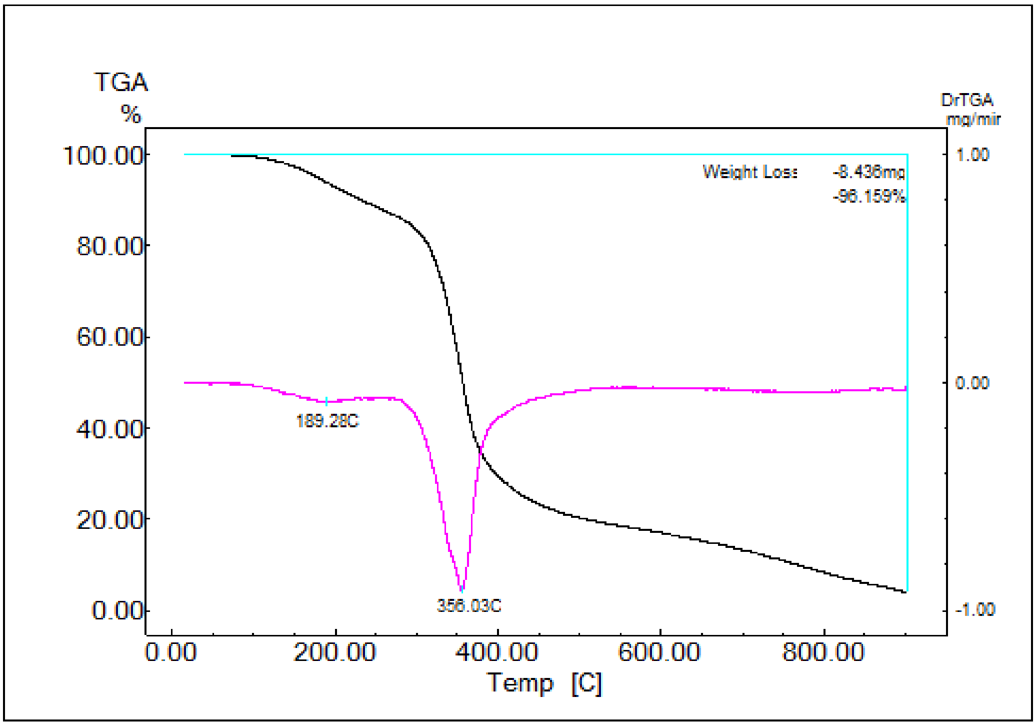

Figure B.9 TG/DTA Thermogram of EP/7.5MP/2.5DPER

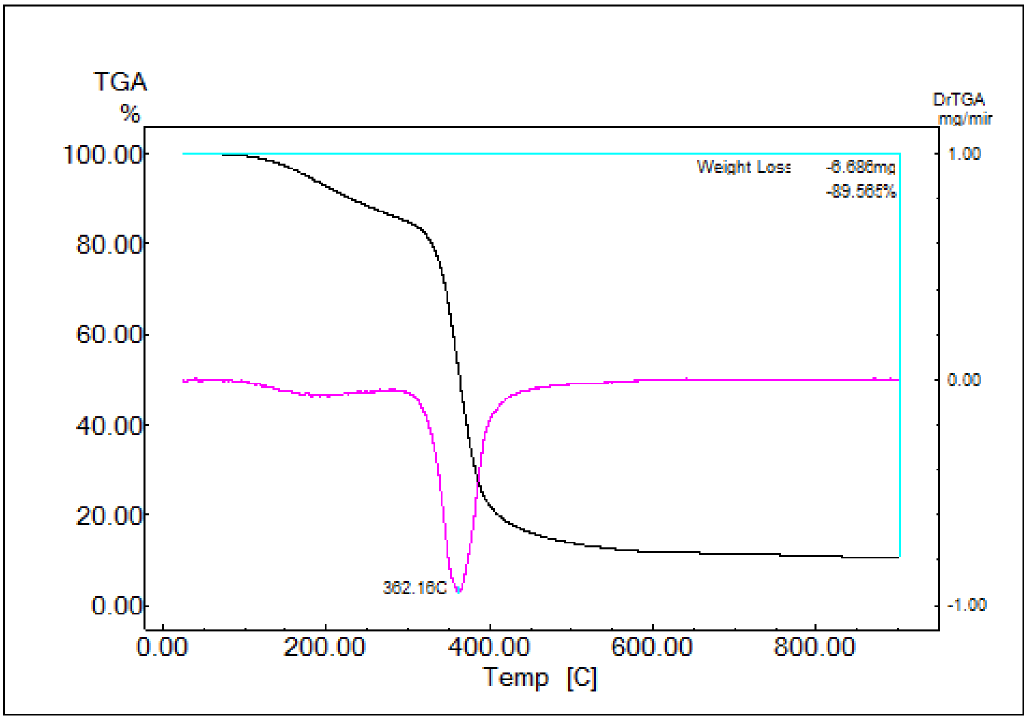

Figure B.10 TG/DTA Thermogram of EP/5MP/5DPER

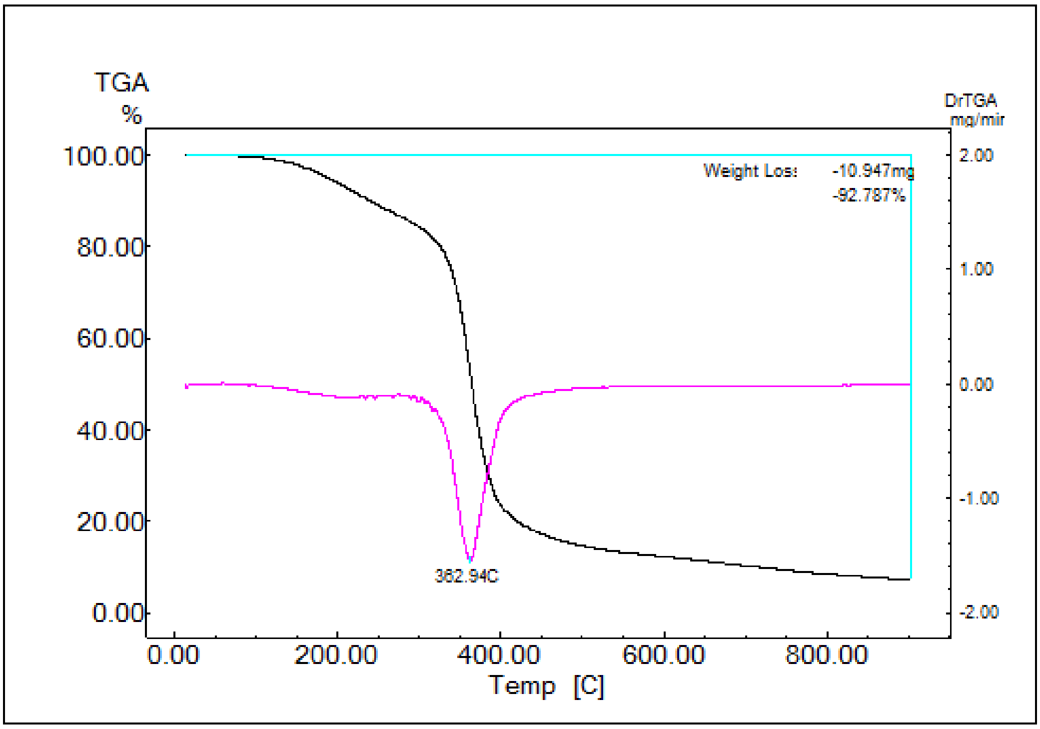

Figure B.11 TG/DTA Thermogram of EP/2.5MP/7.5DPER

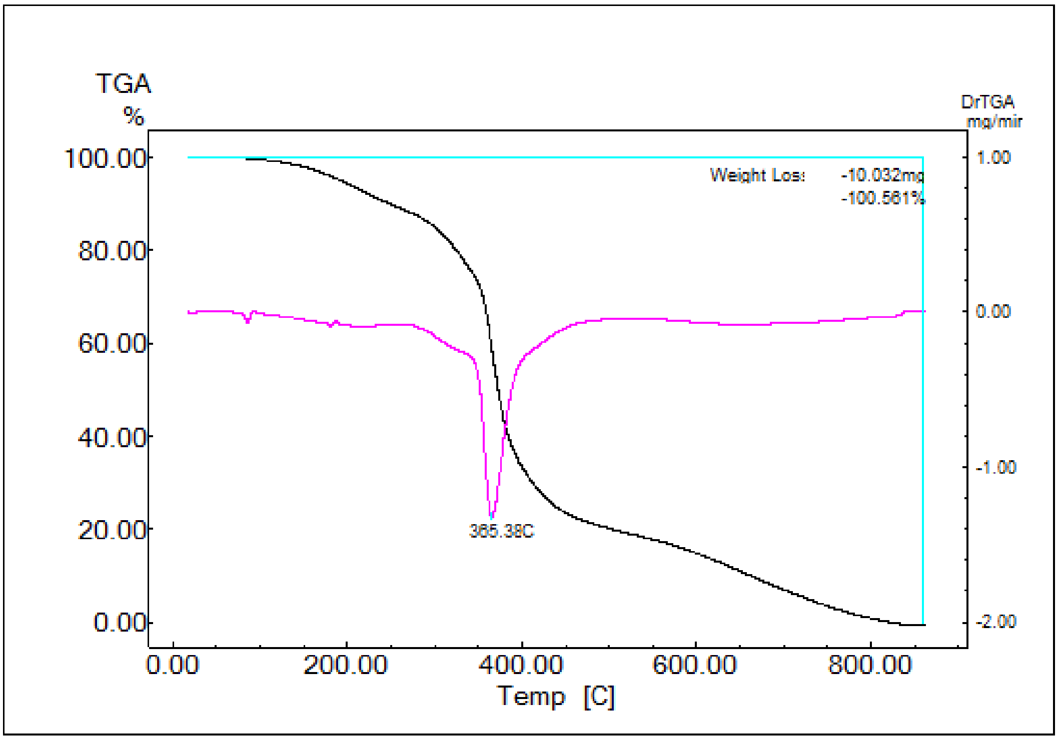

Figure B.12 TG/DTA Thermogram of EP/10DPER

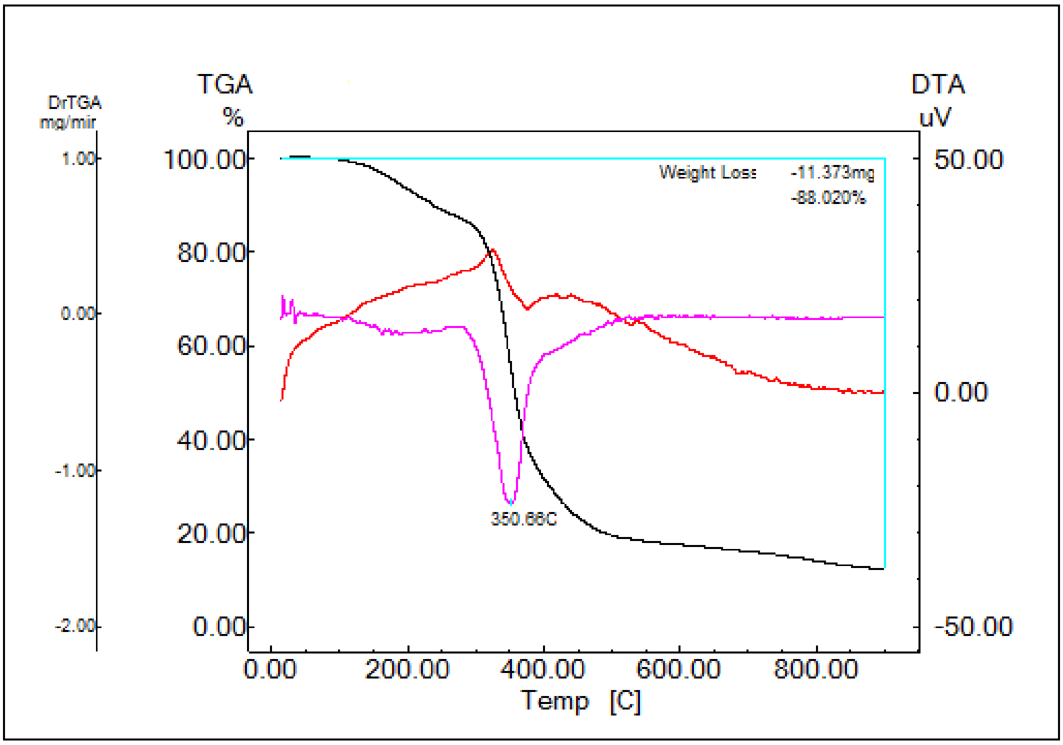

Figure B.13 TG/DTA Thermogram of EP/10MP/0.5BaM

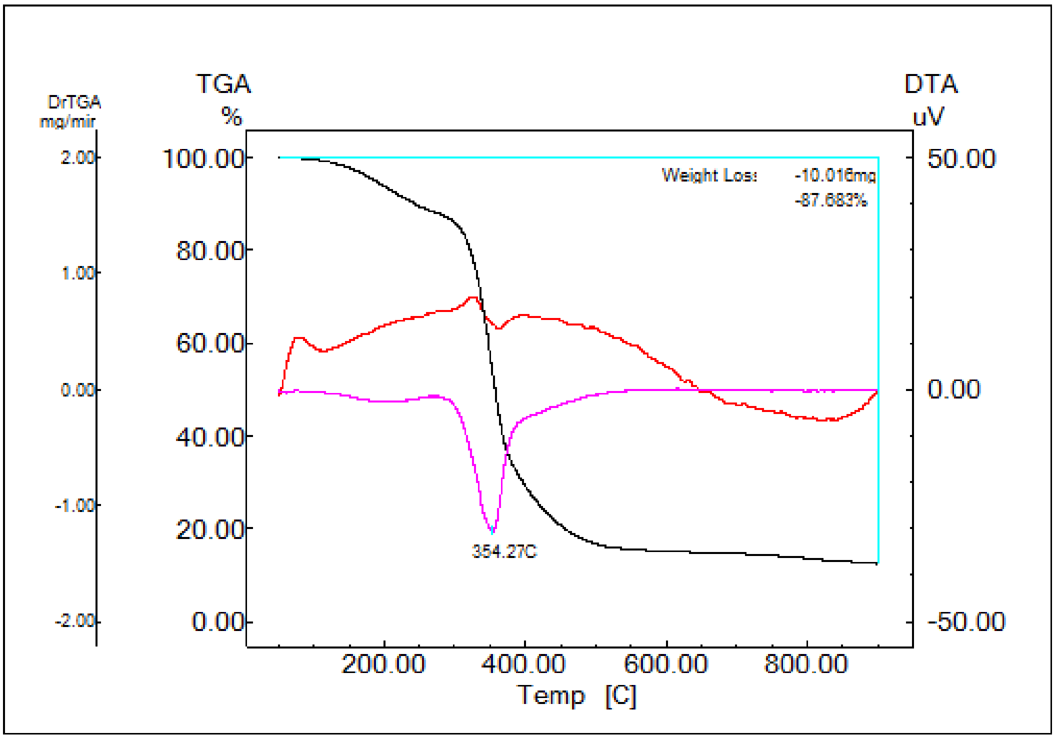

Figure B.14 TG/DTA Thermogram of EP/10MP/1BaM

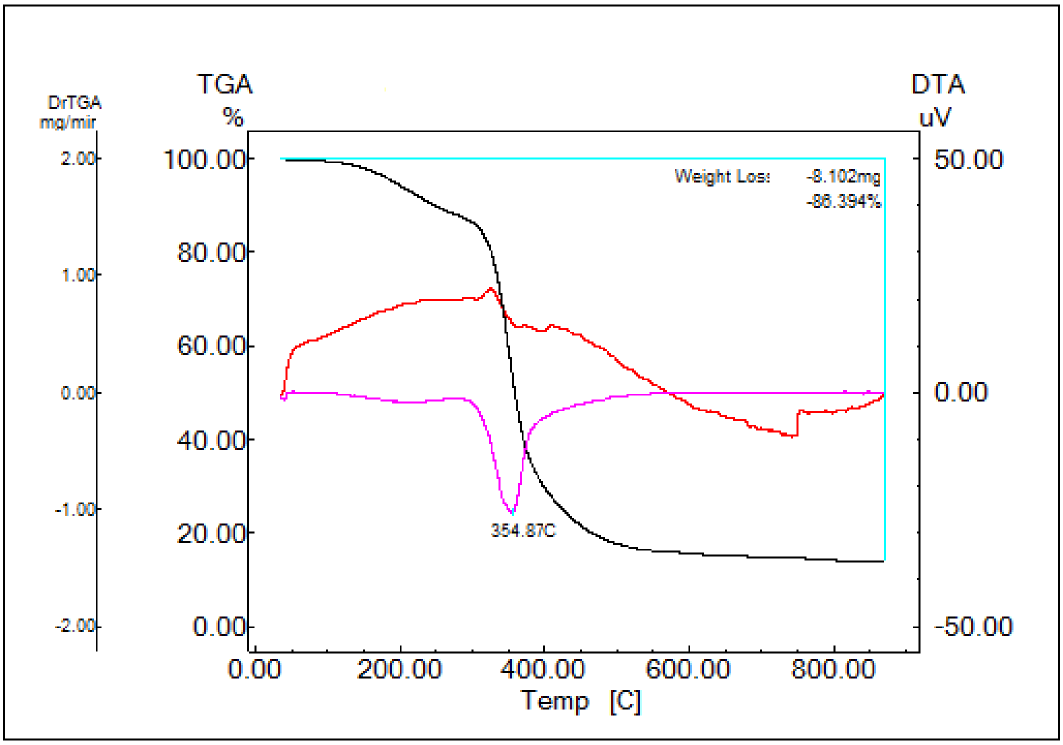

Figure B.15 TG/DTA Thermogram of EP/10MP/3BaM

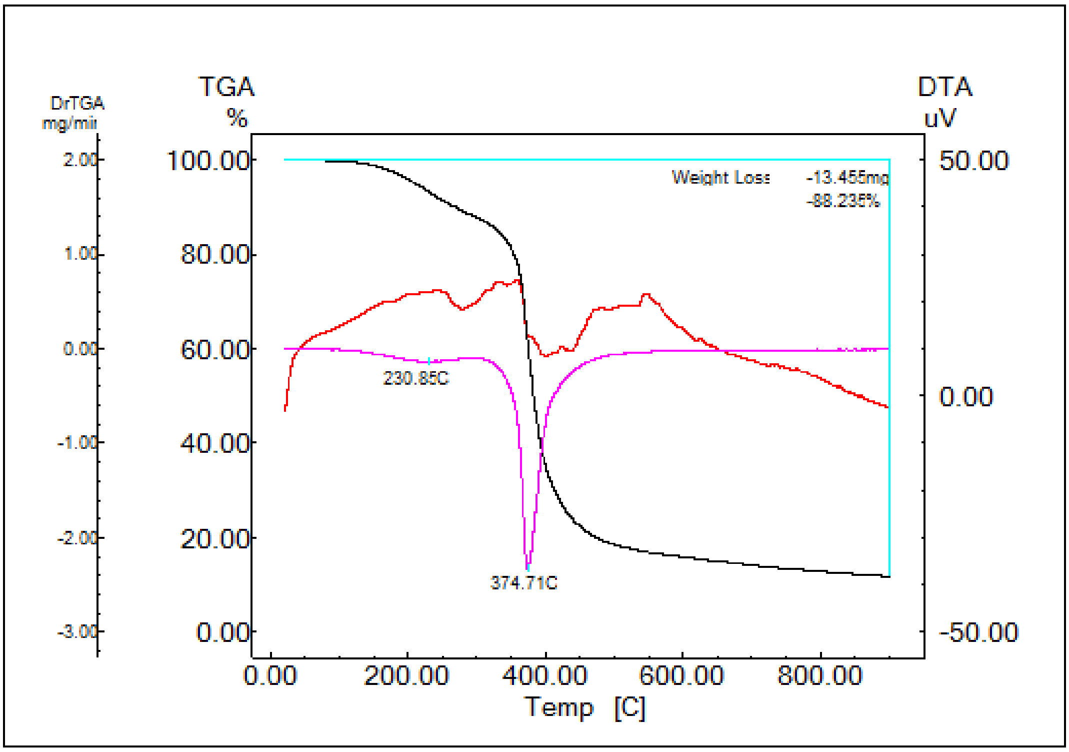

Figure B.16 TG/DTA Thermogram of EP/1BaM/1MEC

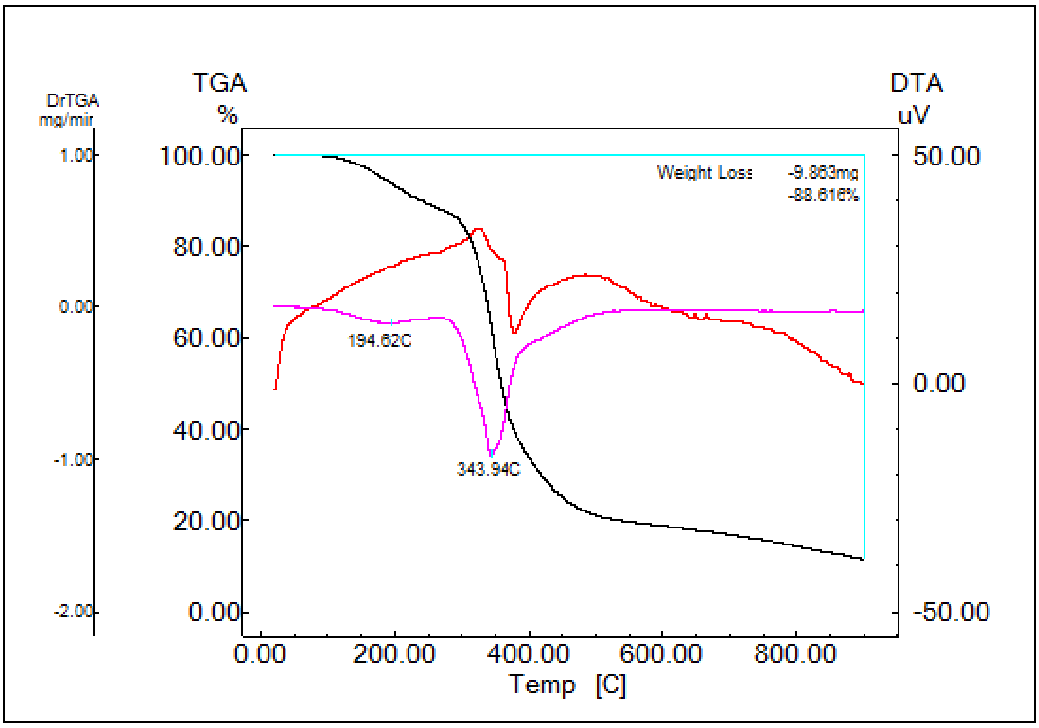

Figure B.17 TG/DTA Thermogram of EP/10MP/1MEC

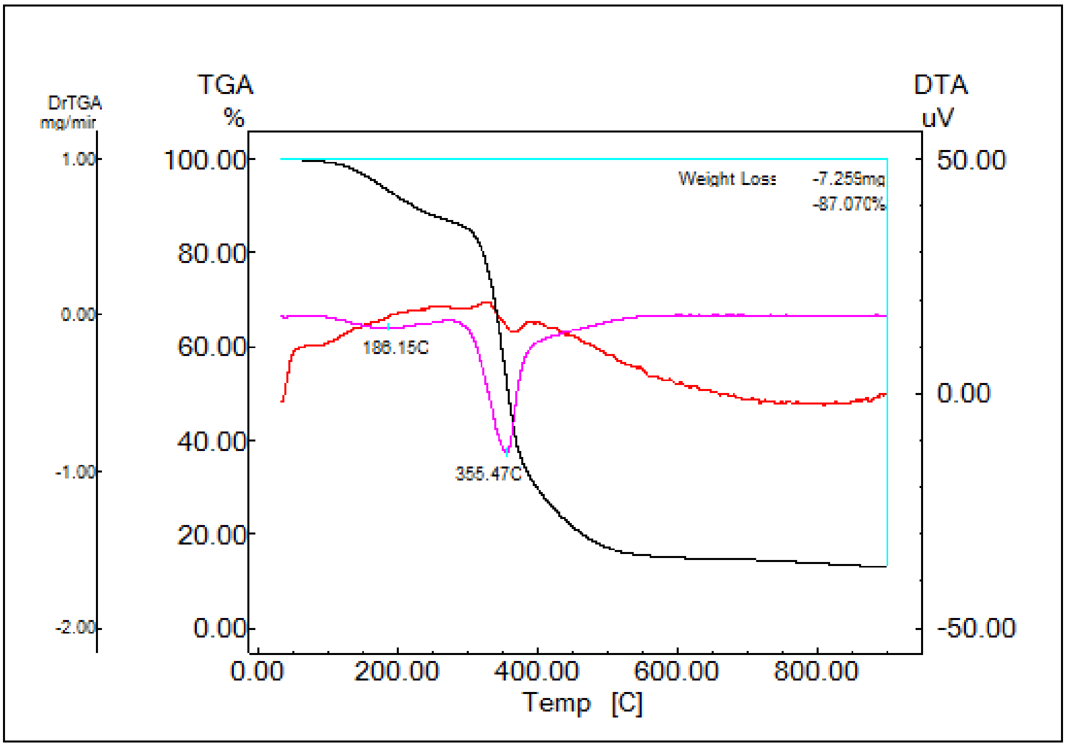

Figure B.18 TG/DTA Thermogram of EP/10MP/1MEC/1BaM

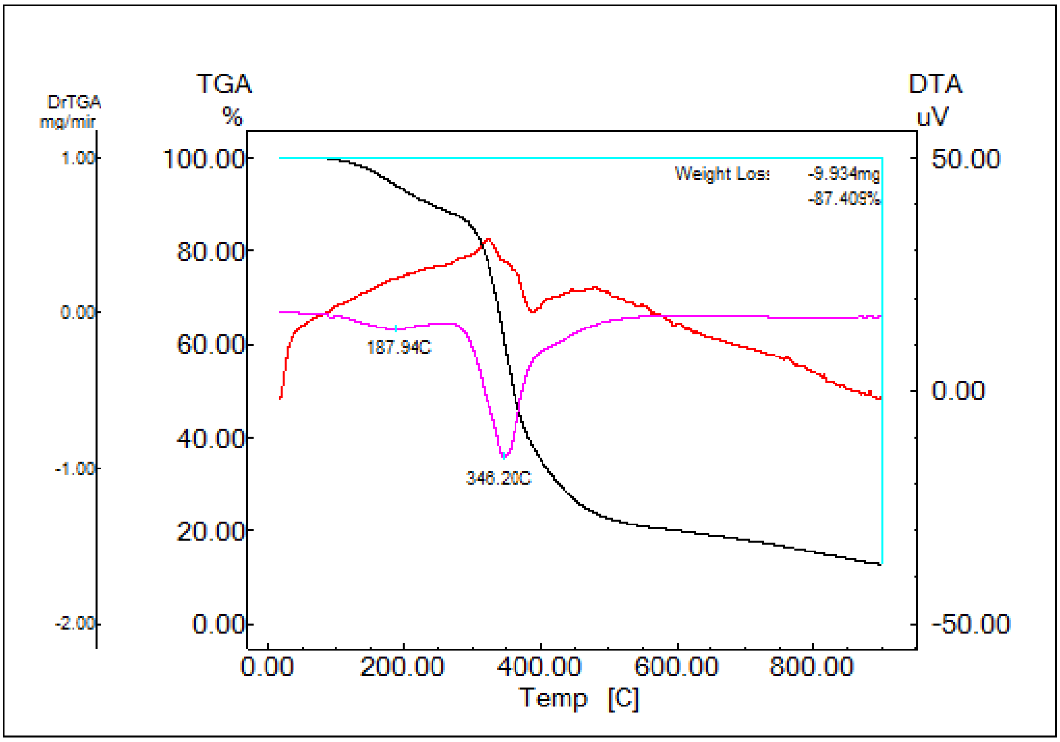

Figure B.19 TG/DTA Thermogram of EP/10MP/1MEC/1ZnB

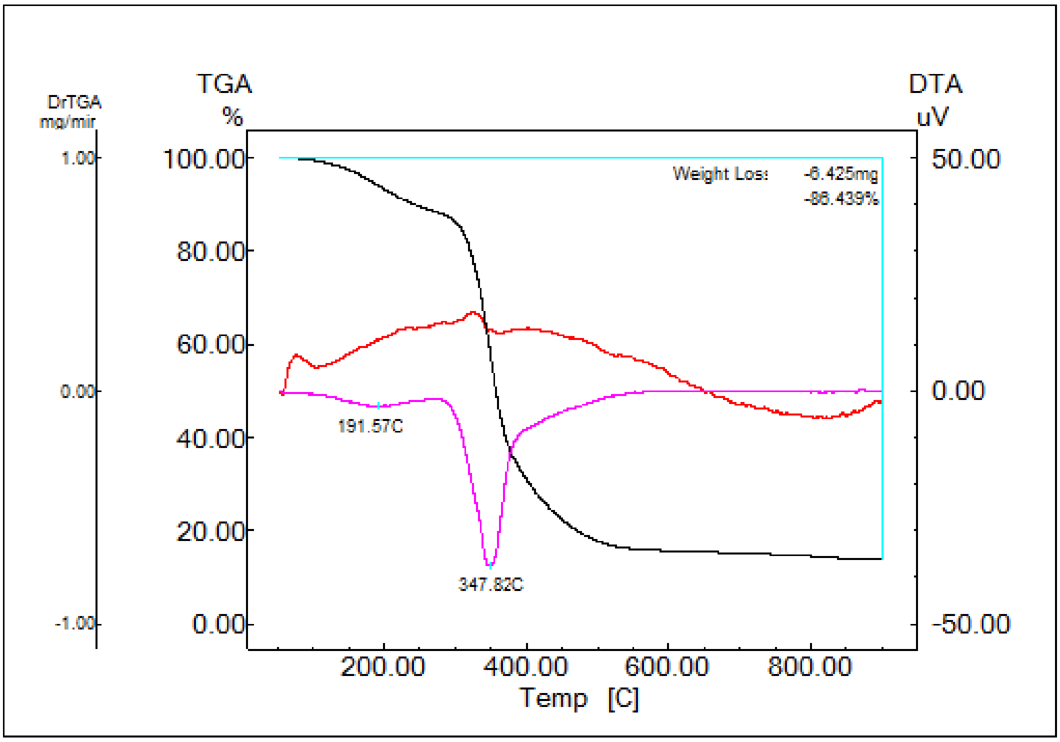

Figure B.20 TG/DTA Thermogram of EP/10MP/1MEC/1CaB

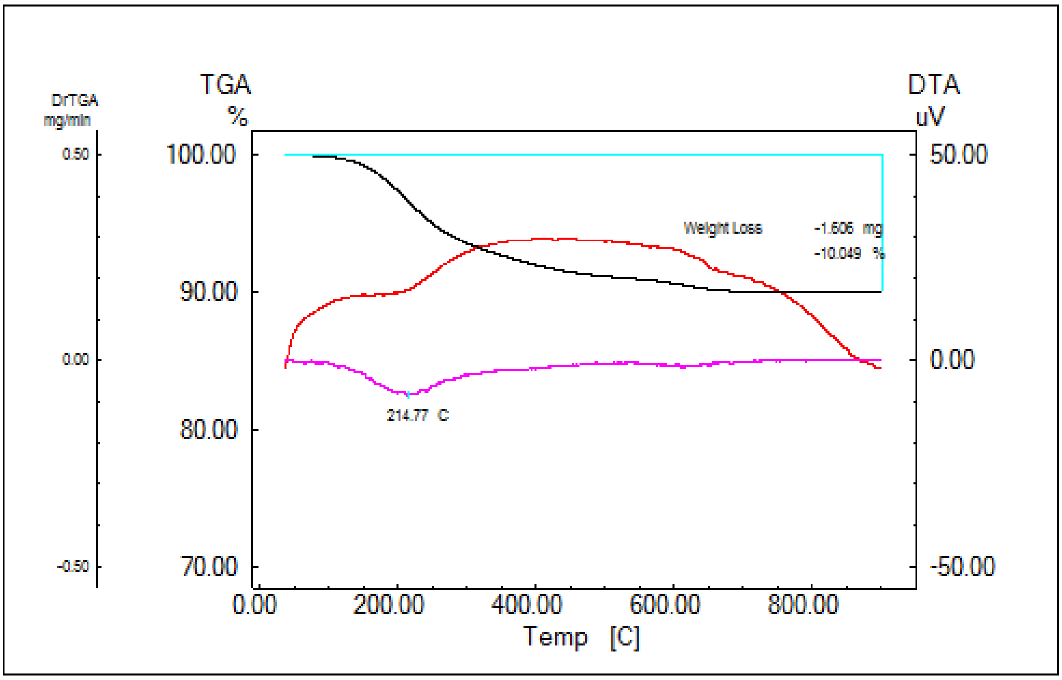

Figure B.21 TG/DTA Thermogram of BaM

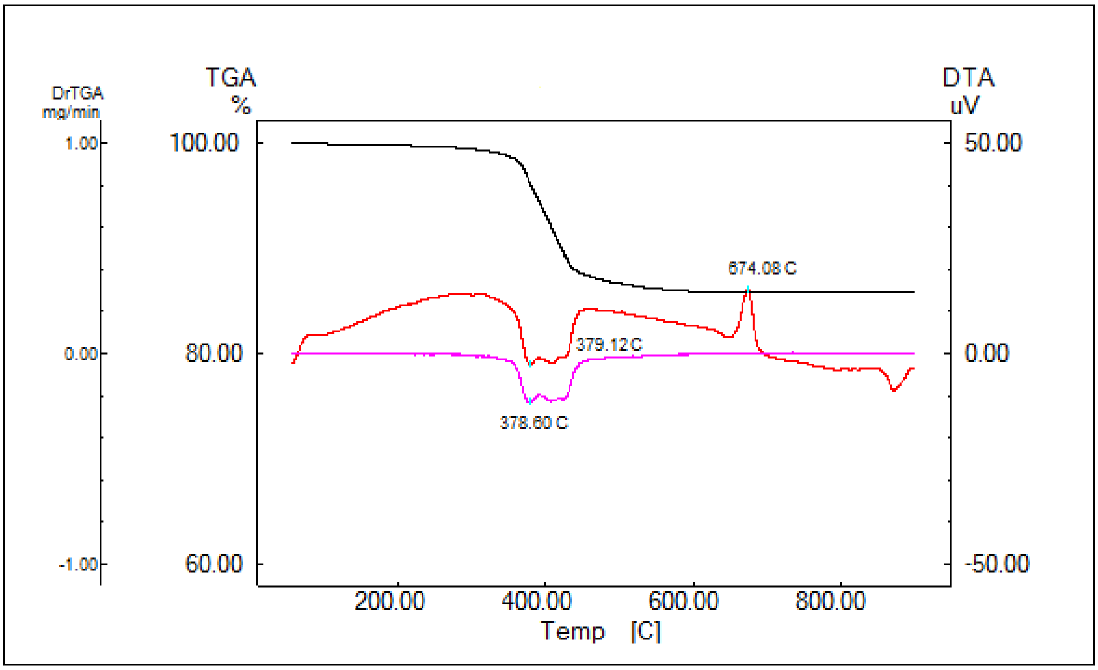

Figure B.22 TG/DTA Thermogram of ZnB

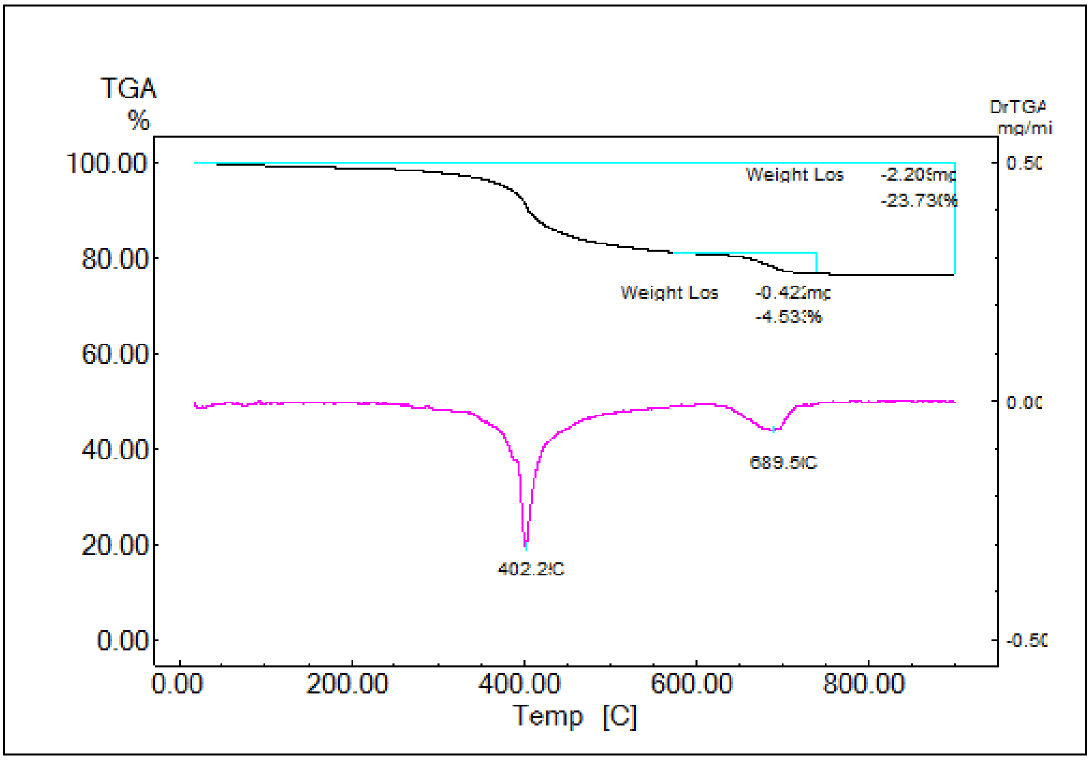

Figure B.23 TG/DTA Thermogram of CaB

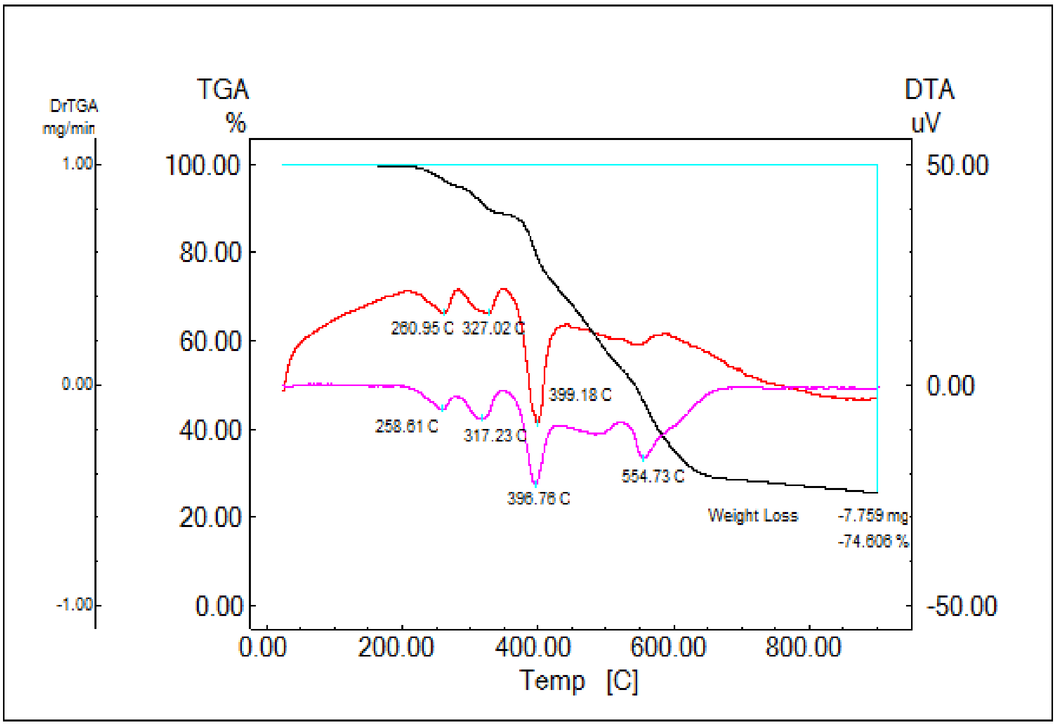

Figure B.24 TG/DTA Thermogram of MP

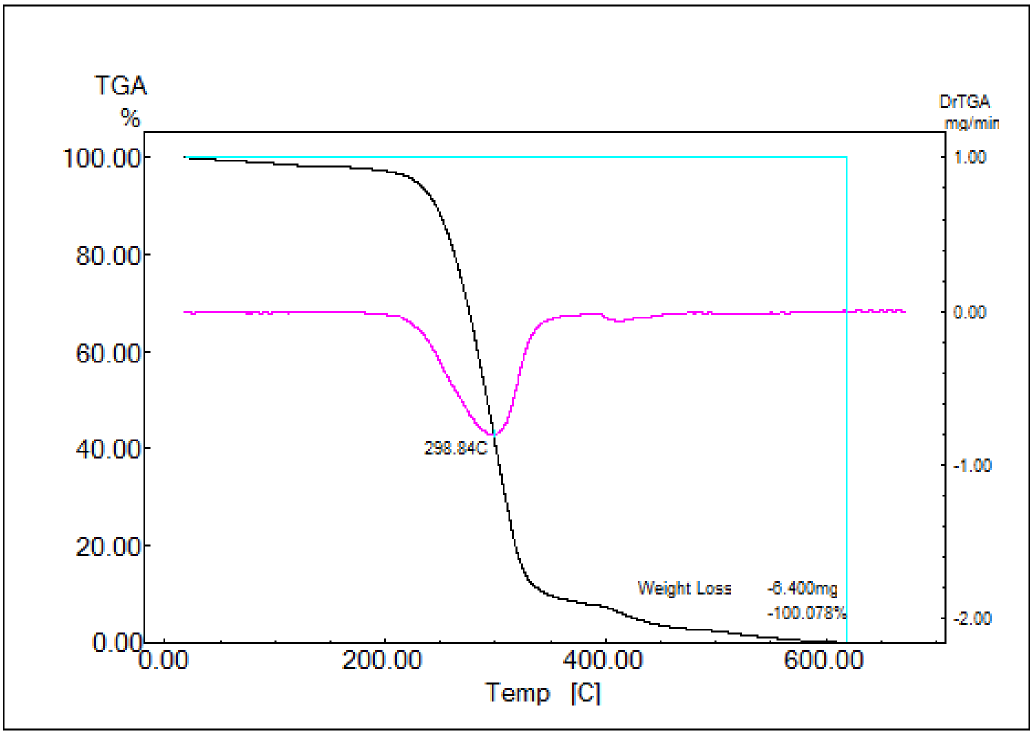

Figure B.25 TG/DTA Thermogram of DPER