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EGE UNIVERSITY
Graduate School of Applied and Natural Science

INVESTIGATION OF THE EFFECT OF PHOSPHORIC ACID ADDITION AS FLAME RETARDANT IN NOVOLAC RESIN PRODUCTION

MSc Thesis

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İzmir
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EGE ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ

ETİK KURALLARA UYGUNLUK BEYANI

EÜ. Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Yüksek Lisans Tezi olarak sunduğum "Investigation of the effect of phosphoric acid addition as flame retardant in novolac resin production / Novolak reçine üretiminde alev geciktirici olarak fosforik asit katkısının incelenmesi" başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

17.02.2022

Nur SARAKURT

ÖZET

NOVOLAK REÇİNE ÜRETİMİNDE ALEV GECİKTİRİCİ OLARAK FOSFORİK ASİT KATKISININ İNCELENMESİ

SARAKURT, Nur

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Tez Danışmanı: Doç. Dr. Murat Sert

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Fenolik novolak reçineler, asit katalizörleri yardımıyla asidik bir ortamda kondenzasyon reaksiyonu sonucu sentezlenir. Novolak reçine sentezi için formaldehit/fenolün mol oranı birden az olmalıdır. Bu tezde alev geciktirici özelliğe sahip novolak reçinelerin, fosfatlı katkılar ile alev geciktirici özelliğinin arttırılması incelenmiştir.

Bu deneysel çalışmada 3 tip süreç vardır. İlk iki deneysel çalışma novolak sentezi olup, reçinenin sentez basamaklarında katalizörün mol oranı değiştirilmeden katalizör kullanım oranı ve katalizör tipi; okzalik asit ve okzalik asit yerine okzalik asit ve fosforik asit birlikte kullanılarak sentez yapılmıştır. Birinci çalışmada kondenzasyon reaksiyonu sonucunda oluşan asidik ortam bazik kimyasallar ile pH ayarlaması yapılarak nötrlendirilmiştir. İkinci çalışmada pH ayarlaması yapılmadan devam edilmiştir. Üçüncü çalışmada ise fosforik katkı malzemeleri ve yaygın olarak kullanılan yanma geciktirici ajanlar novolak reçine ile fiziksel olarak karıştırılarak yanma geciktirici özelliğin nasıl etkilendiği araştırılmıştır. Her üç çalışma bölümünde de fosforik asidin okzalik asit ile birlikte kullanımı yanma geciktirici özellik olarak sadece okzalik asite kullanımına göre daha iyi sonuç verdiği saptanmıştır. Her üç çalışma sonuçları karşılaştırılmış ve en uygun deney koşulları belirlenmiştir. Çalışmaların ölçüm analizleri için X-Ray Fluorescence Spectrometer (XRF) analizi, Perkin Elmer (STA 8000) kullanılarak Termal Gravimetrik Analiz (TGA), ISO 3146 standardına

uygun olarak Electrothermal IA9200 cihazı ile erime noktası analizi ve ISO 8619 standardına uygun olarak akma mesafesi analizlerinden yararlanılmıştır.

Anahtar Kelimeler: Novolak reçine, alev geciktirici, fosforik asit, pH ayarlanması

ABSTRACT

INVESTIGATION OF THE EFFECT OF PHOSPHORIC ACID ADDITION AS FLAME RETARDANT IN NOVOLAC RESIN PRODUCTION

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Master Thesis, Chemical Engineering Department

Thesis Advisor: Assoc. Prof. Dr. Murat SERT

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Phenolic novolac resins are synthesis as a result of the condensation reaction in an acidic medium with the help of acid catalysts. The mole ratio of formaldehyde/phenol should be less than one. In this thesis, it was investigated increasing the flame retardant properties of novolac resins with phosphate additives.

There were three types of processes in this studies. This first two experimental studies were the synthesis of novolac resin with acid catalysts. Oxalic acid and instead of the oxalic acid catalyst, oxalic and phosphoric acid were changed the catalyst type and ratio without changing the mole ratio of the catalyst. Firstly, the acidic medium was formed as a result of the condensation reaction was neutralized by adjusting the pH with bases. The second study was continued without pH adjustment. Third study, it was investigated how the fire retardant property was affected by physically mixing phosphoric additives and commonly used fire retardant agents with novolac resin. In all three studies sections, it was determined that the use of phosphoric acid together with oxalic acid gave better results as a fire retardant than just oxalic acid used. All results were compared and optimum reaction conditions were determined. During these studies, X-Ray Fluorescence Spectrometer (XRF), the thermal gravimetric (TG) analysis was carried out using Perkin Elmer STA 8000, melting point analysis accordance with ISO 3146 and flow distance analysis in accordance with ISO 8619 were used.

Key Words: Novolac resin, flame retardant, phosphoric acid, pH arrangement

PREFACE

In this thesis, my manager in Çukurova Kimya Endüstirisi, Dr. Özge AKSIN ARTOK's knowledge and experience in the phenolic resin industry played an important role from the determination of the thesis topic to the evaluation of the results. My thesis supervisor Assoc. Prof. Dr. Murat SERT has consistently been an adviser to me in terms of academic and graduate education process.

İZMİR Nur SARAKURT

17.02.2022

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NOMENCLATURE

Symbol	Explanation
°C	Celsius
%	Percentage
g	Gram
ml	Milliliter
cm	Centimeter
mm	Millimeter

Abbreviations	
Conc.	Concentration
HMTA	Hexamethylenetetramine
FR	Flame Retardant
PA	Phosphoric acid
MAP	Mono Ammonium Phosphate
DAP	Di Ammonium Phosphate
TSP	Trisodium Phosphate Dodecahydrate
ZnB	Zinc Borate
TGA	Thermal Gravimetric Analysis
FTIR	Fourier transform infrared spectroscopy
STA	Simultaneous Thermal Analyzer
XRF	X-ray Fluorescence
F	Formaldehyde
P	Phenol
Min	Minute
Hr	Hour
LOI	Loss on Ignition
Temp	Temperature
Adj	Adjustment

1 INTRODUCTION

1.1 Resins

Resins are typically highly viscous substance of plant or synthetic materials origins. It turns into a rigid structure with a curing process. Resins are usually blended of organic compounds. Synthetic resins can show the same or different properties with natural plant resins. There are many different types of resins such as epoxies, phenolics, acrylics, alkyds, urethanes, silicones. Resins are either thermoplastic or thermoset. Thermoset resins convert from liquid to solid state during the curing process that crosslinking. Cured occurs using a catalyst, heat or a combination of both. Once cured, solid thermoset resins cannot be recycled to their original liquid form. Thermoplastics are softened when heated. Thermoplastics resins are not crosslinked, so the curing process is completely reversible. This property allows the remelting and reshaping of thermoplastics without adversely affecting the physical properties of the material. (Swallowe, 1999).

1.2 Phenolic Resin

Phenolic resin is a type of thermosetting resin. Heating under pressure process makes phenolic resin commercially useful. Phenolic resins have widely application areas like polymer composites, sand binder etc. (Pilato, 2010). After the first commercial synthesis of phenolic resin, its use has spread rapidly all over the world and has been used for commercial applications in Germany in 1909. Enhanced mechanical properties, bonding performance, heat resistance, flexibility, high thermal stability, chemical resistance has made it the material of choice for applications in all industrial applications. In the 20th century, phenolic resins spread across several industries thanks to their superior properties. In order to make them suitable for a wide range of industrial applications, many chemical and physical modifications have been applied.

Types of catalysts, raw materials, molar ratios of formaldehyde to phenol, polymer functional groups affect the end products of phenolic resin. (Figure 1.1). Phenolic resin are synthetic thermoset resins which are synthesized by the condensation reaction of phenol with formaldehyde in the presence of a catalyst. Formaldehyde functionality is two and phenol functionality is three. Phenol react with the OH group at the para and at the two ortho positions. The two meta positions are unreactive (Pilato, 2010).

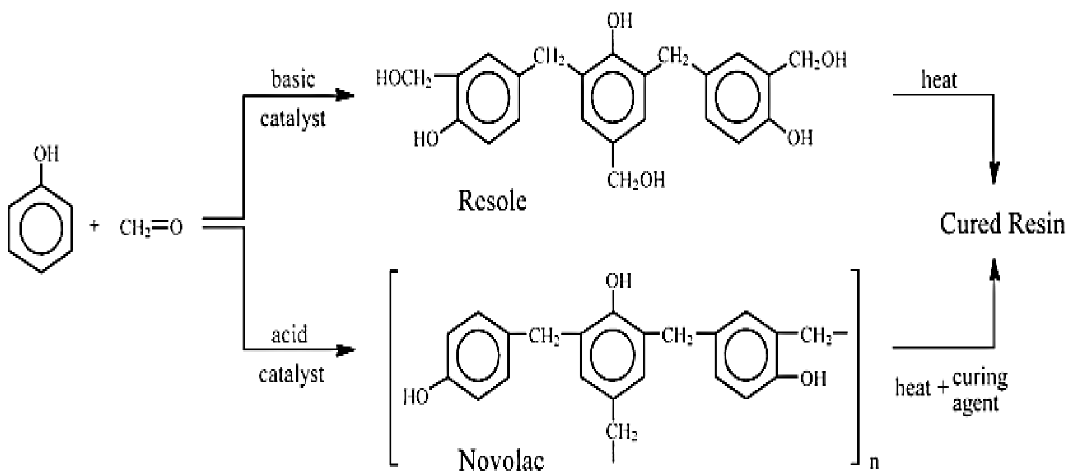

Figure 1.1 Chemical structures of novolac and resol due to medium condition and molar ratio.

1.2.1 Phenol

Phenol is an aromatic organic compound which contains one or more hydroxyl groups that are attached to an aromatic ring. Phenol molecular formula is C_6H_5OH. Phenol is a solid state at the ambient temperatures. They appear like a white amorphous material. Phenol melting point is 40.9 °C. In the molten state, pure phenol is a colorless clear liquid. Phenol becomes liquid at room temperature when mixed with around 6 or 10 wt. % of water. To produce phenolic resins, phenol is most important raw materials. Phenol is due to the presence of a hydroxyl group and an aromatic ring which are complementary to each other in facilitating both electrophilic and nucleophilic type of reactions. Phenol is an extremely reactive. The reactivity provide toward electrophilic substitution and lead to synthesis phenolic resins which is acid catalyst reaction with formaldehyde (Pilato, 2010).

1.2.2 Formaldehyde

Formaldehyde, the first of the series of aliphatic aldehydes which is a naturally occurring organic compound with the formula CH_2O. At ordinary temperatures, formaldehyde is a colorless gas with a pungent odor. It is highly reactive. Its reactivity is reduced with in aqueous solutions containing variable amounts of methanol. Often used in an aqueous solution that mixed with around 25 or 40 weight % of water (Table 1.1) (Subası, 2020).

Table 1.1 Physical and chemical properties of formaldehyde (Subası, 2020)

Chemical name	Formaldehyde
Chemical formula	CH_2O
Molecular weight, g/mol	30.026
Color	Clear, colorless liquid
Density, - 20 °C, g/cm^3	0.8153
Melting point, at 37% conc., °C	93 – 96
Boiling point, at 37% conc., °C	- 15

1.2.3 Condensation reactions

Synthesis of polymers occurs in two different ways. One of them is addition polymerization. Monomers containing multiple bonds link together by addition reactions in addition polymerizations. These polymers are synthesized with bonding of free radical by heat, light and radical initiator.

The other way is condensation polymerization. In this process, as monomers bind together, stable small molecules such as water are released. In condensation reactions monomers must have two or more functional groups. In all cases, when polymers are synthesized, the result is a mixture of long chain molecules of varying lengths.

In crosslinking process, molecular chains joined to each other by covalent bonds. The molecular chains in non-cross-linked polymers will usually slide across each other. When heated, the polymer softens and various shapes are provided with the softening polymers. This types polymers are called thermoplastic polymers. Cross-linked polymers have high hardness, more rigid, and sometimes brittle structure and they are referred to as thermosetting polymers. Phenolic resins are produced as Bakelite with condensation polymerization between phenol and formaldehyde. Crosslinking occurs when the polymer is heated (Askeland, 1996).

1.2.4 Resole resins

When reaction medium is under alkaline condition and the mole ratio of formaldehyde to phenol is greater than one resole resins are occurred. Resole resins have excess formaldehyde. The condensation reaction is carried out at approximately 70 °C. Resole resins are usually dark in color. Their color ranges from yellow to dark red. Resole resins are cured with applied of heat without the use of any additional curing agent or catalyst. Typical alkali metal hydroxide catalysts used in resole resin production and their activity are Magnesium Hydroxide ($MgOH_2$), Calcium Hydroxide ($CaOH_2$), Barium Hydroxide ($BaOH_2$), Lithium Hydroxide (LiOH), Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH), respectively. Resole resin reaction is stopped prior to gelation. Resole resin is usually in liquid form. They have low molecular weight and short shelf life. They usually contain no more than two or three benzene rings. They are soluble in water or alcohol (Allen et al., 2001).

1.2.5 Novolac resins

Novolac resins are produced from the condensation reactions between phenol and formaldehyde under acidic medium. Formaldehyde to phenol mole ratio must be less than one. The novolac reaction terminates as all the formaldehyde is consumed and excess approximately 5 % phenol. Novolacs form at a pH below 7 by protonation of the carbonyl group of the formaldehyde followed by electrophilic aromatic substitution at the ortho or para positions of the phenol (Figure 1.2). The typical acid catalyst in the preparation of novolac phenolic resins are Oxalic Acid ($C_2H_2O_4$), Sulfuric Acid (H_2SO_4), Hydrochloric Acid (HCl). The most widely used acid catalyst is oxalic acid. Oxalic acid is preferred as novolac resin catalyst because of as followed (Shang, 2001);

- Decomposes at high temperatures (> 180 °C) to carbon dioxide, carbon monoxide and water, which easier the removal of this catalyst thermally.
- Light color can be obtained.
- Low using amount and high efficiency.
- Noncorrosive catalyst instead of corrosive materials like Hydrochloric Acid.

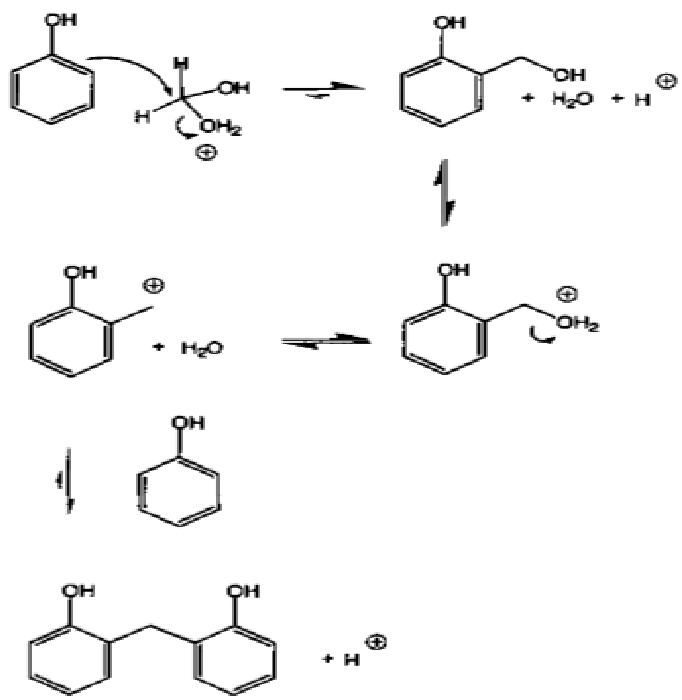

Figure 1.2 Methylolation and condensation in novolacs

Novolac resins are linear thermoplastic polymer in nature. When heated novolac resins are melt but they do not make a cross link or cure. They need the addition of curing agent such as hexamethylenetetramine (HMTA). HMTA is used in order to structure of thermoset that occurs cross linking methylene bridges between molecules. Typically, 5 – 15 % of HMTA are used as curing agent for novolac. Novolac resins have a higher molecular weight of above 1000, branching occurs as the reactions continue between the end groups and unreacted phenol. Novolac resin is generally solid or semi solid form. They are converted to liquid form using different solvents such as Mono Ethylene Glycol, Diethylene Glycol. Novolac phenolic resin according to resole resin has an infinite shelf life at normal conditions (Zhang, 2014).

Novolac resin properties are heat, creep and chemical resistance, dimensional stability.

1.2.6 Novolac resin production

A reactor with an agitator, heating or cooling serpentine, distillation tank, holding tank, raw materials tank which are made of stainless steel, cooling belt conveyor, pastillator are required for production of flake/pastille novolac resin. Phenol (91 %) and acid catalyst are loaded into the reactor and the reactor temperature is increased to 100 °C. The reactor is equipped with a reflux condenser, and stirrer. The Formaldehyde (36 %) is charged into reactor at a certain period of time interval and the reaction is allowed to continue at a temperature of about 100 °C and reflux conditions. The water produced by the condensation reaction is removed by distillation. The distilled water is collected under atmospheric and/or vacuum pressure into distillation tank. After distillation, phenolic novolac resins gains a highly viscous form. Highly viscous novolac resin is transferred into the holding tank which has heating systems. After that, highly viscous novolac resin is fed to flake band systems and is converted to shape of pastille or flake form. At the end of process, novolac resin is filled in big bags and is sent to powder novolac unit (Figure 1.3).

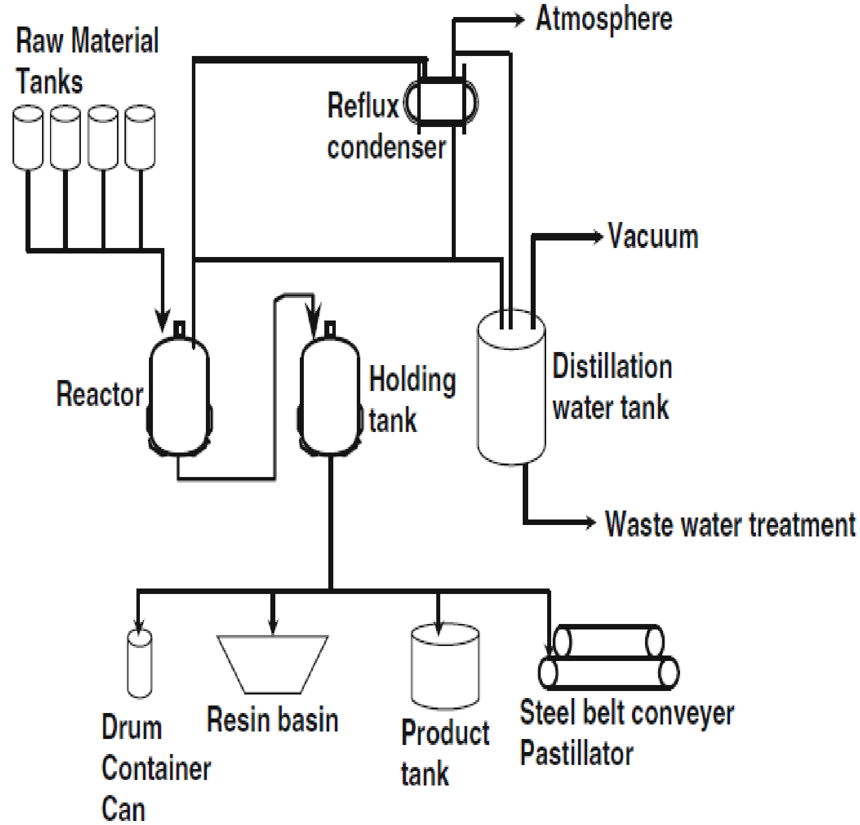

Figure 1.3 Flow diagram of flake or pastille form novolac resin production process

1.3 Flame Retardants

Ignition begins with any source of energy such as heat or a small flame. The ignition source causes the material to burn, break down and released of the flammable gases. Flammable gases, released from the material, are mixed with oxygen from the air. In the combustion zone which contains of fuel, oxygen and free radicals combine to create chemical reactions that cause visible flames to appear. Polymers are substances that can easily burn, and each polymer shows different burning properties. Flame retardants (FR) prevent ignition by different physical and chemical methods. Physical methods are cooling, formation of a protective layer and dilution. Chemical methods are occurred two phases as gas phase and solid phase (Figure 1.4). The interaction of the flame in the gas phase; the radical gas phase combustion process is interrupted by the flame retardant, resulting in cooling of the system, reducing of flammable gases. The interaction of the flame in the solid phase; the flame retardant builds up a char layer and protection the material against oxygen and provides a barrier against the heat source (EPRA, 2007).

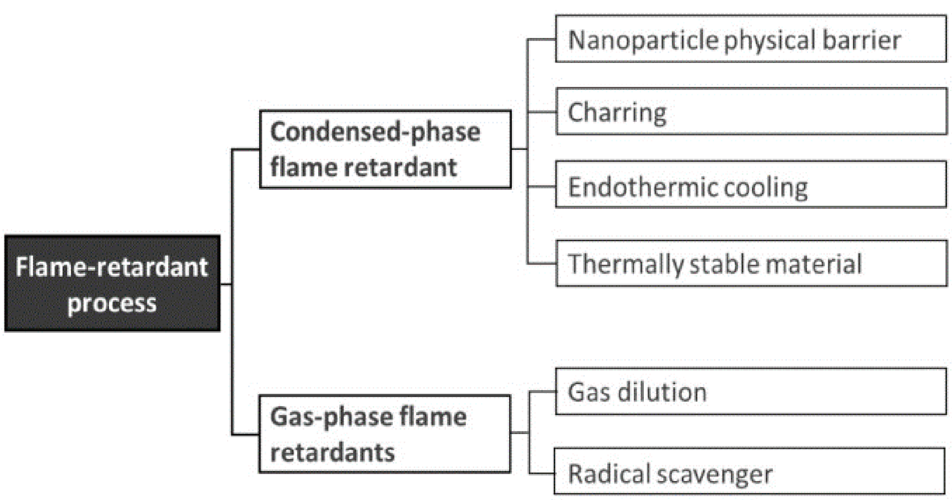

Figure 1.4 Effect of flame retardant additives to fire process (Ahmed et al., 2018)

The most important parameters showing the compatibility of flame retardants with the material are as follows;

- Material properties must be conserved to the greatest possible extent, with price as the most determining factor.

- The FR must be suitable with polymerization process and pyrolysis type

- Health regulations and global direction require that formulations must become sustainable, recyclable and increasingly eco-friendly.

Thermosetting composites resins is approximately be about $ 8 – 10 billion in the global market. Thermosetting composites of fire-resistant resins making up about 10 % of the total. When the resins are separated by the fire resistant resin market, they are ranked as 4 – 5 % phenolic resins, 30 – 40 % vinyl esters composed of resins and 55 – 65 % epoxies. (Pilato, 2010).

There are many types of flame retardants compounds such as Halogens; Bromine, Chlorine etc., Phosphorus, Nitrogen, Minerals; Aluminum Hydroxide (ATH), Magnesium Hydroxide (MDH) etc. and others such as Borax (Table 1.2). Halogenated flame retardants have negative effects on the environment and human health. Some are very persistent, some bioaccumulation in aquatic and terrestrial food chains, and some show serious adverse effects. Today, there is a tendency to use resins with flame retardant additives using phosphorous compounds as synergists instead of halogen containing compounds (Kim et al., 2021).

Table 1.2 Effect of different types of flame retardants materials

Chemicals	Physical Dilution	Chemical Interference	Inert Gas Dilution	Thermal Quenching	Protect Coating
Alumina Trihydrate				*	
Antimony Oxide		*			
Bromine-based		*			
Chlorine-based		*			
Magnesium Hydroxide	*		*		
Phosphorus-based		*			*
Silicone-based					*

1.4 Flame Retardants Types

1.4.1 Phosphorus based flame retardants

Organic and inorganic phosphorus types flame retardants are more environmentally friendly, they have good thermal stability and superior performance thanks to the synergistic effect of P-N. They do not emit toxic gases. Because phosphorus is mostly converted to char. Phosphorous Flame retardants can be reactive (chemically bound) and additive (physical mixing). Phosphorus is not found uncombined in nature but is widely found in compounds in minerals. The strengths of phosphorous flame retardants compared to other flame retardant systems can be summarized as follows (Choudhury et al., 2018).

- Lower density
- Less probable to be stable and bio accumulative residue in the environment
- Less tendency to concentrate smoke obscuration
- Less gas formation in combustion

The fire-retardant properties of phosphorus in novolac resins are as follows (Velencoso et al., 2018). Phosphorus pentoxide generated by the combustion of phosphoric compound reacts with a phenolic hydroxyl group in the linear phenolic aldehyde, and phosphoric acid or metaphosphoric acid and the like are generated simultaneously; and the acids of the type are further used for catalyzing dehydration and char formation of phenolic resin, and are esterified with the phenolic hydroxyl group, so that an organic-inorganic hybrid barrier layer is formed (Yang et al., 2012). Phosphoric acid, Mono Ammonium Phosphate, Trisodium Phosphate Dodecahydrate are the most popular inorganic flame retardants in the phosphate-containing compound family (Table1.3).

Table1.3 Phosphorus Based Flame Retardants (Yang et al., 2012)

	Chemical Classification	**Comment**
Phosphoric acid (PA)	Inorganic	Phosphoric acid has a good fire retardant properties and it select as a worst case control.
Mono Ammonium Phosphate (MAP)	Inorganic	Generally used in commercial formulations as a common chemical.
Trisodium Phosphate Dodecahydrate (TSP)	Inorganic	TSP is not combustible, and does not contribute to the intensity of a fire.

1.4.1.1 Phosphoric acid

Orthophosphoric acid (H_3PO_4) or the other name phosphoric acid is a clear, white liquid. It is derived from phosphate rock. It is a strong acid (Table 1.4). They are used in fire retardant formulations because they are stable and flame resistant, and have a useful and long shelf life. (Buick, 2012).

Table 1.4 Phosphoric Acid properties (Burick, 2012)

Molecular formula	H_3PO_4
Molar Mass, g/mol	98
Melting Point, °C	42.4
Boiling Point, °C	213
Density, g/mL	1.885

When fire temperature is up to 200 to 300 °C, phosphoric acid can give off phosphorus oxides by thermal decomposition. Phosphoric acid loses water at 160 °C. In this temperature phosphoric acid turns into pyrophosphoric acid. Phosporic acid turns into metaphosphoric acid then polyphosphoric acid at over 300 °C.

Phosphoric acid is included many fire retardant materials. After the burning process, heat is occur. Heat is occur flammable volatile polyphosphoric acid. The flammable volatile polyphosphoric acid helps to produce a char layer. The char layer acts as a physical barrier. Physical barrier reduces the formation of gases and the release of heat. (Persianutab, 2020).

1.4.1.2 Mono ammonium phosphate

Mono Ammonium Phosphate (MAP) is white crystal (Table 1.5). It is mainly used as a fire retardant for fertilizer and wood paper fabric. MAP and Di Ammonium Phosphate (DAP) are most desirable for use in dry powder type retardant concentrates (Mosaic, 2022). The commercial ABC type powder fire extinguisher has cooling effects. It compress the free ions of chain reaction, and quickly extinguishes the fire. Such materials have been widely used in the last 50 years (Su et al., 2014).

Table 1.5 Mono Ammonium Phosphate properties (Su et al., 2014)

Molecular formula	$NH_4 \cdot H_2PO_4$
Molar Mass, g/mol	115.026
Melting Point, °C	190
P_2O_5 Content, %	48 – 61

1.4.1.3 Trisodium phosphate dodecahydrate

Sodium phosphate tribasic dodecahydrate is also known as Trisodium Phospate or TSP. TSP is a white, granular or powder crystalline solid. It is highly soluble in water (Table 1.6).

Table 1.6 Trisodium Phosphate Dodecahydrate properties

Molecular formula	$Na_3PO_4 \cdot 12H_2O$
Molar Mass, g/mol	380.12
Melting Point, °C	75 °C
P_2O_5 Content, %	≥ 18.3%

1.4.2 Other types of flame retardants

1.4.2.1 Zinc borate

Zinc borate has a formulation $4ZnO \cdot B_2O_3 \cdot H_2O$. Zinc borate has a high dehydration temperature approximately 415 °C. It is preferred for the polymer and rubber sectors. Recently, the use of inorganic flame retardants, as borate additives flame retardants, has been become common. They replace halogen based additives that have been used in polymers. Zinc borate is suitable for extrusion requiring high processing temperatures. It is also used in paint, electrical and electronic, building and transportation material application areas. (Yalçın et al., 2021).

1.4.2.2 Magnesium Hydroxide

Magnesium hydroxide (MDH) decomposes at around 300 °C.

$$Mg(OH)_2 + 1220 \text{ kj/kg} \longrightarrow MgO + H_2O$$

During the burning process, energy is detracted from the ignition source, as the decomposition is an endothermic reaction. Simultaneously, the released water vapor reduce the temperature the surface of the polymer. Also particularly dilutes the burnable gases in the surrounding. After the burning process occurring metal oxide residue has a high internal surface where sooty particles are absorbed. Additionally, the oxide residue acts like a barrier for retain the further release of low molecular weight decomposing products and heat barrier protecting the polymer against further decomposition (PINFA, 2017).

1.5 Flame Retardant Novolac Resin Application Area

Phenolic resins are famous for excellent flame retardance. However, in some industrial applications fire retardant properties are not sufficient for application to the industry. Therefore, there was a need to improve the flame retardant properties. It is provided with elemental or organic compounds with excellent heat resistance properties.

Novolac resin with enhanced flame retardancy are used in many industrial applications. These are automotive field; lining, felt, non-woven fabrics, insulating materials, composite fields; airplane, ships, panels, walls, electronic field etc. (PINFA, 2010).

2 LITARATURE REVIEW

Phenolic resins are synthesized with the reaction of phenol and formaldehyde. They are well known to have good heat resistance, have excellent flame retardancy, and low toxic gas emission on burning (Kandola et al., 2014). Flame retardant binders has become an important point in many sector such as composite, automotive and felt etc. Automotive, textile and composite etc are some searching innovative solutions to improving product performance, combustion resistance, continuously improving the environmental properties of the products used and sustainable fire safety. Halogens or polymers with halogen atoms, when considered from a health point of view, emit halogen along with carbon, hydrogen or other atoms during the combustion process. These gases are not readily soluble in water. It may enter the respiratory tract by breath. Most of the loss of life in fires is due to the effects of toxic by-products that occur alongside carbon monoxide gases (PINFA, 2010)

Among the fire retardants, halogen-free flame retardant additives such as phosphorus-containing resins, boron-containing resins, Aluminum trihydroxide or magnesium hydroxide-contain resins cause an increase in the amount of char residue, reducing the release of volatile fuel and slow the pyrolysis by carbonizing the surface of the material (Bisschoff, 2001). These compounds are found worthy of research due to reducing the oxygen index of the main substance, being used together with novolac resin used in many sectors against combustion, being easily applied by dissolving with water, being cheap and easy to supply, negligible low toxicity effects to the environment by using halogen in terms of health reasons (Aseeva et al, 2005).

Halogen-free phosphorus containing flame retardant epoxy composites. This thesis investigates reaction between three amines and Phenylphosphonic dichloride and reaction between three amines and Phenyl dichlorophosphate. This synthesized name was FPx. Second synthesized name was FPOx. For characterization analysis, Nuclear magnetic resonance, Fourier transform infrared spectroscopy (FTIR), Differential scanning calorimetry and Termal gravimetric analysis (TGA) were used. The thermal characteristic behavior were investigated and compared between epoxies containing FPx and FPOx. This thesis use the thermal decompositions of epoxies containing FPx occurred at higher temperatures than the epoxies containing FPOx (Zhao, 2017).

Development of Novel Flame-Retardant Thermosets Based on Boron-Modified Phenol–Formaldehyde Resins. This thesis investigates reaction between a phenolic novolac resin with different weight contents of bis(benzo-1,3,2-dioxaborolanyl) oxide. Flame retardant modified phenolic resin investigated point of view thermal and flame-retardant properties. Thermal stability analysis were carried out on a TG analysis with N_2 gas at a ramp rate of 10 °C/min. The results of TG analysis formation boric acid at high temperature was observed. This formation provides a char yields that decreases the degradation and prevention from flame (Martin et al., 2006).

Synergistic Effects of Aluminum Diethylphosphinate and Melamine on Improving the Flame Retardancy of Phenolic Resin. This thesis investigates flame retardancy properties of phenolic resin which that physical mixing with novel flame retardants which are aluminum diethyl phosphinate and melamine. For characterization, TGA, FTIR, scanning electron microscopy were used. When thermo-gravimetric analysis and char yield which means residual carbon content of the test results was investigate 15 wt. % of aluminum diethylphosphinate 4 wt. % melamine addition is the best results (Zhou et al., 2019).

When all studies research were investigated, fire retardant materials were used as chemical reaction or physical additives. Generally, TG analysis was used for characterization methods. Char yields are evaluated. The best results were selected as a result of these evaluations. In this study, investigation of use of phosphorus and phosphorus compounds in novolac resin synthesis or as additives, investigation of mechanical and thermal stability of the end product in the usage sectors.

3 EXPERIMANTAL PROCEDURE

3.1 Materials

Phenol (91 %) (C_6H_6O), Formaldehyde (36.5 %) solution (CH_2O), Oxalic Acid (≥ 99.5) ($C_2H_2O_4$), Phosphoric Acid (85 %) (H_3PO_4), Sodium Hydroxide (10 %) (NaOH), Trisodium Phosphate Dodecahydrate (TSP) (98 %) ($Na_3PO_4.12H_2O$ Merck grade), Mono Ammonium Phosphate ((NH_4) H_2PO_4), Zinc Borate ($B_2O_6Zn_3$), Magnesium Hydroxide ($Mg(OH)_2$) were used for the experimental studies. All chemicals were used without further purification.

3.2 Characterization

3.2.1 Thermal gravimetric analysis

The thermal gravimetric (TG) analysis was carried out using Perkin Elmer Simultaneous Thermal Analyzer (STA 8000) in the temperature range of 30 °C to 750 °C and heating rate of 25 °C/min and flow of nitrogen gas is 20 ml/min.

3.2.2 X-ray fluorescence (XRF) spectroscopy analysis

The quantitative determination of the phosphate compound in novolac resins was carried out using SPECTRO XEPOS X-ray fluorescence (XRF) spectroscopy analysis.

3.2.3 Melting point analysis

Melting point determination was performed based on ISO 3146 standard which that determination of melting behavior of semi crystalline polymers by capillary tube and polarizing-microscope methods. Melting point analysis was carried out using Electrothermal IA9200 Series Melting Point Apparatus.

3.2.4 Flow distance analysis

Flow distance determination was performed based on ISO 8619 standard which that phenolic resin powder - determination of flow distance on a heated glass plate method. Flow distance analysis was carried out using Memmert UFB 110 in the temperature at 125 °C. Analysis method starts with novolac and HMTA weighed at a 9:1 weight ratio and the mixture is loaded into a grinder. After grinding, the powder novolac mixture which included HMTA is converted into pellet form. The pellet size diameter is 14.50 mm ± 0.3 mm, the pellet height is 5 mm ± 0.2 mm. The pellet is prepared as follows. Weighing novolac resin 0.50 g ± 0.01 g and then press into the specified dimensions. The stainless steel inclining apparatus was tempered at 125 °C ± 1 °C in a horizontal position. After placing the pellet on glass plate, hold the plate in a horizontal position for 180 s ± 3 s and then rotate the apparatus 60 degree and continue heating for 20 minutes. Finally, the glass plate is removed from the oven and measured the distance. The measured value is the flow distance. The efficiency of the catalysts enables chain growth of the polymer. Shorter flow distance is showing that the better the polymerization results (Sahinovic et all., 2020).

3.3 Procedure

Novolac resin setup was prepared as below Figure 3.1. In a 2000 mL four-neck round-bottom flask provided with IKA Eurostar 60 Digital high speed laboratory stirrer, Electrothermal heating equipment, digital thermometer and a reflux condenser, dropping funnels materials were used for preparation experimental setup. IKA M 20 universal mill which milling chamber can be cooled with top water.

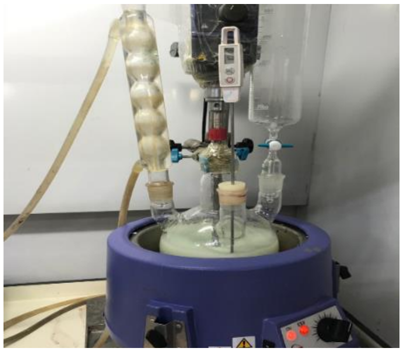

Figure 3.1 Novolac resin production setup

3.4 Experiments

3.4.1 Different catalyst types and catalyst ratio with pH adjustment

The desired Formalin/Phenol mol ratio was 0.78. 922.24 g Phenol (8.9 mol) and 0.003 mol oxalic acid was place in 2000 ml four-neck heavy wall round-bottom flask. 571.12 g of Formalin 36.5% (6.9 mol) was added dropwise to the round-bottom flask for 90 minutes. The mixture was stirred and refluxed for 120 minutes. A novolac resin was obtained, in which two layers were formed. After refluxing the pH dropped to between 1 and 2. NaOH and TSF was added to the flask to adjust the pH to between 4.5 and 5.5. The top layer is water produced by the condensation reaction, which was collected by atmospheric and/or vacuum distillation. The top layer is water produced by the condensation reaction, which was collected by atmospheric and/or vacuum distillation. The bottom layer is novolac resin. The Novolac resin was kept under vacuum at 180 °C for 1 hour. Steam distillation was performed to reduce free phenol monomers. The final novolac resin was transferred to the aluminum container until it cooled and solidified. Novolac resin synthesis was started with 100% oxalic acid catalyst as Reference 1. In the continuation of the study, phosphoric acid was used as a catalyst for the synthesis of novolac resin. Experimental studies were continued by changing the catalyst type without changing the mole ratio of the catalyst. The catalyst mole ratio was started with 100 % oxalic acid and was continued as 25 % phosphoric acid – 75 % oxalic acid, 50 % phosphoric acid – 50 % oxalic acid, 75 % phosphoric acid – 25 % oxalic acid and 100 % phosphoric acid. For all experimental studies, pH was adjusted after reflux process. Sodium Hydroxide (NaOH) and Trisodium Phosphate Dodecahydrate (TSF) were chosen for pH adjustment.

3.4.2 Different catalyst types and catalyst ratio without pH adjustment

The desired F/P mol ratio was 0.76. 937.11 g Phenol (9.1 mol) and 0.008 mol oxalic acid was place in 2000 ml Four-neck heavy wall round-bottom flask. 569.63 g formalin 36.5 % (6.9 mol) was added dropwise to the round-bottom flask for 90 minutes. The mixture was stirred and refluxed for 120 minutes. A novolac resin was obtained, in which two layers were formed. When after refluxing the pH was dropped to between 1 and 2, experimental studies was continued without pH adjustment. Distillation steps was continued as specified in 4.2.1.

3.4.3 Additive effect on thermal stability of phenolic novolac resins

The novolac resin obtained in the above-mentioned step was physically mixed with additives containing different flame retardants. Phosphorus-containing flame retardants such as Mono Ammonium Phosphate and Trisodium Phosphate Dodecahydrate and the other commercial flame retardants such as Zinc Borate, Magnesium Hydroxide was used in this experimental studies. In this experimental study, 5 %, 10 % and 15 % by mass of flame retardant materials were added to the phenolic resin.

4 RESULTS

In section 3.4.1 and section 3.4.2, different catalyst types and catalyst ratio, with and without pH adjustment, oxalic acid and instead of the oxalic acid catalyst, oxalic acid and phosphoric acid was added to synthesis with different ratio. Novolac synthesis was performed without changing the main mole ratio of the catalyst. In section 3.4.1, additive effect on thermal stability of phenolic novolac resins, it was investigated how the fire retardant property was affected by physically mixing phosphoric additives and commonly used fire retardant agents with novolac resin.

4.1 Different Catalyst Types with pH Adjustment Phenolic Novolac Resin Synthesis

Oxalic acid and Phosphoric acid was selected catalyst for phenolic novolac synthesis. Novolac resin synthesis was started with using oxalic acid catalyzed resin production as a Reference 1. In the continuation of the study, phosphoric acid was used as a catalyst for the synthesis of novolac resin. Experimental studies were continued by changing the catalyst type without changing the mole ratio of the catalyst. The catalyst mole ratio was started with 100 % oxalic acid (Reference 1) and was continued as 25 % phosphoric acid – 75 % oxalic acid (Experiment 1), 50 % phosphoric acid – 50 % oxalic acid (Experiment 2), 75 % phosphoric acid – 25 % oxalic acid (Experiment 3) and 100 % phosphoric acid (Experiment 4). Sodium Hydroxide (NaOH) and Trisodium Phosphate Dodecahydrate (TSF) were chosen for pH adjustment. Table 4.1 shows the catalyst types and catalyst ratio with pH adjustment for synthesis of novolac resin.

Table 4.1 Different catalyst types and catalyst ratio with pH adjustment

	Ref. 1	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
Catalyst Ratio and Types	100 % Oxalic Acid	75 % Oxalic Acid	50 % Oxalic Acid	25 % Oxalic Acid	–	–
	–	25 % Phosphoric Acid	50 % Phosphoric Acid	75 % Phosphoric Acid	100 % Phosphoric Acid	100 % Phosphoric Acid
pH Adjustment	Sodium Hydroxide					TSF

The reflux process, it has been measured that the pH drops approximately 1 – 2. Then NaOH and TSF were added to adjust the pH between 4.5 and 5.5. Table 4.2 shows the results of weight loss, total weight loss and pH value after base addition. The effectiveness of the catalysts provide chain growth of the polymer. Shorter flow distance is showing that the better the polymerization results. When compare the flow distance and melting point results Experiment 3 is the most appropriate polymerization structure (Figure 4.1).

Table 4.2 Results of different catalyst types and catalyst ratio with pH adjustment

	Reference 1	Exp. 1	Exp. 2	Exp. 3	Exp. 4	Exp. 5
pH, After Reflux	1.60	1.20	1.65	1.09	1.00	1.50
pH, After addition of base	4.61	4.60	4.50	4.78	5.10	5.00
Weight Loss, % at 632.72 °C*	35.97	34.22	41.36	33.29	32.98	34.96
Total Weight Loss, % at 750 °C	41.96	39.98	43.87	39.49	39.32	40.91

*Reference 1 loss on ignition peak temperature

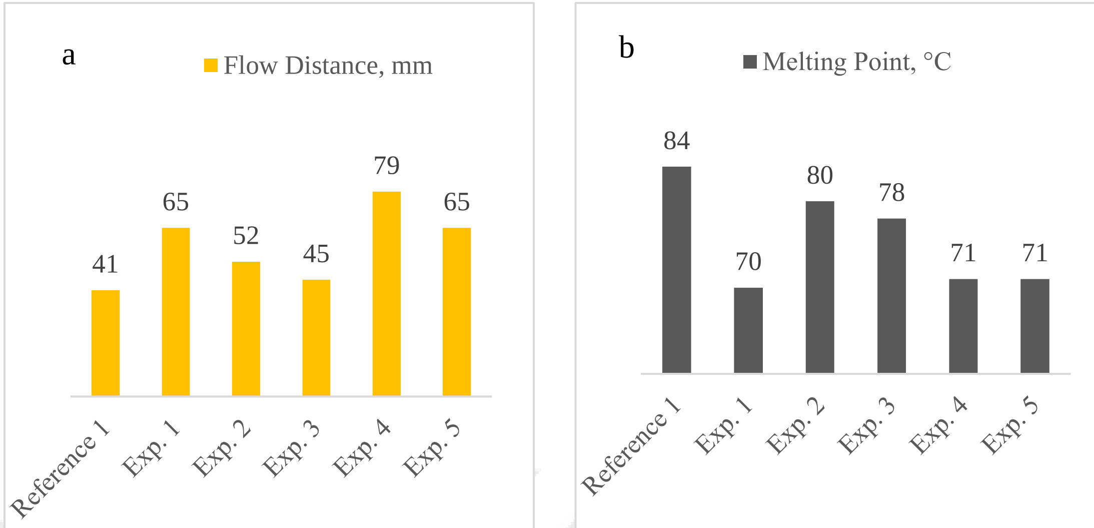

Figure 4.1 Graph of flow distance (a) and melting point (b) in different catalyst types with pH adj.

The char formation of the phenolic resin forms an organic-inorganic hybrid barrier layer. The hybrid barrier is in the solid phase in the char layer, providing resistance to heat source. The smaller the total weight losses, the higher the coal layer formation (Yang et all., 2012). TG analyzes are given below between Figure 4.2 and Figure 4.7. The results of all the experimental studies was performed in section 4.1 are given in Table 4.2. When the total weight losses were compared, it was determined that the results of Experiment 3 and Experiment 4 were better than Reference 1 (Table 4.2). However, when the flow distance and melting point results were evaluated, it was determined that Experiment 3 was the best result. In the same molar ratio, it was determined that the use of 50 % phosphoric acid together with 50 % oxalic acid gave better results as a fire retardant than 100 % oxalic acid used. In all 3.1 section production times were approximately 24 hours.

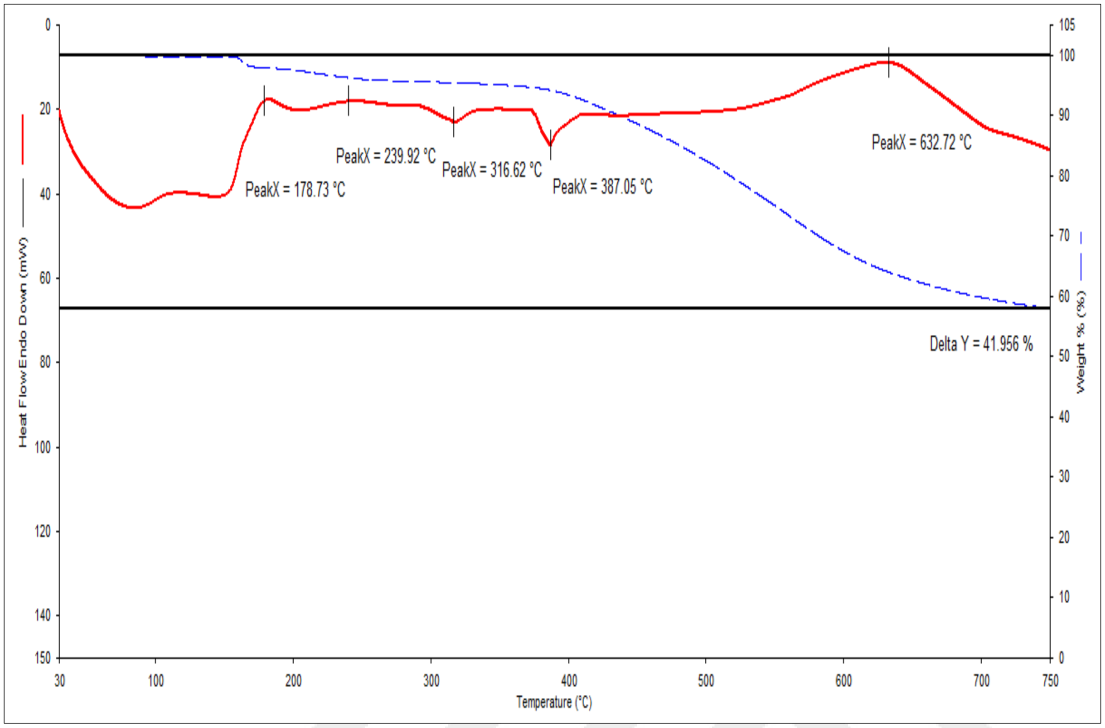

Figure 4.2 Reference 1 Oxalic acid catalyst, catalyst ratio 100 %, pH adj. with NaOH

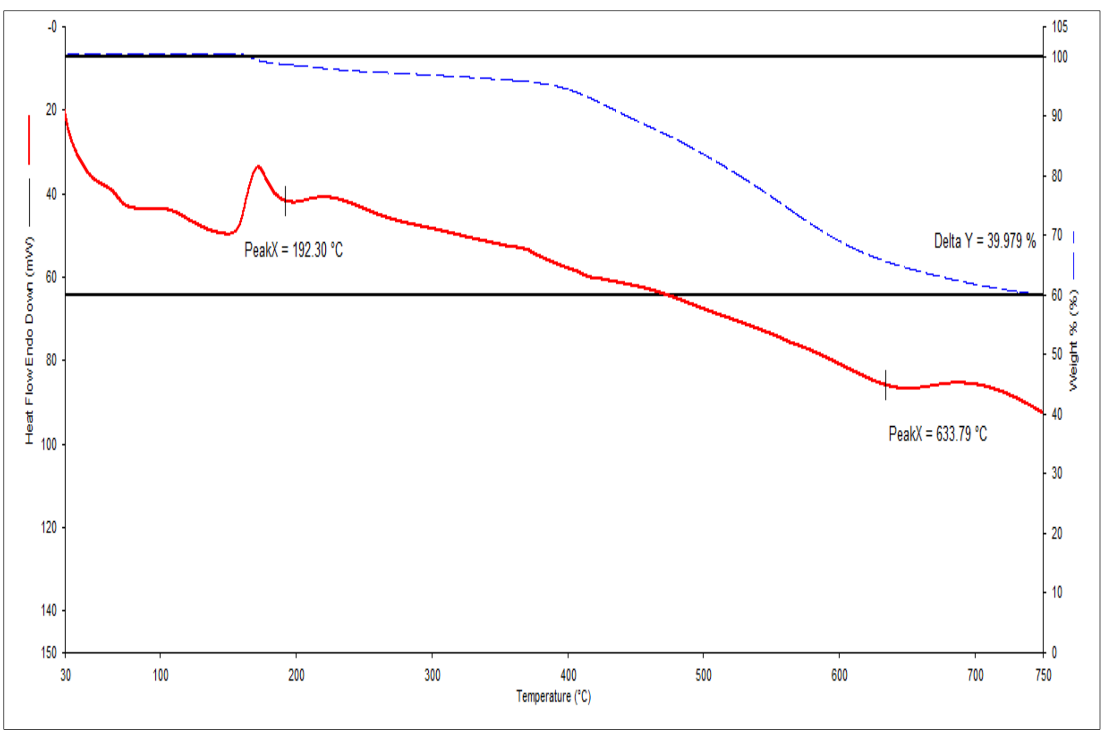

Figure 4.3 Exp 1. Oxalic acid and phosphoric acid catalyst, catalyst ratio 75 % - 25 %, pH adj. with NaOH

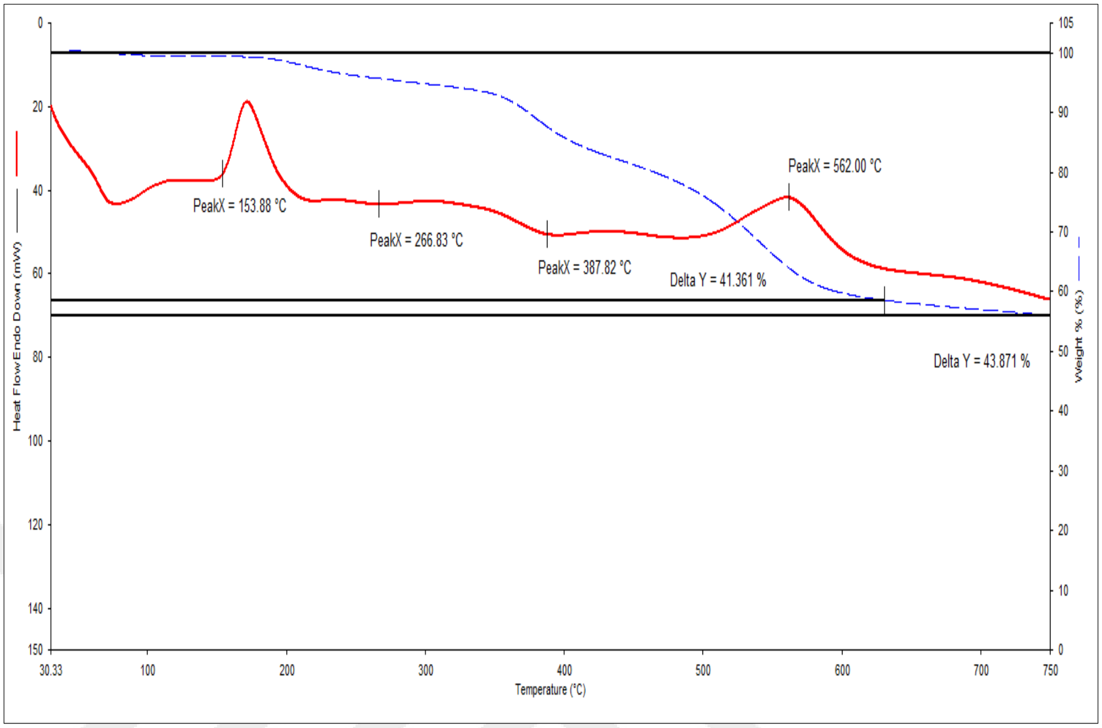

Figure 4.4 Exp 2. Oxalic acid and phosphoric acid catalyst, catalyst ratio 50 % - 50 %, pH adj. with NaOH

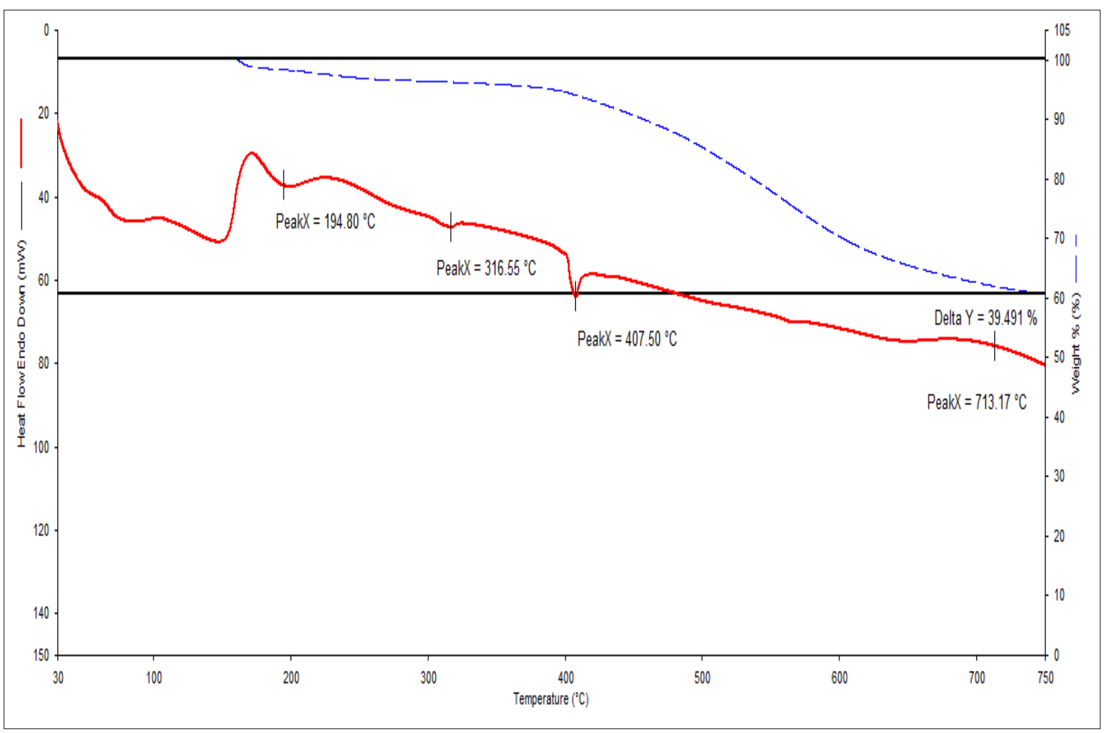

Figure 4.5 Exp. 3 Oxalic acid and phosphoric acid catalyst, catalyst ratio 25 % - 75 %, pH adj. with NaOH

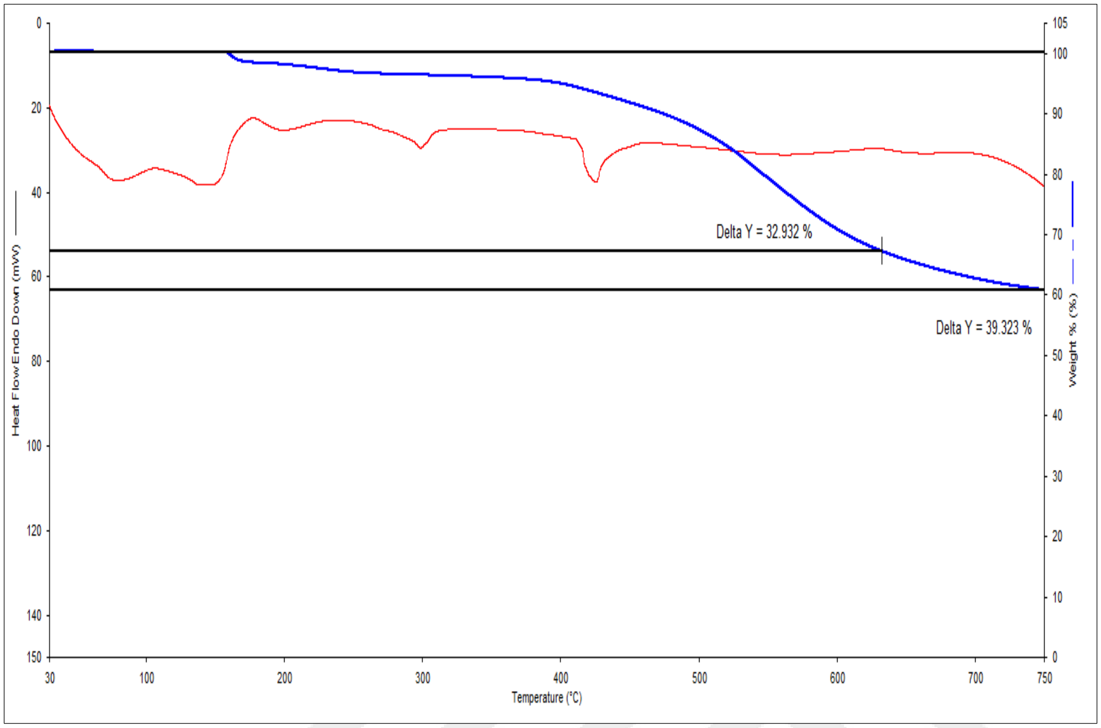

Figure 4.6 Exp. 4 Phosphoric acid catalyst, catalyst ratio 100 %, pH adj. with NaOH

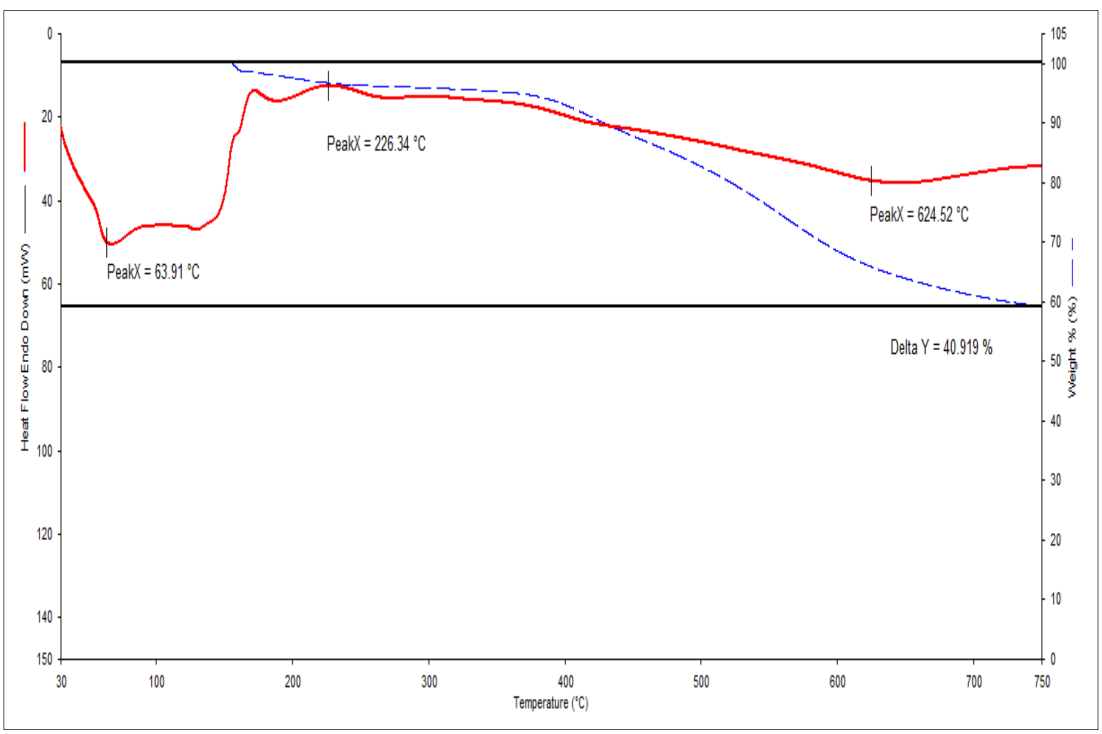

Figure 4.7 Exp. 5 Phosphoric acid catalyst, catalyst ratio 100 %, pH adj. with TSF

4.2 Different Catalyst Types without pH Adjustment Phenolic Novolac Resin Synthesis

All experimental were repeated as mentioned in section 3.4.1. The catalyst mole ratio starts with 100 % oxalic acid (Reference 2) and continues as 25 % phosphoric acid – 75 % oxalic acid (Experiment 6), 50 % phosphoric acid – 50 % oxalic acid (Experiment 7), 75 % phosphoric acid – 25 % oxalic acid (Experiment 8) and 100 % phosphoric acid (Experiment 9). However after reflux process was continued without pH adjustment in this Experimental studies. The pH adjustment was removed to see the phosphoric acid catalyst effect without neutralization. Table 4.3 shows the catalyst types and catalyst ratio without pH adjustment for synthesis of novolac resin.

Table 4.3 Different catalyst types and catalyst ratio without pH adjustment

	Reference 2	**Exp. 6**	**Exp. 7**	**Exp. 8**	**Exp. 9**
Catalyst Ratio and Type	100 % Oxalic Acid	75 % Oxalic Acid	50 % Oxalic Acid	25 % Oxalic Acid	–
	–	25 % Phosphoric Acid	50 % Phosphoric Acid	75 % Phosphoric Acid	100 % Phosphoric Acid
pH Adjustment	–				

Reference 1 and reference 2 were compared and the results of this two references were observed to be close to each other. All studies in section 4.2 without pH adjustment has been shown to give better results than section 4.1 with pH adjustment. These results has been shown that there was no needed for pH adjustment in this experimental studies. Removal of pH adjustment from the process was provided both time and financial convenience. All studies in section 4.2 production times were performed approximately 16 hours. For all this reasons, reference 2 has more improvable features. Improvement studies of Reference 2, we were seen that Experiment 7 was given the best results such as low flow distance, high melting point and low weight loss and highest ignition temperature peak result. TG analyzes were given below between Figure 4.9 and Figure 4.13. The results of all the experimental studies was performed in section 4.2 are given in Table 4.4.

Table 4.4 Results of different catalyst types and catalyst ratio without pH arrangements

	Reference 2	**Exp. 6**	**Exp 7**	**Exp 8**	**Exp 9**
pH, After Reflux	1.63	1.13	1.15	1.18	1.40
Weight Loss, % at 630.65 °C*	33.90	32.68	31.66	32.28	33.39
Total Weight Loss, % at 750 °C	40.59	39.28	37.65	38.45	39.59

*Reference 2 loss on ignition peak temperature

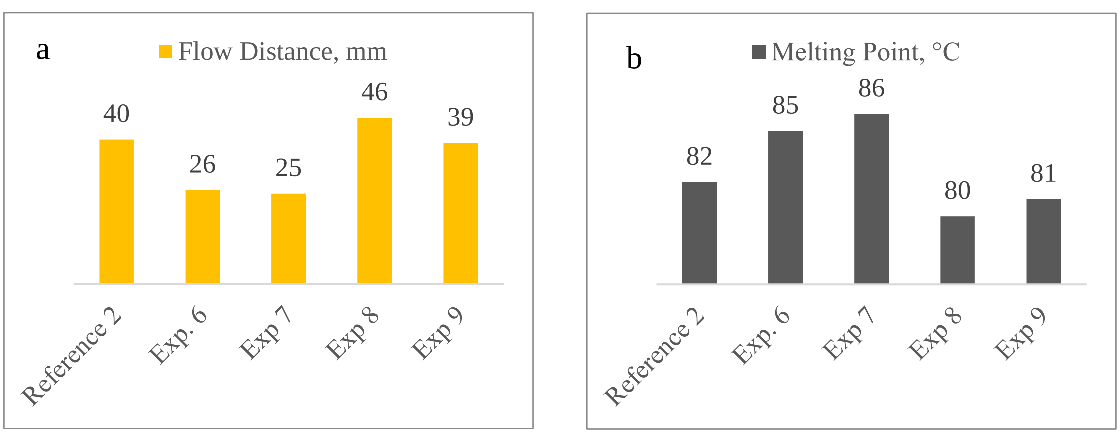

Figure 4.8 Graph of flow distance (a) and melting point (b) in different catalyst types without pH adj.

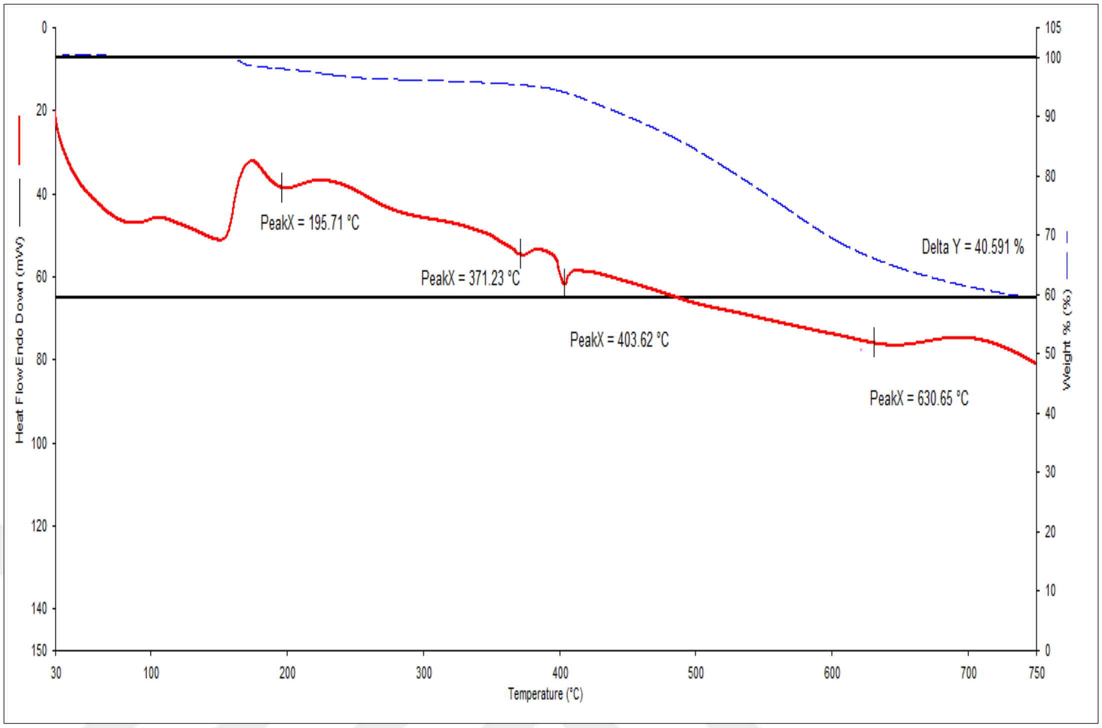

Figure 4.9 Referance 2 Oxalic acid catalyst, catalyst ratio 100 %, without pH adjustment

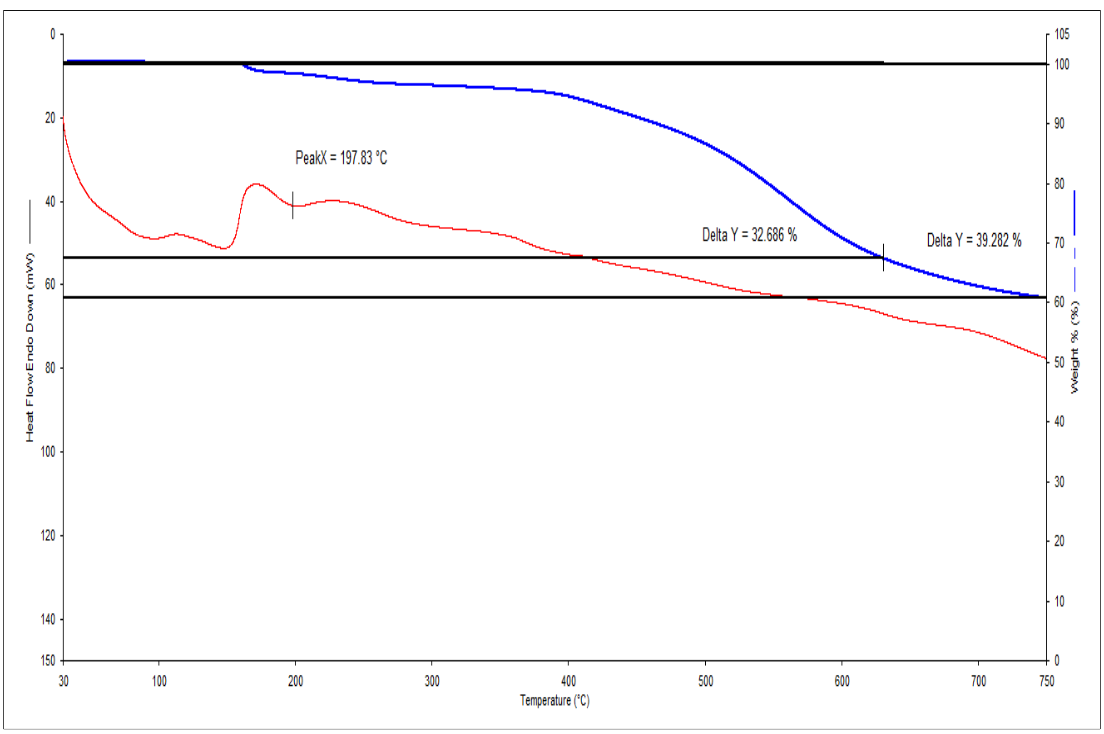

Figure 4.10 Exp. 6 Oxalic acid and phosphoric acid catalyst, catalyst ratio 75 % - 25 %, without pH adj.

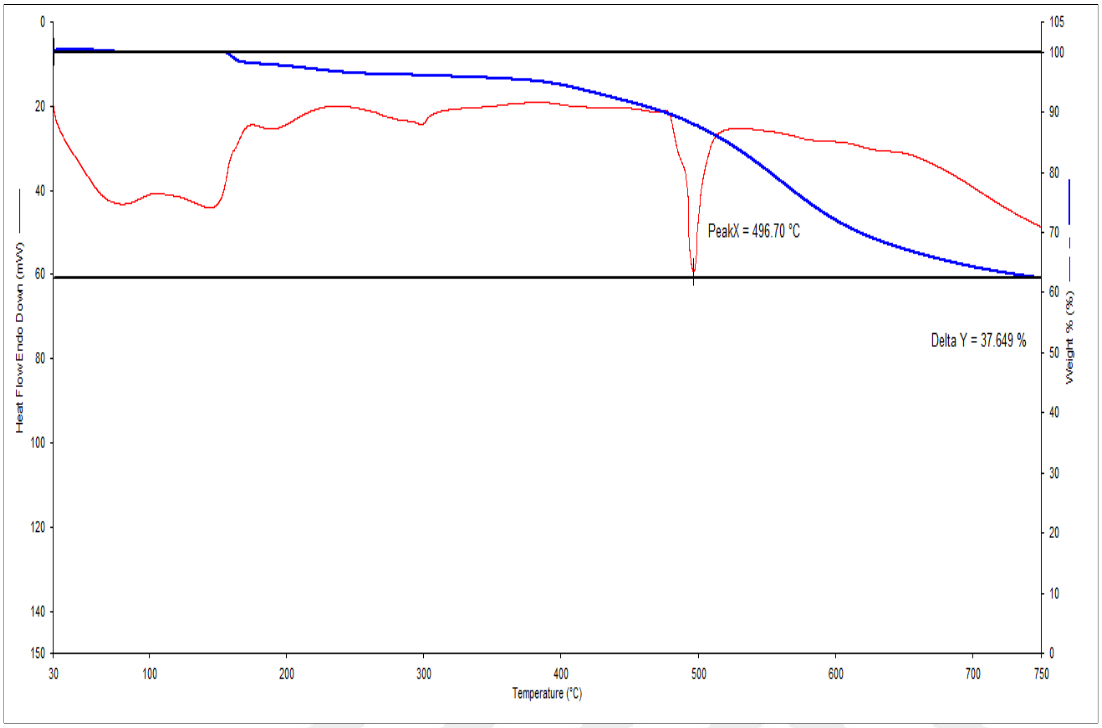

Figure 4.11 Exp. 7 Oxalic acid and phosphoric acid catalyst, catalyst ratio 50 % - 50 %, without pH adj.

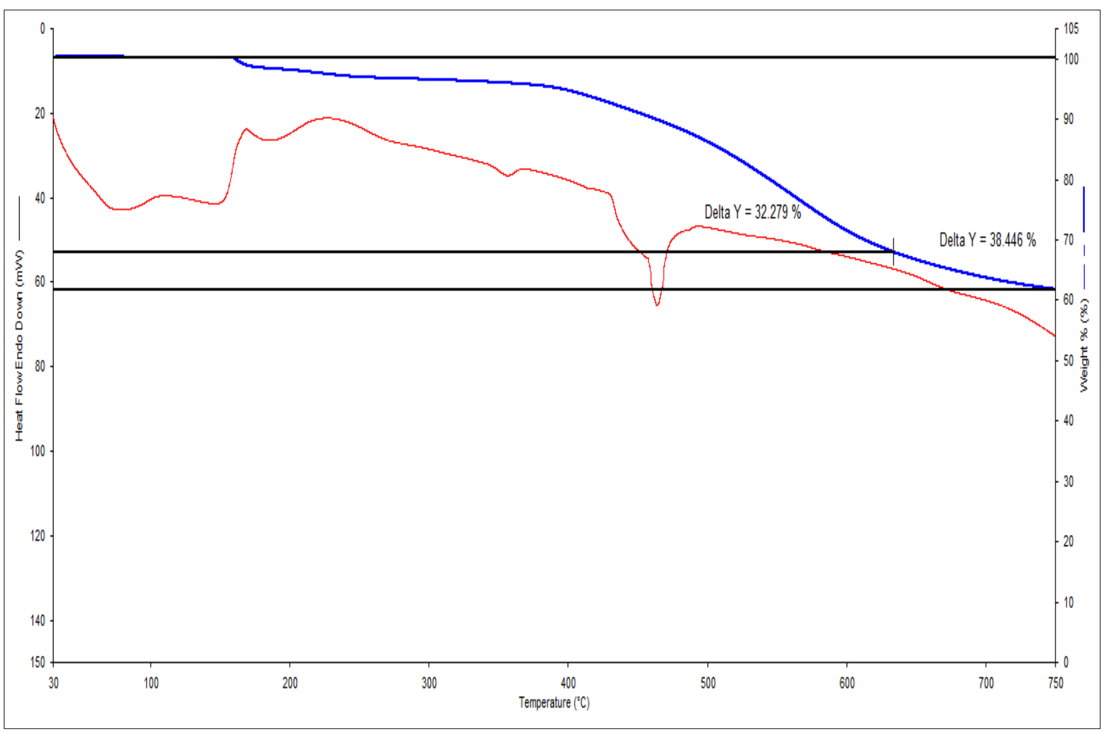

Figure 4.12 Exp. 8 Oxalic acid and phosphoric acid catalyst, catalyst ratio 25 % - 75 %, without pH adj.

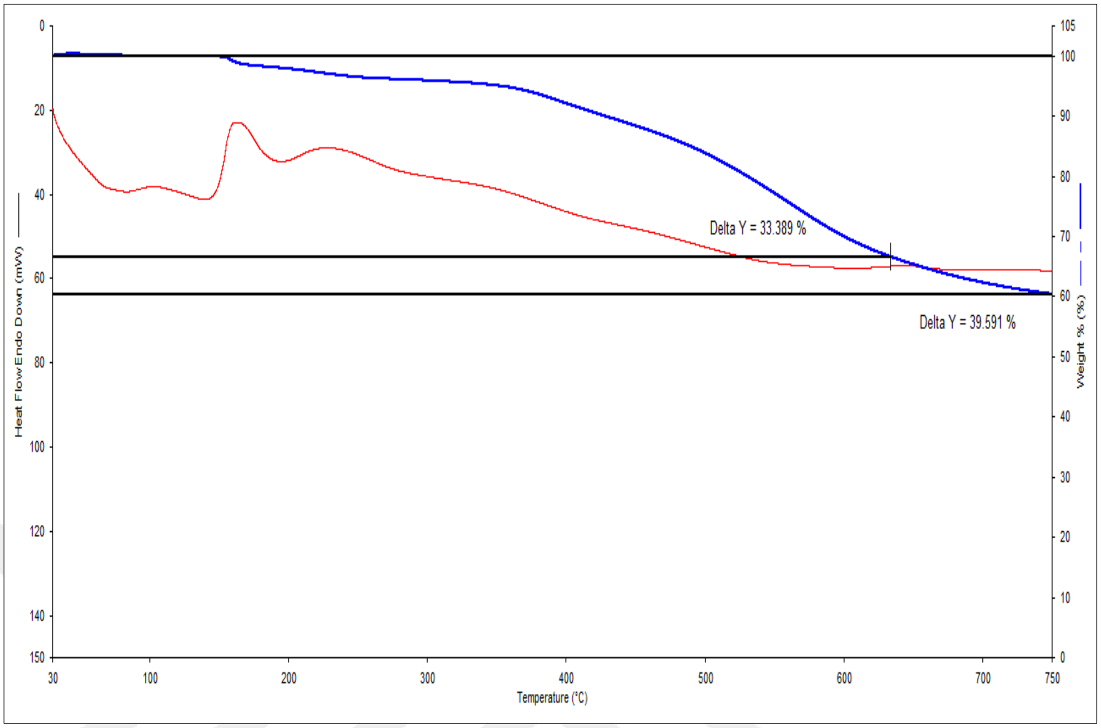

Figure 4.13 Exp. 9 Phosphoric acid catalyst, catalyst ratio 100 %, without pH adjustment

4.3 Additive Effect on Thermal Stability of Phenolic Novolac Resins

This experimental section covers the results of phosphate-containing flame retardant compounds and the most popular commercial flame retardants physically mixed with novolac. Flame retardant was added by different weight ratio. Mono Ammonium Phosphate (MAP), Trisodium Phosphate Dodecahydrate (TSF) were used as phosphate containing flame retardants. Apart from these, different inorganic flame retardants such as Zinc Borate ($B_2O_6Zn_3$), Magnesium Hydroxide $Mg(OH)_2$ were used. These flame retardants were tested by adding 5 %, 10 % and 15 % by mass to the phenolic resin. Table 4.5 shows the summary of the in this experimental studies.

Table 4.5 Types of additives and percentage of additive amount

Type and Percentage of Additive Amount	**Exp. 10**	**Exp. 11**	**Exp. 12**
	5 % MAP	10 % MAP	15 % MAP
	Exp. 13	**Exp. 14**	**Exp. 15**
	5 % TSF	10 % TSF	15 % TSF
	Exp. 16	**Exp. 17**	**Exp. 18**
	5 % Zinc Borate	10 % Zinc Borate	15 % Zinc Borate
	Exp. 19	**Exp. 20**	**Exp. 21**
	5 % $Mg(OH)_2$	10 % $Mg(OH)_2$	15 % $Mg(OH)_2$

Table 4.6 Results of 5 % additive effect on thermal stability

	Exp. 10	Exp 13	Exp. 16	Exp. 19
Flow Distance, mm	54	55	58	58
Melting Point, °C	79	79	76	75
Total Weight Loss, % 750 °C	42.36	43.87	42.39	61.21

Table 4.7 Results of 10 % additive effect on thermal stability

	Exp. 11	Exp. 14	Exp. 17	Exp 20
Flow Distance, mm	43	44	48	48
Melting Point, °C	79	81	77	77
Total Weight Loss, % 750 °C	41.84	42.39	42.12	53.95

Table 4.8 Results of 15 % additive effect on thermal stability

	Exp. 12	Exp. 15	Exp. 18	Exp. 21
Flow Distance, mm	30	32	43	41
Melting Point, °C	83	83	79	79
Total Weight Loss, % 750 °C	40.85	40.64	38.63	52.43

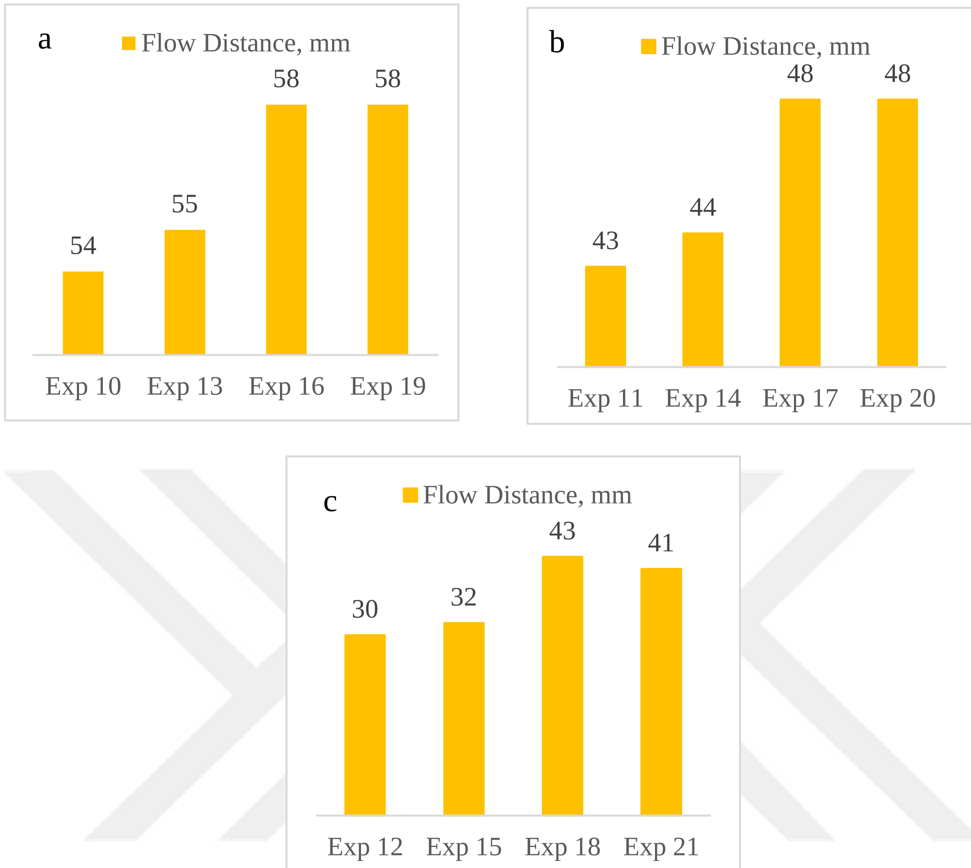

Figure 4.14 Flow distance on 5 % (a), 10 % (b), 15 % (c) additive effect on thermal stability

The results of all the experimental studies was performed in section 4.3 are given in Table 4.6, Table 4.7 and Table 4.8, respectively. Table 4.6, Table 4.7 and Table 4.8 were shown the analysis results of novolac resins with flame retardant added ratio 5 %, 10 % and 15 % by mass, respectively. The flow distance analysis results of four different additives used in different weight ratios were given in the graphics above (Figure 4.14). The melting point increased as the amount of addition increased. All selected chemicals were used to increase the flame retardant property of novolac resin. The additives were physically mixed with the novolac resin but were not included in the polymerization. It has been measured that additive effect provide the shorter flow distance of the compared to the pure novolac resin. Because additives act as impurities in the novolac resin.

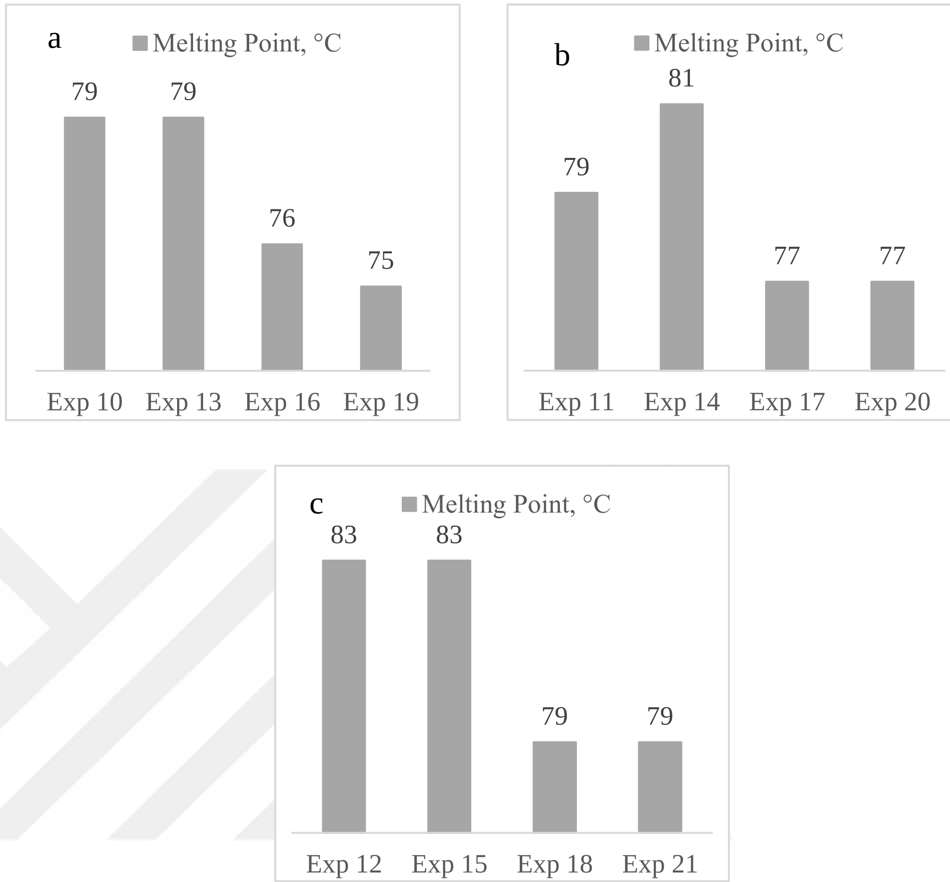

Figure 4.15 Melting point on 5 % (a), 10 % (b), 15 % (c) additive effect on thermal stability

The melting point analysis results of four different additives used in different weight ratios were given in the graphics above (Figure 4.15). As the amount of addition was increased, the melting point was increased. Considering the effect of different flame retardant additives on the melting point temperature, it was determined that used 15 % weight ratio of Mono Ammonium Phosphate additive was given the highest result. TG analyzes were given below between Figure 3.16 and Figure 3.27. All results were compared in section 4.3. Experiment 12 was performed the best result with low flow distance, high melting point and low weight loss and highest ignition temperature.

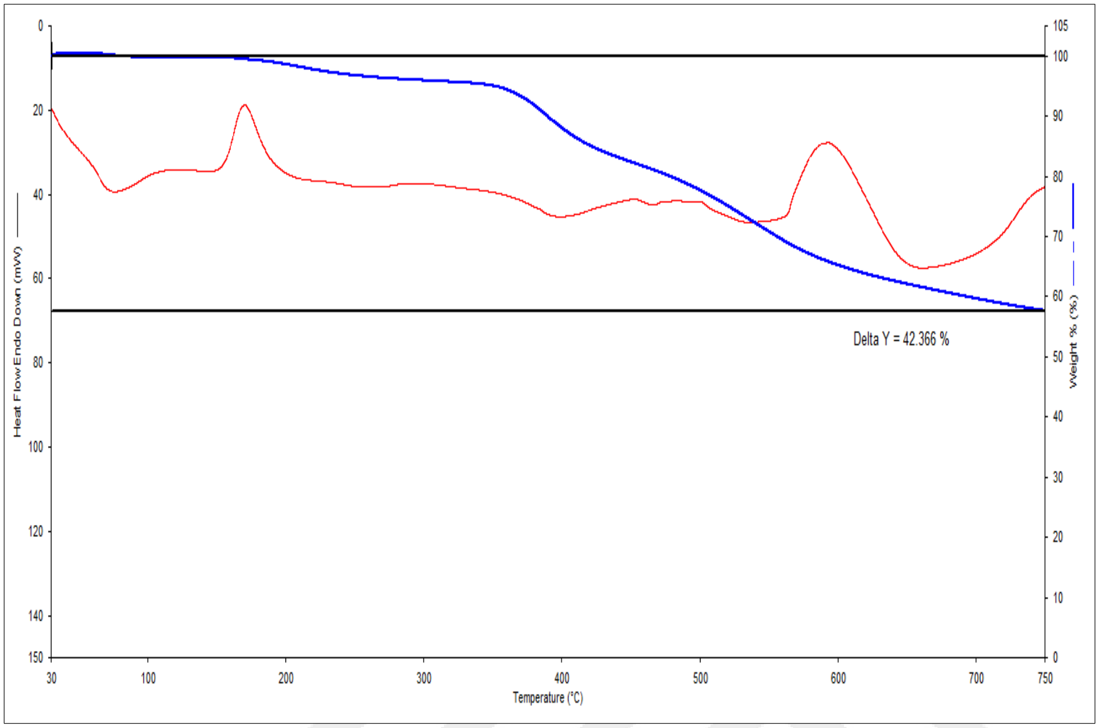

Figure 4.16 Exp. 10 Addition of MAP, 5 % additive amount

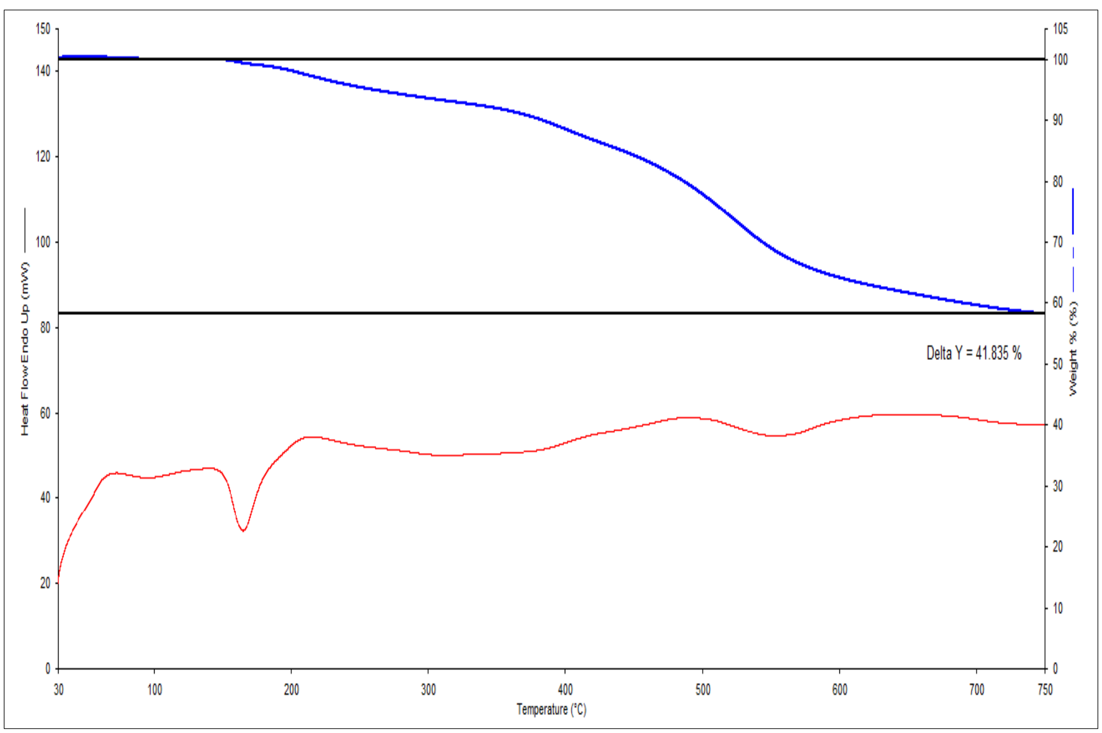

Figure 4.17 Exp. 11 Addition of MAP, 10 % additive amount

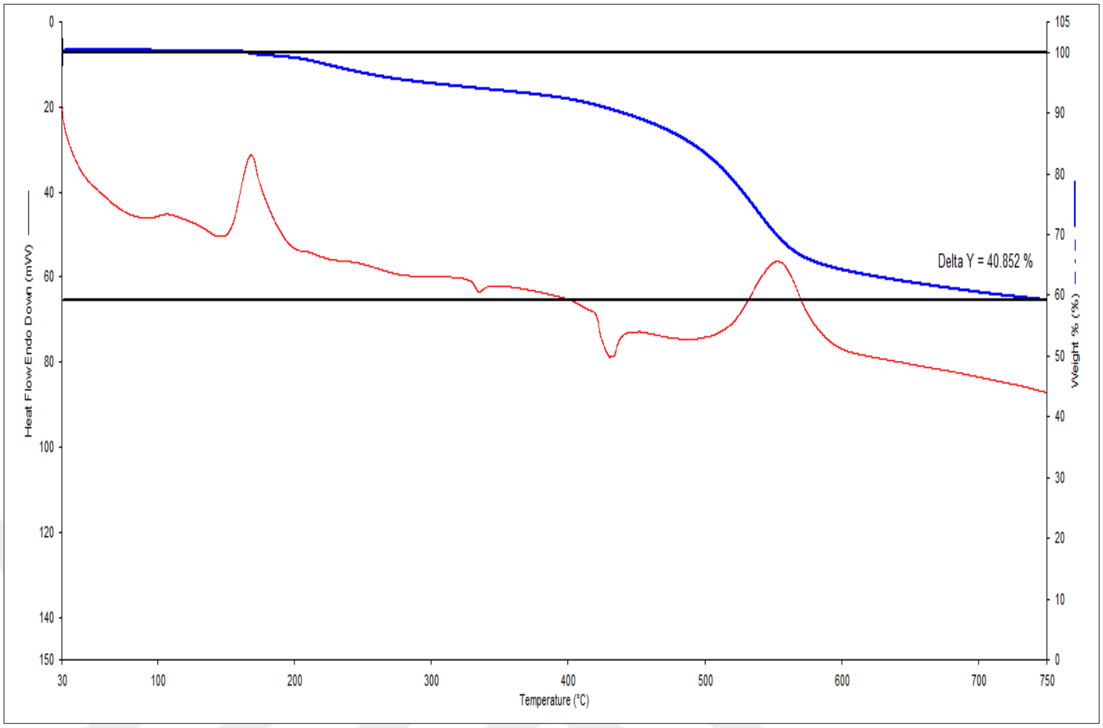

Figure 4.18 Exp. 12 Addition of MAP, 15 % additive amount

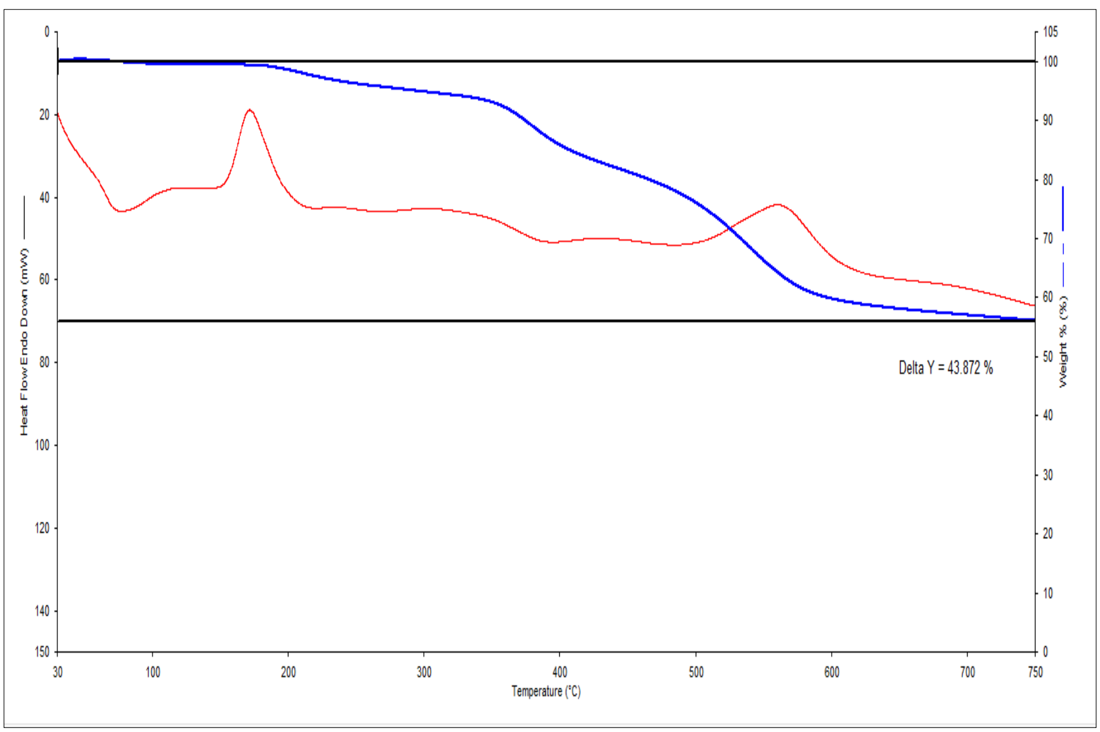

Figure 4.19 Exp. 13 Addition of TSF, 5 % additive amount

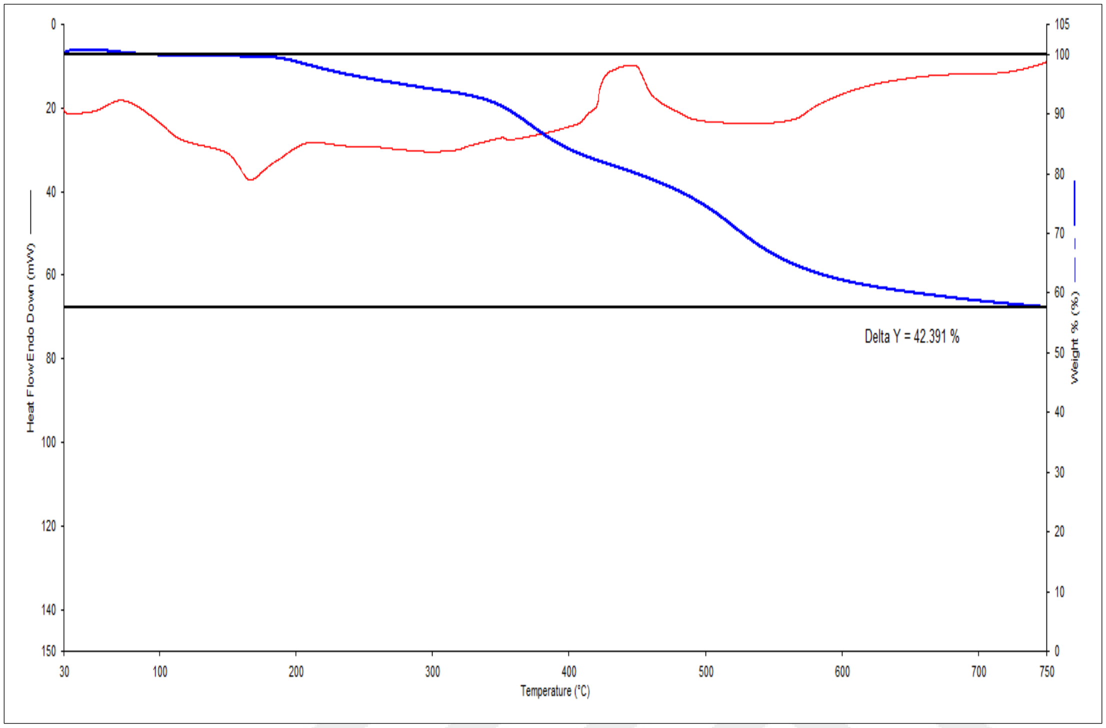

Figure 4.20 Exp. 15 Addition of TSF, 15 % additive amount

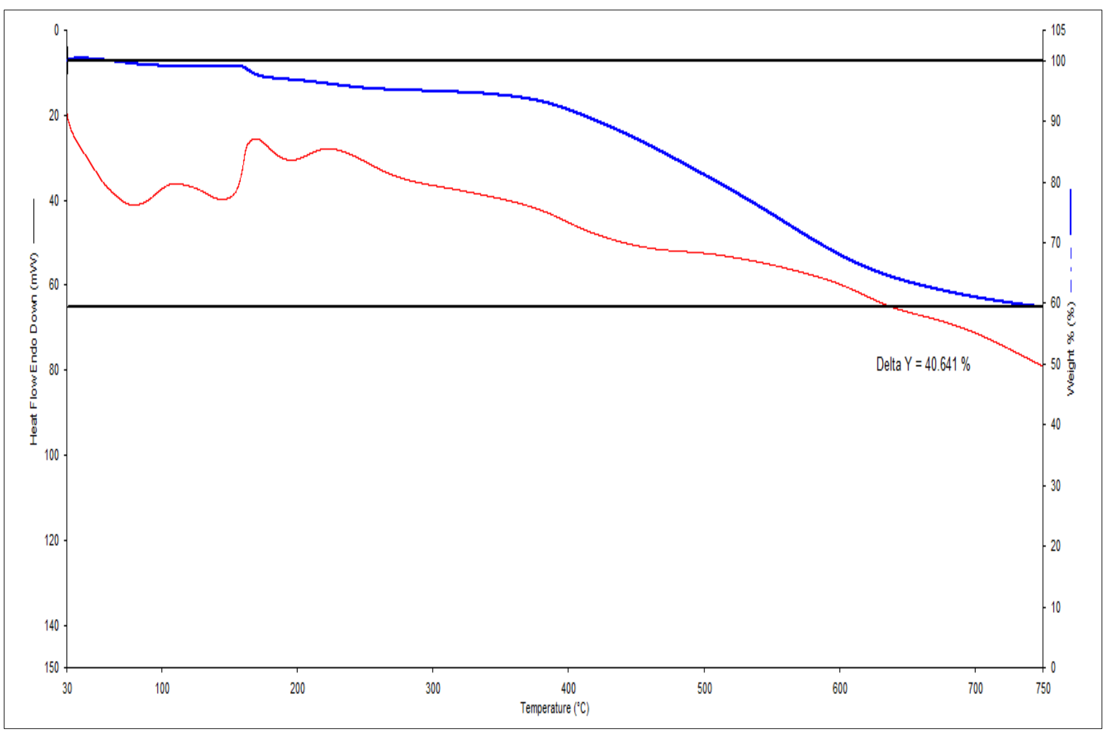

Figure 4.21 Exp. 14 Addition of TSF, 10 % additive amount

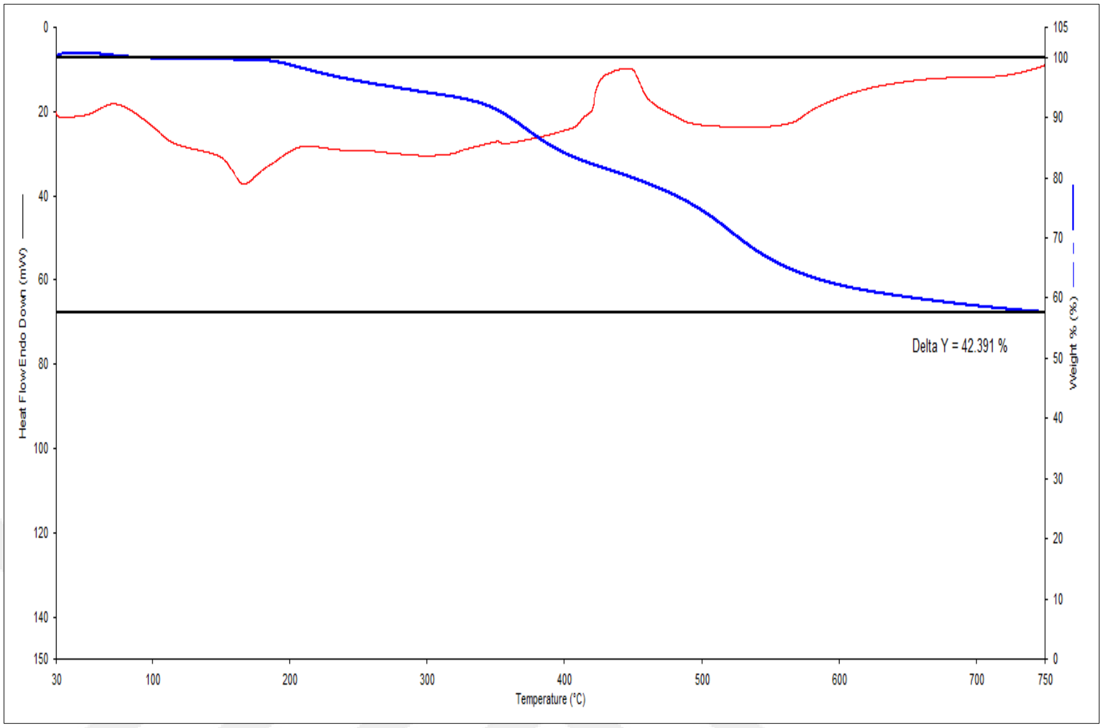

Figure 4.22 Exp. 16 Addition of ZnB, 5 % additive amount

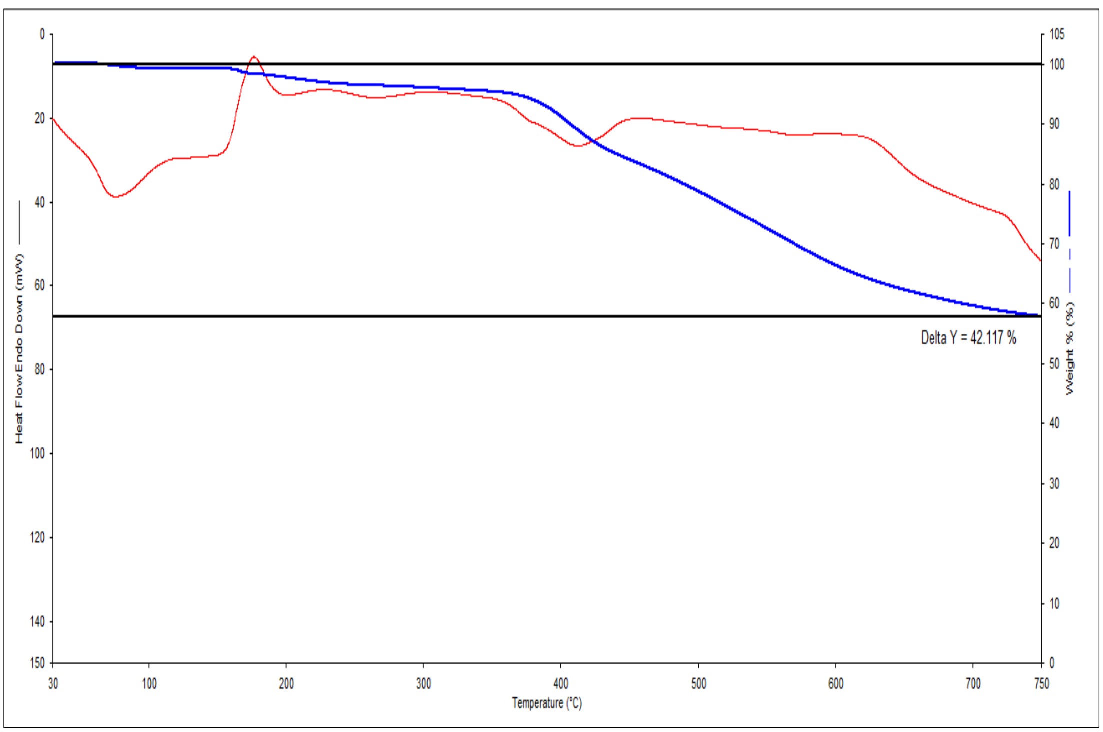

Figure 4.23 Exp. 17 Addition of ZnB, 10 % additive amount

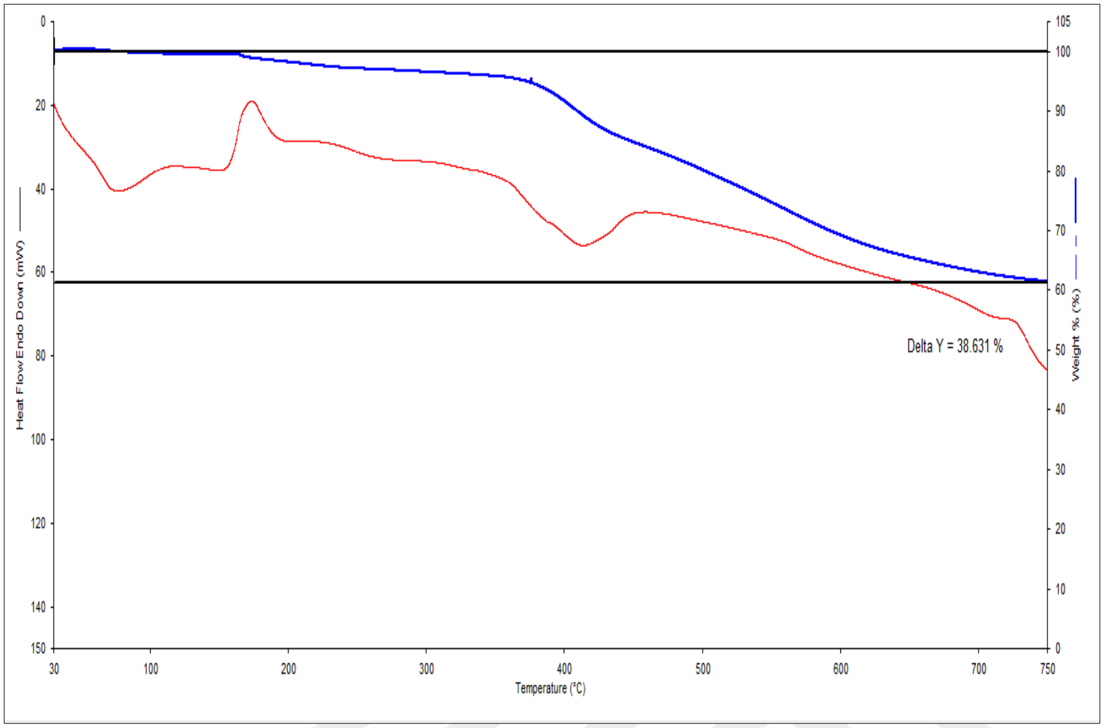

Figure 4.24 Exp. 18 Addition of ZnB, 15 % additive amount

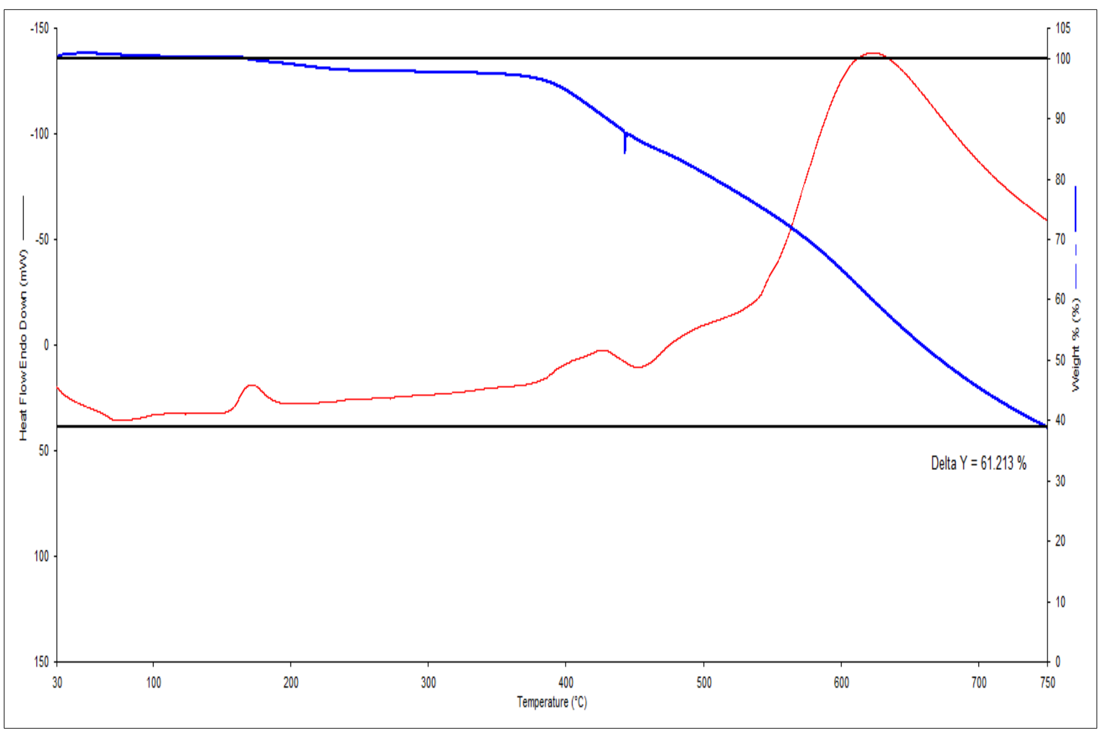

Figure 4.25 Exp. 19 Addition of $Mg(OH)_2$, 5 % additive amount

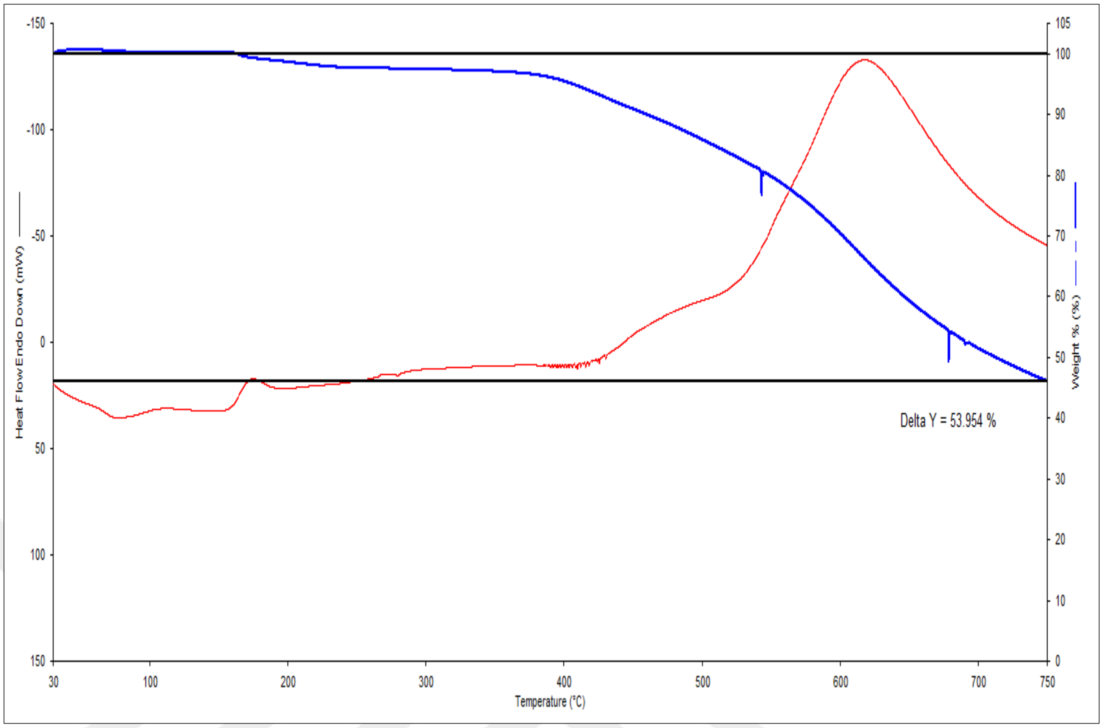

Figure 4.26 Exp. 20 Addition of $Mg(OH)_2$, 10 % additive amount

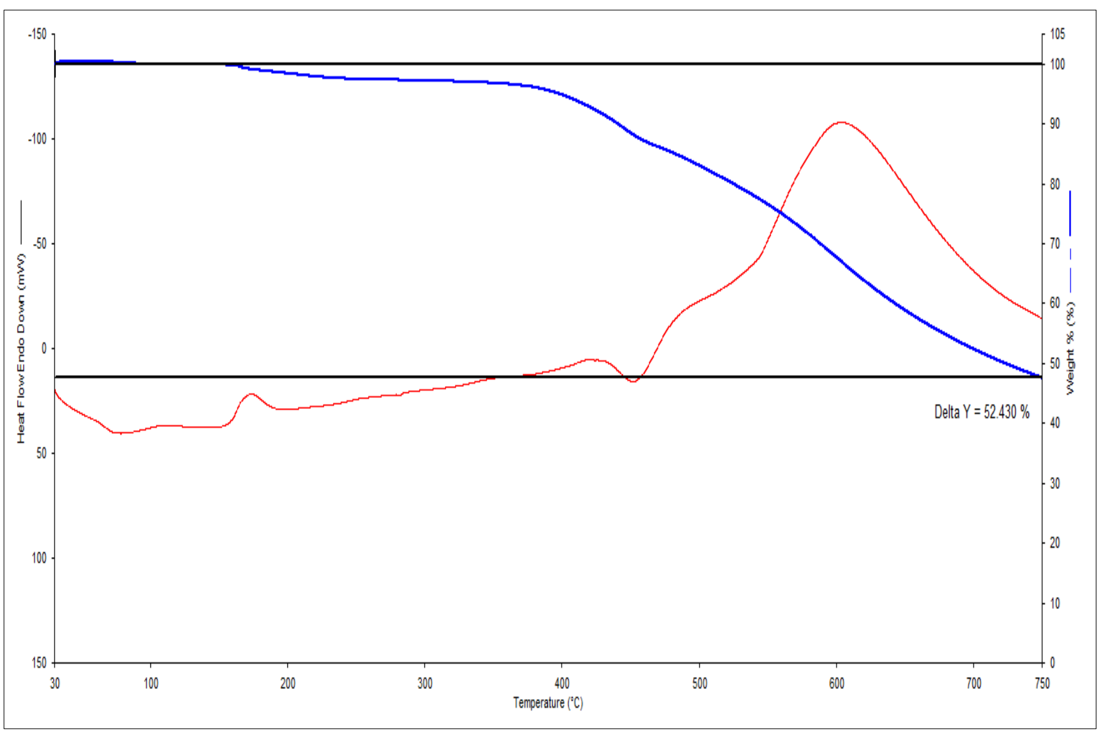

Figure 4.27 Exp. 21 Addition of $Mg(OH)_2$, 15 % additive amount

5 CONCLUSION

In this thesis, it was investigated increasing the flame retardant properties of novolac resins with phosphate additives. There were three types of processes in this experimental study. The first two experimental studies were the synthesis of novolac resin with acid catalysts. Oxalic acid and instead of the oxalic acid catalyst, as oxalic acid and phosphoric acid were changed the catalyst type and ratio without changing the mole ratio of the catalyst. The studies were continued in this order. Firstly, the acidic medium formed as a result of the condensation reaction was neutralized by adjusting the pH with bases. The second study was continued without pH adjustment. In the third study, it was investigated how the fire retardant property was affected by physically mixing phosphoric additives and commonly used fire retardant agents with novolac resin. During these studies, determination flow distance analysis in accordance with ISO 8619 standard, determination phosphate amount with X-Ray Fluorescence Spectrometer (XRF), determination melting point analysis with an accordance with ISO 3146 standard methods were used.

The effectiveness of the catalysts provide chain growth of the polymer. Short flow distance is showing that the better the polymerization results. Char formation of phenolic resin create organic-inorganic hybrid barrier layer is formed. Hybrid barrier, char layer is solid phase, provide against the heat source. Lower total weight losses, the higher the char layer formation. When compared in different catalyst types with pH adjustment phenolic novolac resin synthesis section, the flow distance which has appropriate polymer structure, highest melting point temperature and the weight loss obtained as a result of TG analysis was investigated that the best result was Experiment 3. Melting point is 78 °C, flow distance is 45 mm and total weight loss is 39.49 % are determined at Experiment 3.

In without pH adjustment phenolic novolac resin synthesis section, Experiment 7 was given the best results. The melting point was determined as 86 °C. The flow distance was determined as 25 mm and total weight loss was determined as 37.65 % at Experiment 7. The production time of Experiment 7 was determined as 16 hours.

Considering the effect of different additives on the melting point temperature section, it was determined that used Experiment 12 which is 15 % weight ratio of Mono Ammonium Phosphate additives gave the highest result on the melting point and lowest loss on ignition. The melting point was determined as 83 °C. The flow distance was determined as 30 mm and total weight loss was determined as 40.85 % at Experiment 12. The production time of Experiment 12 was determined to be approximately 30 hours.

The best results of the experimental studies carried out in 3 different processes were compared. It was determined that Experiment 7 had more developable features, shorter production time and better experimental results compared to Reference 1, Reference 2, Experiment 3 and Experiment 12.

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