ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

SYNTHESIS OF COMPOSITE RESOL RESINS AND APPLICATION FOR GLASS WOOL PRODUCTION

M.Sc. THESIS

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Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

KOMPOZİT RESOL REÇİNELERİNİN SENTEZİ VE CAM ELYAF ÜRETİMİNDE KULLANIMI

YÜKSEK LİSANS TEZİ

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Ümran Burcu Alkan, a **M.Sc.** student of ITU **Institute of / Graduate School of Science and Technology** student ID **515131025**, successfully defended the **thesis** entitled "**SYNTHESIS OF COMPOSITE RESOL RESINS AND APPLICATION FOR GLASS WOOL PRODUCTION**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my parents,

FOREWORD

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May 2015 Ümran Burcu ALKAN
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ABBREVIATIONS

AA : Alendronic Acid
BP : Bisphosphonate
DSC : Differential Scanning Calorimeter
F : Formaldehyde
FTIR-ATR : Fourier Transform Infrared Spectroscopy
P : Phenol
PFR : Phenol Formaldehyde (Resol) Resin
SEP : Sepiolite Clay
PF : Phenol-Formaldehyde
PFR-AA : Alendronic Acid Modified Resol Resin
PFR-AA-SEP : Alendronic Acid and Sepiolite Modified Resol Resin
PFR-SEP : Sepiolite Modified Resol Resin
PR : Phenolic Resins
SEM : Scanning Electron Microscopy
TGA : Thermogravimetric Analysis
XRD : X-Ray Diffraction Analysis

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SYNTHESIS OF COMPOSITE RESOL RESINS AND APPLICATION FOR GLASS WOOL PRODUCTION

SUMMARY

This study can be divided into two parts. The first part aims to synthesis resol nanocomposites that can be used for thermal insulation materials, coatings, molding compounds, foundry materials, wood products and aerospace components due to their high strength, thermal stability, heat resistance and solvent resistance. In this study, resol resins were modified with alendronic acid and sepiolite in the presence of base catalyst.

Sepiolite is a needle like clay that improves the thermal stability, mechanical properties of polymers and used in the matrix of polyethylene, polypropylene, polyurethane, polyamide, polyvinylalcohol and epoxy resins, however there is not any research that include sepiolite and resol. Alendronic acid that is a phosphorus compound mostly used in drug sector for treatment of hypercalcemia, Paget’s disease, parasitic diseases, hypercholesterolemia and atherosclerosis. On the other hand phosphorus containing compounds used as flame retardant materials in engineering plastics, polyurethane foams, phenolic resins, polyamides, coatings and textiles.

The influence of sepiolite content and alendronic acid content on spectroscopic, thermal and microscopic properties of resins have been researched and determined. For this reason, with adding the different clay amounts of sepiolite (3wt%, 5wt%, 8 wt%, 10wt%, 15wt%, 20 wt%, 30 wt% and 50wt%) and different amounts of alendronic acid (5wt% and 10wt%) were synthesized. Furthermore, the synergist effect of sepiolite and alendronic acid were studied with 5wt% sepiolite and 5wt% of alendronic acid. In this part the synthesized resins formed the structure of nanocomposites. The characterization of the resin nanocomposite samples have been researched and determined. The characterization of the resin samples were performed by Fourier Transform Infrared Spectroscopy (FTIR-ATR), Thermogravimetric Analysis (TGA), X-ray Diffraction (XRD) and Scanning Electron Microscope (SEM). In addition, the solvent behaviour of these resins were investigated with the solvents of acetone, methanol, tetrahydrofuran (THF), dimethylformamid (DMF), chloroform and dimethyl sulfoxide (DMSO).

In FTIR-ATR measurements, with the characteristic peaks of neat resol (PFR), Si-O-Si vibrating characteristics of sepiolite and phosphorus peaks of alendronic acid were obtained in nanocomposite resin samples.

The DSC technique was used for determining the maximum cure temperatures and onset of cure temperatures. The cycle was heated from 30°C to 200°C with 10 °C/min heating rate. Due to sepiolite clay and alendronic acid loading, the curing temperarutres were enhanced.

The thermal attitude of resins were determined by TGA analysis. All resin samples heated at linear heating rate of 10 ^oC/min up 30^oC to 700^oC temperature. The weight loss of the resins were calculated with TGA. The obtained all residues at 700^oC were higher than 50%wt of initial resin.

The structures and the variations of spacing of the PFR, SEP, PFR-AAs, PFR-SEPs and PFR-AA-SEP were detected by X-ray diffraction. The d-spacings were calculated by Bragg’s Equation. All of the PFR-SEPs exhibited intercalated structure. As the loading of sepiolite was increased, the interlayer distance did not change very much due to the layers of sepiolite were bonded covalently and resol has thermoset structure even before curing. In PFR-AAs the nanocomposite structure was changed from exfoliated to intercalated with increasing alendronic acid content.

Distribution of clay particles in polymeric resol resin matrix and morphology of resin samples were determined with SEM analysis. The sample that contained 10wt% sepiolite loading had good dispersion in resol matrix that supports the strong interaction between silanol (Si-OH) groups of sepiolite and methylol ($-CH_2OH$) groups of resol.

The solubility tests were done with six different solvents that were acetone, methanol, THF, chlorofom, DMF and DMSO. All of the resin samples were not solve in acetone, methanol, THF and chloroform. The neat PFR were soluble in DMF and DMSO. Alendronic acid including nanocomposite resins were soluble in DMF however sepiolite including nanocomposite resins were not soluble in DMF. In DMSO not only PFR-AAs but also most of PFR-SEPs and PFR-AA-SEP were soluble. However, increased sepiolite contents of PFR-SEPs reduced the solubility.

The second part of this study aimed to obtain production of glass wool insulation materials with sepiolite and alendronic acid modified phenol formaldehyde resol resins to improve thermal properties. Glass wool that is a fluffy material of discontinuous fibers in random lenghts is very useful in thermal insulation sector. For producing glass wool composites of resol samples in a batch mixer the major ingredients (silica sand, limestone, soda ash, cullet) were blended at 1100^oC-1300^oC. From the reactor the molten glass was poured into the spinner that consisted of 2000 small holes. The fluid mixture were constrained and fibers were manufactured, owing to the centrifugal force of spinner.

To bind glass wools the synthesized liquid nanocomposite resol resins were sprayed. After this step, the glass wool was dried in the curing oven at 180-250^oC to obtain composite glass wool – modified resol resin product. Length and width trimmers were cut the size of the composite glass wool insulation product At the end of process glass wool composites gained the colour of resin samples.

KOMPOZİT RESOL REÇİNELERİNİN SENTEZİ VE CAM YÜNÜ ÜRETİMİNDE KULLANIMI

ÖZET

Bu çalışma iki bölümden oluşmaktadır. İlk bölümde yüksek mukavemetleri, termal olarak dayanıklıkları, ısıya ve çözücüye karşı dirençlerim sebebiyle; izolasyon malzemesi, kaplama, döküm, ahşap üretim malzemesi ve uzay-havacılık malzemesi olarak kullanılabilecek nanokompozit resol reçinelerinin sentezini amaçlamaktadır. Bu çalışmada resol reçineleri alendronik asit ve sepiyolit ile modifiye edilmiştir.

Polimer biliminde kompozitler ve nanokompozitlere son yıllarda büyük bir ilgi vardır. Bunun nedeni polimerlere eklenen mikro ve nano boyuttaki taneciklerin polimerin sertliğini, tokluğunu, termal dayanıklılığını ve boyutsal stabilitesini arttırmasıdır. Bir diğer sebep de bu taneciklerin ucuz olması ve az miktarda bulunan veya pahalı olan polimerleri miktar olarak çoğaltmasından kaynaklanmaktadır.

Sepiyolit polimerlerin termal ve mekanik dayanımlarını artıran çubuksu yapıdaki bir kildir ve polietilen, polipropilen, poliüretan, poliamit, polivinilalkol ve epoksi reçinelerinde bu amaçlarla kullanılmışlardır. Ancak sepiyolitin resol reçineleri üzerinde etkisini inceleyen bir araştırma daha once yapılmamıştır. Alendronik asit çoğunlukla ilaç sektöründe hiperkalsemi, Paget hastalığı, parazitik rahatsızlıklar, hiperkolestrolemi ve ateroskleroz gibi hastalıkların tedavisinde kullanılan fosfor bileşenli bir malzemedir. Ancak, diğer bir taraftan fosfor içerikli maddelerin polimerlerin termal dayanıklıklarını arttırdıkları da bilinmektedir. Bunlara örnek olarak poliüretan köpükler, fenolik reçineler, poliamitler, kaplamalar ve tekstiller verilebilir.

Tezde sepiyolit kili ve alendronic asit içeriklerinin etkisi spektroskopik, termal ve mikroskopik olarak incelenmiştir. Bu sebeple farklı kil içerikleri (3wt%, 5wt%, 8 wt%, 10wt%, 15wt%, 20 wt%, 30 wt% and 50wt%) ve farklı alendronik asit içerikleri (5wt% and 10wt%) bulunduran resol reçineleri sentezlenmiştir. Buna ek olarak sepiyolit kili ve alendronik asitin birlikte olan etkisi kütlece 5% sepiyolit ve kütlece 5% alendronik asit içeren yeni bir reçine örneği ile incelenmiştir. Bu aşamada elde edilen tüm reçineler nanokompozit yapıdadır.

Elde edilen nanokompozitlerin karakterizasyonu için FTIR-ATR spektrometre, diferansiyel taramalı kalorimetre (DSC), termogravimetrik analiz cihazı (TGA), X-ray ışığı kırınımı cihazı (XRD) ve taramalı elektron mikroskobu (SEM) kullanılmıştır. Bunlara ek olarak reçinelerin çözünürlükleri aseton, metanol, tetrahidrofuran, dimetilformamid, kloroform ve dimetil sülfoksit içerisinde 25^{o}C ve 50^{o}C sıcaklıklarda incelenmiştir.

FTIR-ATR spektroskopik ölçümlerinde resol reçinesinin karakteristik piklerinin yanında, sepiyolit kilinin Si-O-Si bağı titreşimleri ve alendronik asitin fosfor pikleri nanokompozit reçine örneklerinde görülmüştür. Yine, artan madde miktarı ile beraber ilgili piklerin şiddetinin arttığı da elde edilen sonuçlardan belirlenmiştir.

DSC ölçümleri ile elde edilen reçinelerin kürlenmeye başladıkları sıcaklık ve maksimum kür sıcaklıkları belirlenmiştir. Artan sepiyolit içeriği ve alendronik asit içeriği ile her bir nanokompozit grubunun kendi içerisinde sıcaklık artışları görülmüştür. Ancak alendronik asit ve sepiyolit kilinin etkileri karşılaştırıldığında sepiyolit kilinin kürlenme sıcaklığını daha fazla yükselttiği söylenebilmektedir. Öte yandan sepiyolit ve alendronik asitin birlikte kullanımının da kürlenme sıcaklığını yükselten etkenlerden biri olduğu görülmüştür.

Reçine örneklerinin termal bozunma davranışı TGA ile belirlenmiştir. Bunun için bütün reçineler 30^{o}C den 700^{o}Cye kadar sıcaklık dakikada 10^{o}C arttırılarak devam edilmiştir. Nanokompozit reçine örneklerinin kütle kaybı (%) termogravimetrik analiz (TGA) ölçümleri ile hesaplanmıştır. Her bir örnek için 700^{o}C de kalıntı miktarının ilk kütlenin %50sinden fazla olduğu görülmüştür. Buradan termal olarak oldukça dayanıklı nanokompozit reçinelerin elde edildiği söylenebilmektedir.

Resol reçinesinin, sepiyolitin ve modifiye olmuş tüm reçinelerin yapıları ve katmanlar arasındaki uzaklığı X-ray difraksiyonu ile elde edilmiştir. Katmanlar arasındaki uzaklık Bragg denklemi yardımıyla hesaplanmıştır. Reçinelerde alendronik asit miktarı arttıkça intercalated yapıdan exfoliated yapıya olan geçiş görülmüştür. Elde edilen verilerden kil içeren bütün reçinelerin intercalated yapıda olduğu belirlenmiştir. Sepiyolit miktarı arttıkça katmanlar arasındaki aralığın çok fazla değişmediği elde edilen sonuçlardandır. Bunun sebebi sepiyolit tabakalarının birbirleriyle kovalent bağlarla bağlanması ve resol reçinesinin kürlenmeden önce bile termoset olmasından kaynaklanmaktadır.

Kil parçacıklarının polimerik resol reçinesi matrisindeki dağılımı ve reçine örneklerinin morfolojisi taramalı electron mikroskobu (SEM) ölçümleri ile belirlenmiştir. Kütlece 10% sepiyolit içeren reçinede kilin homojen olarak dispersiyonu görülmektedir. Bu durum resol reçinesinin metilol grupları ile sepiyolit kilinin silanol grupları arasındaki etkileşimi destekler niteliktedir.

Reçinelerin çözünürlük testleri endüstride sıkça kullanılan altı farklı solventle gerçekleştirilmiştir. Bunlar aseton, metanol, tetrahidrofuran, kloroform, dimetilformamid ve dimetik sülfoksittir. Bütün reçinelerin aseton, metanol, tetrahidrofuran ve kloroformda sıcaklık arttırılsa bile çözünmedikleri gözlemlenmiştir. Saf resol reçinesinin sadece DMF ve DMSOda çözündüğü görülmüştür. Alendronik asit içeren reçineler de tıpkı saf resol reçinesi gibi DMF ve DMSO da çözünmüşlerdir. Ancak sepiyolit içeren reçineler için artan kil miktarına oranla kısmi çözünürlük ve çözünmezlik söz konusudur. DMSO için hem alendronik asit içeren reçineler hem de sepiyolit içeren çoğu reçine çözünürlük konusunda olumlu sonuç vermiştir. Ancak artan kil oranına bağlı olarak 30% ve 50% kil içeren reçinelerin çözünürlüğü sağlanamamıştır.

Bu çalışmanın ikinci bölümünde cam yünü izolasyon malzemelerinin sentezlenen reçinelerle üretimi amaçlanmıştır. Böylelikle laboratuarda elde edilen reçinelerin endüstriyel hayata da uygulanması sağlanmıştır. Sentezlenen nanokompozit reçinelerin bu alanda kullanılmasının nedeni termal dayanıklıklarının saf resol reçinesinden yüksek olmasıdır. Cam yünü görünüş olarak kabarık bir yapıdadır ve çeşitli uzunluklarda fiberler içermektedir. Endüstriyel olarak ısı yalıtımında kullanılmı yaygındır. Resol reçineleri de bu üretim sırasında bağlayıcı görevini üstlenmektedir.

Cam yünü üretimi için öncelikle fabrika ortamında silika kumu, kireç, soda külü ve artık cam parçaları bir reaktör içerisinde 1100^{o}C-1300^{o}C lerde eritilir. Reaktörden çıkan eriyik malzeme üzerinde 2000 adet mikrometrik delik bulunduran bir silindire gönderilir. Silindirin dönmesiyle beraber sıvı haldeki cam eriyik burada sıkıştırılır ve fiber şeklindeki çubuksu yapı elde edilir. Bu aşamada elde edilen cam yünleri birbirlerinden ayrık bir haldedir. Bunları biraraya getirmek için bağlayıcı olarak ilk aşamada elde edilen reçineler sıvı halinde cam yününün üzerine püskürtülerek uygulanmıştır. Bu aşamadan sonra, cam yünü üzerindeki reçinelerin kürlenmesi için sıcaklığı 180-250^{o}C lerdeki fırın kullanılmıştır. Son olarak elde edilen ürünün boyu, eni ve kalınlığı doğrayıcı makinelerle ayarlanmıştır. Proses sonunda oluşan malzeme cam yünü - modifiye edilmiş resol kompozitidir ve bu malzeme ilk aşamada üretilen nanokompozit reçinenin rengine sahiptir.

1. INTRODUCTION

Phenolic resins (PR) which are known as the oldest thermosetting polymers have been irreplaceable materials for industrial applications, such as wood products, coatings, laminates, structural adhesives, moulding compounds, thermal insulation materials and composites. Most of these applications are due to the fact that their low-cost, easily processability, high chemical resistance, fine dimensional stability, good temperature resistance and superior mechanical strength characteristics [1-8].

Glasswool is a fluffy material made from discontinuous fibers that can be used for thermal insulation. It is commonly found in ship and submarine bulkheads; automobile engine compartments and body panel liners; in furnaces and architectural partitions [9]. For binding glass wool, phenol–formaldehyde resole resins are widely used [10].

In polymer science, composites and nanocomposites have attracted great attention as a result of performance improvements of polymers through the incorporation of micro and nanosized fillers [11]. Typically, the main advantage is to enhance strength, stiffness, toughness, temperature resistance or dimensional stability by embedding particles in a matrix. Second advantage is to use cheap, readily available fillers to extend of scarce or expensive resin [12].

Among the different clays which are convenient as candidates for nanocomposite production, surely sepiolite is a valuable nanofiller [13]. Currently, many studies have been investigated nanocomposites based on sepiolite as a needle-like nanoclay species[14-17] because it is believed that needle-like nanofiller can be dispersed more easily in polymeric matrices due to its lower specific contact surface area compared with platelet-like clays with the same aspect ratio [16-17]. Today, sepiolite has been used for the preparation of nanocomposites using different polymers as matrix [13-23].

Bisphosphonates (BPs) are an important drug class of phosphorus compounds for various bone- and calcium-related pathologies and are used for the clinical treatment of metabolic bone diseases, such as tumor-induced hypercalcemia, Paget's disease, and osteoporosis [24]. Among the bisphosphonates, alendronic acid (or alendronate) is one of the most effective drugs used for the clinical treatment of osteoporosis, caused by osteoclastic bone resorption [25-26]. Additionally, the presence of phosphorus compounds has been reported in literature to improve the flame retardancy and thermo oxidative resistance of phenolic resins [27-29].

On the other hand, phenolic resins have three dimensional (3D) molecular structure even before curing, therefore the synthesis of phenolic resin nanocomposites is rather difficult. This situation limits the number of studies on these resins, compared to other thermosetting resins such as epoxy and unsaturated polyester [30-33]. Nevertheless, phenolic resin nanocomposites have attracted considerable attention in both scientific and industrial fields on account of their unexpected hybrid properties [33].

In this study, sepiolite and alendronic acid effects of resole nanocomposite resins were investigated by *in situ* method. Moreover, these materials have introduced the fabrication of insulation material to produce modified resol and glass wool composites. Spectroscopic, thermal, and microscopic properties of the final nanocomposite samples have been searched and determined by Fourier Transform Infrared (FTIR-ATR) spectroscopy, Differential Scanning Calorimetry (DSC), Thermogravimetric Analyzer (TGA), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

2. THEORETICAL PART

2.1 Resins

Resin is a versatile term that is not sharply defined. Initially, the term was defined as yellowish to brown colored, transparent to opaque, soft to brittle, tacky and noncrystallizable low molecular mass natural materials that can be soluble in most common organic solvents and virtually insoluble in water. As chemical industry has improved, this term has also been expanded to define synthetic materials that are used substitutes for natural resins with similar characteristics.

In the international standards, ISO 472 and ISO 4618/3 resins are described similarly, 'i.e., as solid, semisolid, or pseudosolid organic materials that have an indefinite and often high molecular mass, and generally soften or melt over a range of temperatures on heating'. Resins can be divided into two groups.

Natural Resins: In ISO 4618/3, natural resins are defined as resins of vegetable or animal origin. Natural resins includes rosins (gum, wood, or tall-oil rosins from tree and plant exudates; wood extracts), fossil resins such as amber; mined resins such as asphaltite; shellac as secretion product from an insect; and their main derivatives.

Synthetic Resins: In ISO 4618/3, synthetic resins are defined as resins resulting from controlled chemical reactions such as polyaddition or polycondensation between well-defined reactants that do not themselves have the characteristics of resins. Furthermore, synthetic resins can be obtained by polymerization (ISO 472) of unsaturated monomers. Phenol-formaldehyde, phenol-urea, and phenol-melamine resins are some of the most important synthetic resins [34-36].

2.2 Thermoset Resins

Thermoset resins, as the name implies, can be cured, set or hardened into a permanent shape. Curing is an irreversible chemical reaction also known as crosslinking. It usually occurs under the influence of heat, pressure and/or catalyst and leads to a three dimensional rigidized chemical structure. For some thermosetting materials, curing is initiated or completed even at room temperature. Although the cured part can be softened by heat, it cannot be remelted or restored to the flowable state that existed before curing. Continued heating for long times leads to degradation or decomposition. The major commercial thermoset resins include phenolic resins, aminoplasts, epoxy resins, polyester resins, vinyl ester resins, polyurethanes and silicones [37-38].

Thermoset resins provide some advantages which are listed below [37]:

- Excellent resistance to solvents and corrosives
- Resistance to heat and high temperature
- Ease of manufacturing
- Low raw material cost
- Fatigue strength
- Tailored elasticity
- Excellent adhesion
- Excellent finishing (polishing, painting, etc.)

Thermoset polymers are prepared in two stages. The first step is the formation of long chain molecules, which are capable of further reaction with each other. The second stage is the application of heat, pressure and/or the addition of curatives, which cause a reaction to occur between the chains, thus producing a complex cross-linked polymer [38-39].

The thermoset resin itself is not recyclable, because a thermosetting resin, once synthesized, it cannot be reshaped or reformed. However, there are a few new companies who have successfully removed the resin through pyrolization and are able to reclaim the reinforcing fiber [37].

2.3 Phenolic Resins

Phenol-formaldehyde resins (phenolic resins, phenolplasts), the first thermosetting plastics, are considered to be the first truly synthetic commercially available resins [40-42]. Phenolic resins were discovered by Von Baeyer in 1872, via acid-catalyzed reactions of phenols and acetaldehyde. In 1891, Kleeberg found that resinous products could also be formed by reacting phenol with formaldehyde. Later, Lederer and Manasse studied phenol and formaldehyde reactions under basic conditions in 1894, resulted the formation of ortho and para methylol phenols. At that time, the importance of the highly reactive intermediates were taken account a little interest. In 1905, Leo H. Baekeland worked with different phenol and formaldehyde ratio to synthesize the first cross-linkable resins. He synthesized base catalyzed resols (known as Bakelite resins) and acid catalyzed novolac products. In 1907, he filed 117 patents on phenol/formaldehyde resin systems [38,43-44].

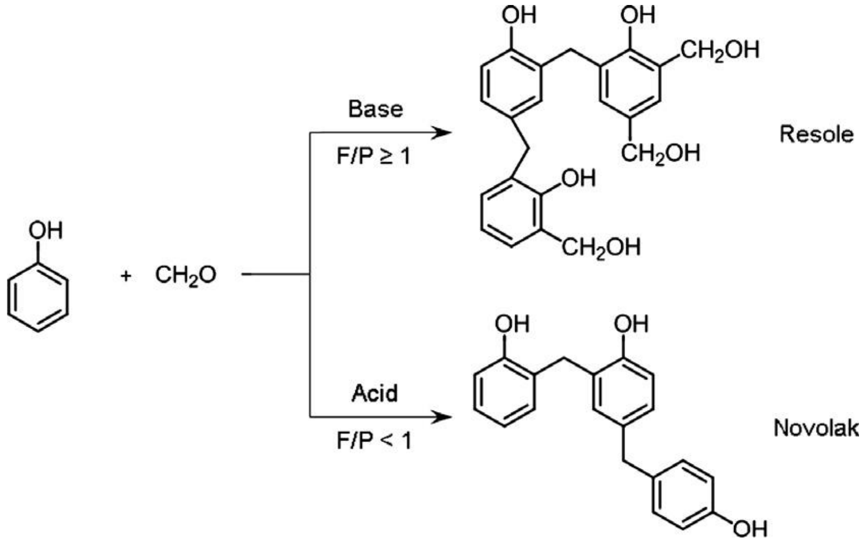

Figure 2.1 : Resol and novolac structures.

The use of phenolic resins was popularized by the “heat and pressure” patents [45-48] of Dr. Leo H. Baekeland in 1907; hence, he is known as the “father of phenolic resins.” Today, some of the most popular phenolic resins bear the trade name “Bakelite” in reference to the company (General Bake-lite Company) he formed in 1910. Bakelite Corporation became a subsidiary of Union Carbide in 1939 [45]. Baekeland’s patents involved the use of:

1. High pressure and a closed mold to overcome the problems of bubble formation and the evolution of gases and steam.

2. Fillers, such as wood flour, to overcome the problem of the brittleness of cured phenolic resin.

Phenolic resins are thermosetting resins produced by the condensation of a phenol with an aldehyde wherein water is produced as a by product. Typically, the phenol is phenol itself and the aldehyde is formaldehyde, but substituted phenols and higher aldehydes have been used to produce phenolic resins with specific properties such as reactivity and flexibility. The variety of phenolic resins available is quite large as the ratio of phenol to aldehyde, the reaction temperature, and the catalyst selected can be varied [49]. Phenolic resins fall into two broad classes:

1. Novolak resins
2. Resol resins

Resol resins are single stage resins and novolak resins are two-stage resins. Resol resins are typically produced with a phenol, a molar excess of formaldehyde, and an alkaline catalyst. The reaction is controlled to create a non-crosslinked resin that is cured by heat without additional catalysts to form a three-dimensional crosslinked insoluble, infusible polymer. In contrast, novolak resins are typically produced with formaldehyde, at molar excess of phenol, and an acid catalyst [43].

2.3.1 Applications of Phenolic Resins

Phenolic resins are useful for many applications. The list is very long, however, the major uses are wood binders, glass insulation binders, moulding compounds, laminates, foundry binders, coatings, friction linings, abrasives, and oil well propants [50-54]. They have found their way into a number of new, high technology uses such as rocket motor wear parts, military armour, sports equipment, photoresists for computer chip manufacture, circuit board binders and microchip module packaging. There has been a renewal of interest in the use of phenolics for aircraft construction because of their excellent flame resistance and low smoke generating properties [3].

2.3.2 Trade Names of Phenolic Resins

Trade names of phenolic resins were giving according to the literature [55].

- Bakelaque is a rigid laminate or tube made from phenolic resin on a substrate cotton fabric, paper or glass.

- Bakelite is made from Phenol resin and wood flour.
- Novotext is cotton fibre-reinforced phenolic, using randomly oriented fibres.
- Oasis is "an open-celled phenolic foam that readily absorbs water and is used as a base for flower arrangements."
- Paxolin Paperstone and Richlite are made from phenolic resin and paper.
- Trymer Green is a rigid cellular phenolic thermal insulation.
- Tufnol is made from phenolic resin and woven cotton or linen fabric.

2.4 Resol Resins

2.4.1 Synthesis of Resol Resins

Resol is obtained by the base catalyzed reaction of phenol and formaldehyde. Resol synthesis mechanism consists of three steps which are activation of phenol, methylolation and condensation (or chain extension) respectively [56].

Three basic stages are recognized in the phenolformaldehyde reaction:

1. A-stage or resole.

2. B-stage or resitol.

3. C-stage or resite

At the A-stage, the initial condensation products are mainly alcohols. The resin at this point is thermoplastic and soluble in inorganic solvents. At the B-stage, there is a higher degree of condensation and some cross-linking, with a consequent increase in molecular weight and viscosity, and a decrease in solubility. The resin is not fully cured; it is soft and fusible when hot, but hard and brittle when cold. At the C-stage, the degree of polymerization and cross-linking is very high, and there is almost a complete cure. The resin is infusible and insoluble [40].

Resole synthesis is commonly catalyzed with strong bases (pKa > 14; e.g. NaOH, Na_2CO_3, KOH, $Ba(OH)_2$, K_2CO_3), also weaker bases such as amines and carbonates (pKa ~ 10-11) can be used. In addition to catalysis, the strong base supports aqueous solubility to the polymer when it is strong enough. Generally, resoles are kept in aqueous solution until the application of a substrate to be glued or saturated.

Under basic conditions, phenolate rings are the reactive species for electrophilic aromatic substitution reactions. In the first step, phenol reacts with base to form the salt that has enhanced electron density at the reactive ring positions. This situation causes the activation of phenol. In Figure 2.2, the electron charge is dispersed along the ring at the positions of *ortho* and *para* to the original phenol structure. It should be noted that this mechanism does not account for pH effects, the type of catalyst. Mixtures of mono-, di-, and trihydroxymethyl-substituted phenols are produced.

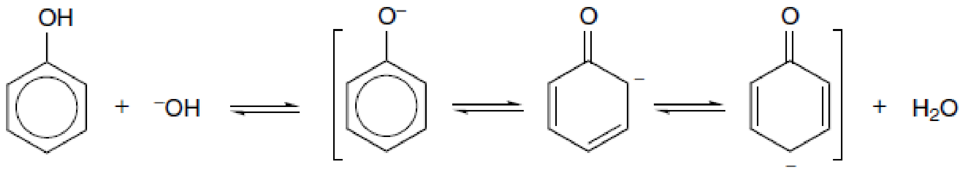

Figure 2.2 : Phenol activation by base.

The second step is reaction of the activated phenol with formaldehyde to form hydroxymethyl phenol and the process is known as methylolation (Figure 2.3).

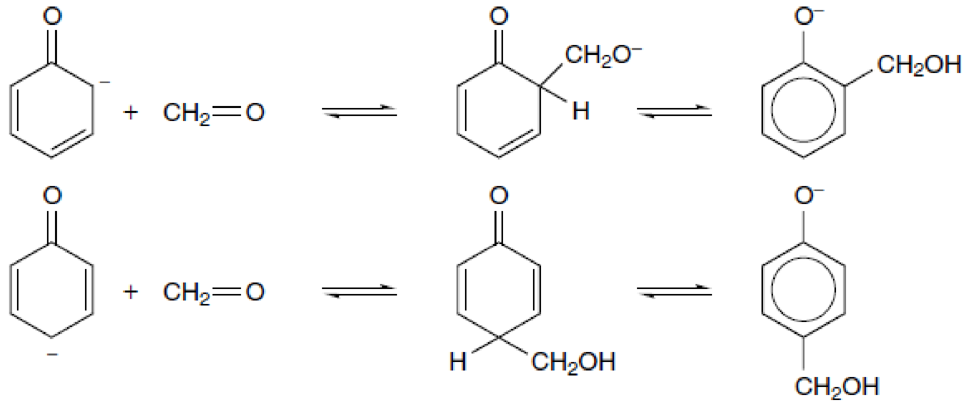

Figure 2.3 : Methylolation reaction under alkaline conditions.

Resoles are synthesized with excess formaldehyde, so more than one substitution can be seen on the ring. Monohydroxymethyl-substituted phenols, react with formaldehyde to form di- and trihydroxymethyl-substituted phenols (Figure 2.4.). In methylolation reaction maximum three methylol groups can be substituted.

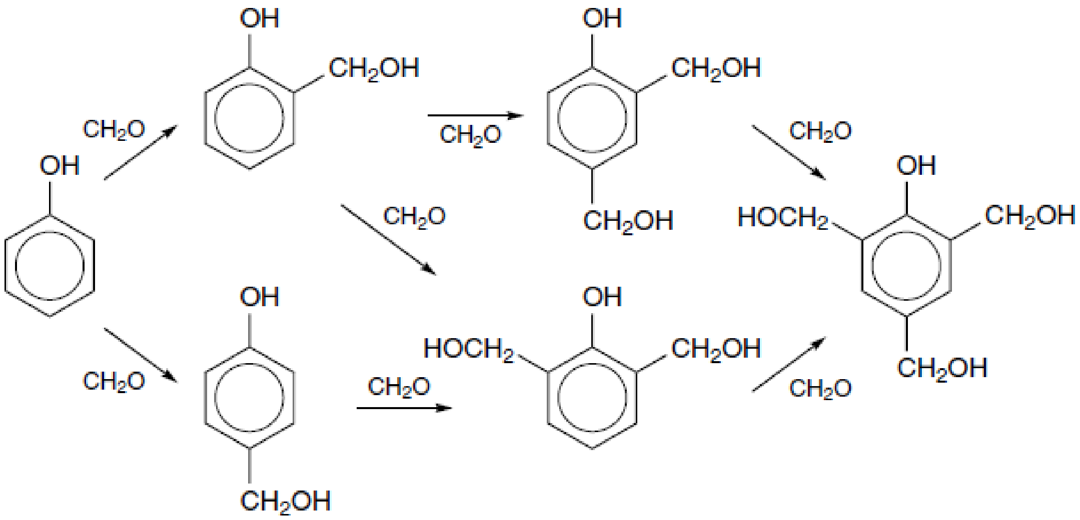

Figure 2.4 : Methylolation reaction pathways for further phenol–formaldehyde reactions under alkaline conditions.

The third and final step of resole manufacture is named as the condensation step or chain extension (Figure 2.5). In this process, hydroxymethyl phenol intermediates combine with each other to form oligomers hence molecular weight increases.

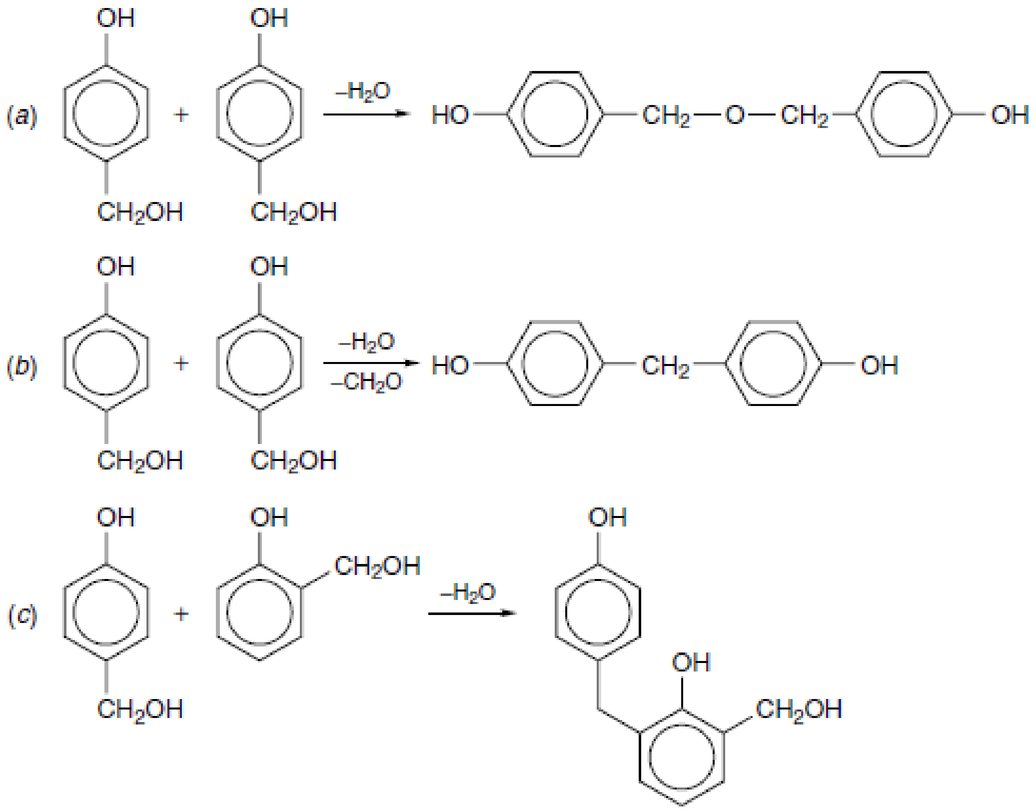

Figure 2.5 : Condensation of hydroxymethyl groups.

There are three general mechanisms through which condensation may take place. Condensation reactions can occur between two hydroxymethyl substituents that remove water to form ether linkages (Figure 2.5.(a)) or remove both water and formaldehyde to form methylene linkages (Figure 2.5.(b)). Furthermore, condensation reactions between hydroxymethyl groups and reactive ortho or para ring positions establish methylene bridges between phenolic rings (Figure 2.5.(c)). Hydroxymethyl condensation reactions under basic conditions strongly favor the formation of para–para and ortho–para methylene linkages. Ether formation is common under neutral or acidic conditions [56-57].

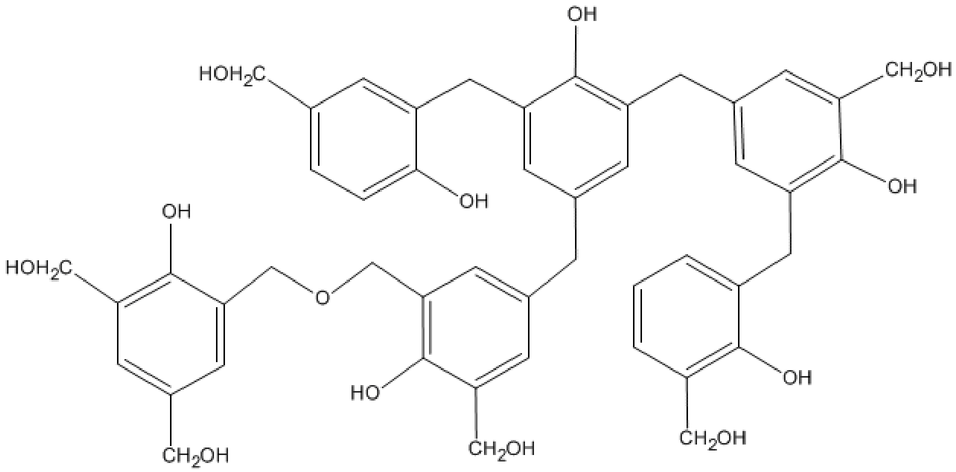

Figure 2.6 : Resol structure.

The activation energy of condensation is higher than methylolation. At temperatures below 70^oC, it is accepted that methylolation occurs. However, this is not to say that condensation does not happen at temperatures below 70^oC. Only, it means that methylolation occurs much faster than condensation at this temperature. Above 70^oC condensation reaction leads to prepolymer and the desired resole resin synthesizes. Table 2.1. shows the properties of methylolation and condensation steps [10,56].

Table 2.1 : Methylolation and condensation steps for resol resin.

Properties	**Methylolation**	**Condensation**
Temperature	<70^oC	>70^oC
ΔH_f	-20 kJ/mol	-99 kJ/mol
pH	8-9	9-11
Water diluability	∞	Low
Viscosity	50-100	~5000

2.4.2 Curing of Resol Resins

One of the most valuable features of the phenolic resins is the ease and rapidity with which they may be converted to well-knit, highly cross-linked products. For resole resins curing process can be defined as the formation of an insoluble and infusible product, is effected by raising the temperature and by the addition of acidic reagents. In Figure 2.7. an outline of synthesis process and curing process were shown.

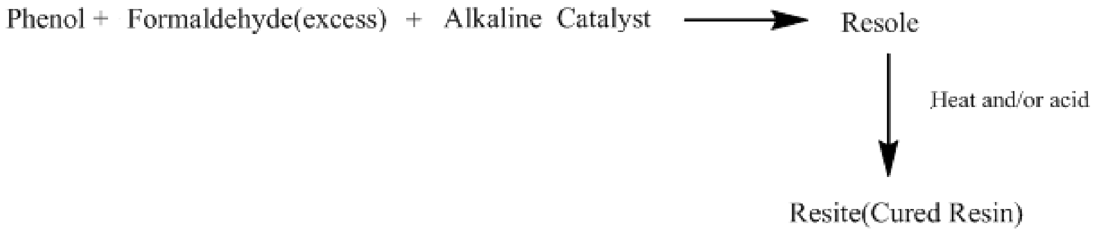

Figure 2.7 : Resol resin processes.

Unlike many polymeric systems where cure results by repetition of a single process, the cure of a phenolic resin is extremely complex, involving as it does a number of competing reactions each of which may be profoundly influenced by the reaction conditions and the structure of phenol used to prepare the resin. A further complicating factor is introduced by the possibility of reaction at either or both the ortho an para positions of the phenol. In view of complexity of the system it is not surprising that knowledge of the curing process fell far behind the commercial development of phenolic resins.

The studies of phenol alcohols have revealed among other things that the nature of the reactions is dependent on temperature. Below about 170^{o}C the condensation reactions take place that has been mentioned before.

At temperatures between 170^{o}C and 250^{o}C, further reactions arise from of dibenzyl ethers and occasionally from a phenol alcohol that has not already reacted at a lower temperature. During this period the number of dibenzyl ether linkages decreases rapidly while the number of methylene bridges usually increases. The reactions are characterized by little or no loss of formaldehyde and frequently involve no loss of water. They are accompanied by a strong brown or reddish brown discoloration of the resin and involve the formation of quinone methides and their polymerization and oxidation-reduction products along with aldehyde and methyl end groups. It is also possible that the quinone methides may result from loss of phenol at the end of resin chain. These reactions lead to extremely complex products.

Resol resins particularly those used as adhesives and casting resins, are frequently employed where cure at low or even room temperature is desirable. This is accomplished by the addition of acids, often sold under the name of ‘hardener’ to the resins. Acids also have been used to promote the cure of baked phenolic surface coatings. The hardeners can be prepared by dissolving acids, such as hydrochloric or phosphoric, in glycerine or glycols.

The phenol combined with formaldehyde under alkaline conditions and the resol obtained then hardened by the addition of acid. Acid hardening occurs best at relatively low pH values. However, the most stable resins are obtained in the pH range 3-5 [58]**.**

2.4.3 Effects of Synthesis Conditions

A large number of studies have assessed PF properties on the basis of reaction conditions [59,60]. lt has long been established that catalyst choice and reagent ratios significantly impact resol characteristics. Likewise, synthesising procedures have been empirically developed to respond to novel end use specifications [60]. The important parameters on PF synthesis/structure/properties relationships are presented below.

2.4.3.1 Catalyst

Catalyst is an important influence on the resol structure and hence on its properties. For instance, preferential ortho substitution increases in the following sequence of catalysts KOH< NaOH< LiOH< $Ba(OH)_2$< $Sr(OH)_2$< $Ca(OH)_2$< Mg(OH) [61]. Ammonia-based catalysts are believed to favour more linear resols [62]. Sodium hydroxide enhances PF solubility in water thus lowering viscosity. Consequently more advanced resols can be manufactured by increasing the sodium hydroxide content while maintaining adequate flow properties. Likewise, reagent dilution can be adjusted to permit more advanced resols with adequate flow properties.[60].

Tertiary amines are good catalysts for the resol synthesis reactions, although their activities are not as high as that for sodium hydroxide. The advantages of the resols obtained in the presence of trialkylamines are longer gelation time, least ash content after incineration and improved hydrolysis resistance. The main drawback for these catalysts is their emission from resins in the setting process. Tetraalkyl ammonium hydroxides can also be used as potential catalysts for resol synthesis [61]. But the catalytic activity is lower than that of sodium hydroxide. Tetraalkyl ammonium hydroxide catalysed resins have similar properties of trialkyl amine catalysed resins with the added advantage of better binding ability. Ammonia and amine catalysed resols have limited miscibility with water and these are generally soluble in alcohols and oils. Thermal degradation, flammability and mechanical performance of resol resins are strongly dependent on the nature of the catalyst used in their synthesis [63].

Usually alkaline NaOH is used as catalyst in an amount up to one mole per mole phenol (molar ratio NaOH/P), which corresponds to a portion of alkali in the liquid resin of approximately 10 mass%. The pH of a phenolic resin is in the range 10-13. The biggest part of the alkali is free NaOH, a smaller part is present as sodium phenate. The alkali is necessary to keep the resin water soluble via the phenate ion formation in order to achieve a degree of condensation as high as possible at a viscosity that still can be used in practice. Additionally, the alkali significantly drops the viscosity of the reaction mix. Hence the higher the alkali content, the higher the possible degree of condensation of the resin. Therefore the higher hardening reactivity of the resin which results the shorter the necessary curing time.

Higher alkali content, however, also has some important disadvantages. The equilibrium moisture content in humid climates increases with the alkali content as well as some hygroscopic (longitudinal stability, thickness swelling, water absorption) and mechanical properties (creep behavior) become worse [40].

2.4.3.2 Reagent ratio

PF resol properties are largely governed by the initial F:P molar ratios [64-69]. Generally, high F:P ratios produce highly branched resins whereas low F:P ratios favour more linear structures. So et al. utilized Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and NMR to obtain detailed information on PF characteristics as a function of F:P molar ratios. As expected, higher F:P ratios were found to enhance hydroxymethylation and increase the degree of polymerization [69]. As the F:P molar ratio increased, the molecular weight and activation energy increased while the gel time, peak temperature, resin pH, and nonvolatile solids content decreased [70]. More surprisingly, a synergy between F:P ratio and cure temperature on PF chemical structure was reported. Specifically, higher cure temperatures were required to convert methylene ether to methylene bridges when high F:P ratios were utilized [69]. While So et al. reported no F:P ratio influence on the resol isomeric structure, another study suggests direct correlation between ortho substituted proportions and F:P molar ratio [68].

Holopainen and coworkers detected greater proportions of o-substitution and p~p' methylene bridges with increasing F:P molar ratio. The authors further confirmed greater degrees of polymerization with greater F:P molar ratios, whereas polydispersity exhibited the opposite trend. The study also assessed F:P ratio influence on resol cure properties with differential scanning calorimetry (DSC). It was found that hydroxymethylation and condensation reactions lead to more reaction steps with increasing F:P molar ratios. These studies reveal that the F:P ratio is a key factor to tailor PF morphology, molecular weight and curing properties [55].

2.4.3.3 Phenols and aldehydes.

Simple phenol is most commonly used for the synthesis of PF resins. Other phenols are used only for the synthesis of specialty applications. Alkyl phenols (o-cresol, p-cresol and m-cresol) are used for the production of coating resins because of their good compatibility with natural oils and increased flexibility or as cross-linking agents in the rubber industry [38].

Resorcinol, a dihydric phenol (1,3-dihydroxybenzene), is a very interesting material for the production of PF resin. However, the relatively high price limits its application to where high performance is required. The reaction rate with formaldehyde is considerably higher compared to that of phenol [71]. This is of great technical importance for the preparation of cold setting adhesives [72].

Formaldehyde is the almost exclusively used carbonyl component for the synthesis of technically relevant phenolic resins [73]. Special resins can also be produced with other aldehydes, for example acetaldehyde, but have not achieved technical importance. Ketones are very seldom used instead of aldehydes [38].

2.4.3.4 Additives

In the production of industrial PF resins a variety of additives are utilized to modify the storage, application and cure properties of resols. Methanol is commonly added at the onset of the synthesis in order to control the polymerization exotherm. The addition of urea at the end of resol synthesis is also a common practice of PF manufacturers [60]. Urea not only reduces the resin cost but also plays the role of free formaldehyde scavenger. Urea is also useful for lowering the preparation viscosity thereby allowing for more advanced resols which require less cure to achieve their final properties. Other additives include plasticizers, antifoams, starches and tackifiers [60]. Aromatic amines like aniline, ortho-, para- and meta-phenylenediamine, aliphatic diamides and thioamides are also used to synthesize mixed copolymer resins exhibiting superior properties over conventional phenolic resins [74-75].

The properties of phenolic resins can be enhanced by the use of additives; the type of additives used depends on the application(s) for which the material is formulated. The additives typically used with phenolic resins are given below [40]:

- Wood flour is the cheapest of the fillers has high volume usage and provides low heat conductivity, good tensile strenght and poor impact strength.
- Clays enhance heat and chemical resistance, dimensional stability and viscosity control.
- Silica (SiO_2) is used for abrasive, electrical, and heat insulation properties, viscosity enhancement, shrinkage and crack reduction.
- Cellulose is typically used for good impact strength.
- Synthetic fibers (e.g. orlon, nylon, teflon) provide improved impact and tensile strength and vibration dampening.
- Graphite fiber is produced from the pyrolysis of stretched polyacrylonitrile or rayon and it has more than 99% carbon content. Graphite fiber improves strenght frictional properties (lubrication).
- Glass fiber has the composition of 55% silica, 20% Ca-Mg oxides, 14% alumina, 10% borates and 1% Na-K oxides. Glass fiber supports impact strength, heat and electrical insulation properties.

- Talc is a mineral filler that is a form of hydrated magnesium silicate and it improves stiffness, creep resistance, and heat resistance.
- Polyaramid fibers Kevlar and Nomex are the most popular ones commercialized by Du Pont. Kevlar is an organic reinforcing fiber with high tensile strenght. Nomex is valued mainly for its heat and electrical properties.

2.4.4 Production of Resol Resins

In the manufacture of resols a molar excess of formaldehyde (1.5-2.0: 1) is reacted with the phenol in alkaline conditions. In these conditions the formation of the phenol alcohols is quite rapid and the condensation to a resol may take less than an hour [41,76]. A schematic of a reactor vessel used for the typical bulk polymerization process of phenol-formaldehyde resins is shown in Figure 2.8. The steam jacket provides the temperature condition needed for the polycondensation reaction of phenol and formalin. The condenser facilitates the condensation and removal of water vapor resulting from the phenol/formalin reaction. The removal of water from the system enhances the phenol/formalin reaction and causes formation of more phenol-formaldehyde resin. If the water was not removed, the formation of phenol-formaldehyde resin would be suppressed [40].

The resin kettle may be constructed from copper, nickel or stainless steel. The reaction mixture is heated and allowed to reflux, under atmospheric pressure at about 100°C. At this stage valve A is open and valve B is closed. Because the reaction is strongly exothermic initially it may be necessary to use cooling water in the jacket at this stage. When the resin reaches the requisite degree of condensation as indicated by refractive index measurements, the valves are changed over (i.e. valve A is closed and valve B is opened) and water present is distilled off. [41]. The product at this point is an intermediate resole phenol-formaldehyde resin (B-staging). If a solid product is desired, the intermediate is dried by healing under a vacuum for 3 to 4 hours to prevent heat hardening. Resole phenol-formaldehyde resin is a water soluble methylol (-CH_2OH) bearing thermoplastic. The curing process to the final thermoset material can be initiated by just heating the resole in a mold above its gel point. The resole resins formed have reactive methylol and hydroxyl groups. When heated, resoles form larger molecules with methylene cross-links without the use or addition of a curing agent. The phenol-formaldehyde resin resinification reaction is a typical polycondensation reaction since water is given off as a by-product. Resole phenolic resins have a short shelf life: less than 1 year (less than 60 days in most cases). They are referred to as one-step phenolics because they do not require curing agents, only heat. Casting resins, bonding resins, and resins for laminating paper and wood are made in this way [40,59,77].

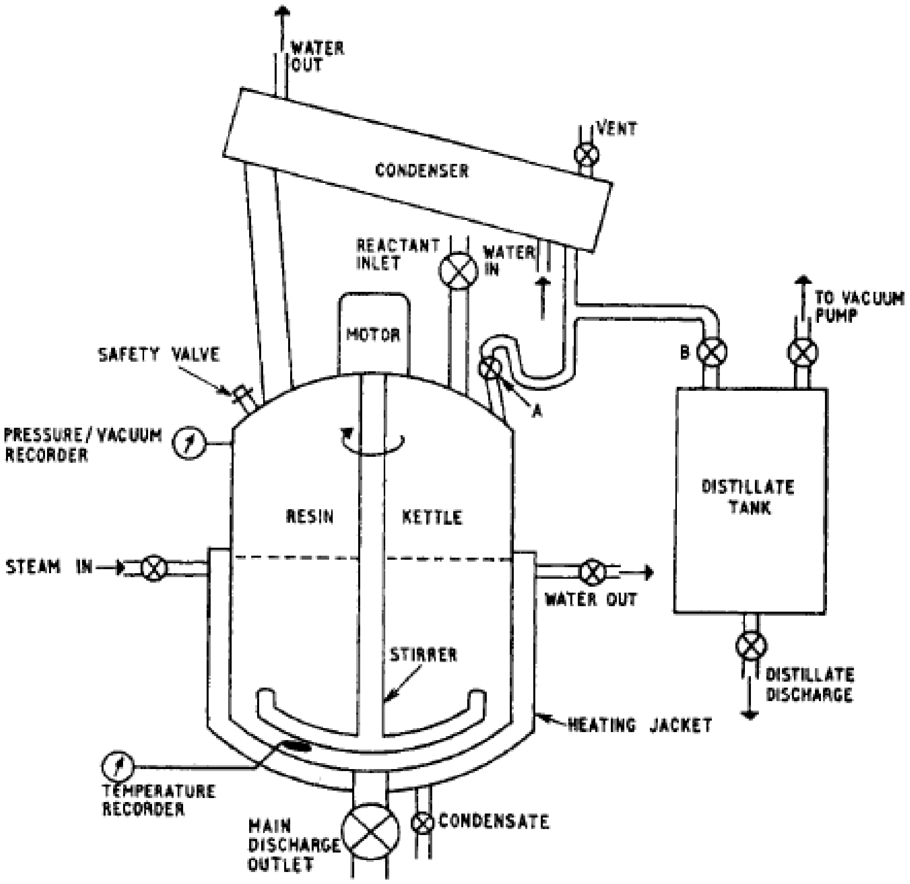

Figure 2.8 : Diagrammatic representation of resin kettle and associated equipment used for the preparation of phenolic resin.

2.5 Composites and Nanocomposites

Composite materials are engineered or naturally occurring materials made from two or more constituent materials with significantly different physical or chemical properties which remain separate and distinct within the finished structure [78]. Most composites have strong, stiff fibres in a matrix which is weaker and less stiff. The objective is usually to make a component which is strong and stiff, often with a low density [79,80].

Natural composite materials in the world, wood is a good example, combination of cellulose fiber and lignin. The cellulose fiber provides strength and the lignin is the "glue" that bonds and stabilizes the fiber. The another example is bamboo**,** a very efficient wood composite structure. The components are cellulose and lignin, as in all other wood, however bamboo is hollow. This results in a very light yet stiff structure [81].

Figure 2.9 : Wood and bamboo.

The polymer composites are any of the combinations or compositions that comprise two or more materials as separate phases, at least one of which is a polymer. By combining a polymer with another material, such as glass, carbon, or another polymer, it is often possible to obtain unique combinations or levels of properties. Typical examples of synthetic polymeric composites include glass-, carbon-, or polymer-fiber-reinforced, thermoplastic or thermosetting resins, carbon-reinforced rubber, polymer blends, silica- or mica-reinforced resins, and polymer-bonded or -impregnated concrete or wood. It is also often useful to consider as composites such materials as coatings (pigment-binder combinations) and crystalline polymers (crystallites in a polymer matrix). Typical naturally occurring composites include wood (cellulosic fibers bonded with lignin) and bone (minerals bonded with collagen). On the other hand, polymeric compositions compounded with a plasticizer or very low proportions of pigments or processing aids are not ordinarily considered as composites [12].

Nanocomposites are a new class of composites, that are particle-filled polymers for which at least one dimension of the dispersed particles is in the nanometer range [82]. It is now accepted to name a heterogeneous material a ‘nanocomposite’ when at least one of the component domains has a dimension ranging from some angstroms to several nanometres [83].

One can distinguish three types of nanocomposites, depending on how many dimensions of the dispersed particles are in the nanometer range. When the three dimensions are in the order of nanometers, we are dealing with isodimensional nanoparticles, such as spherical silica nanoparticles. When two dimensions are in the nanometer scale and the third is larger, forming an elongated structure, we speak about nanotubes or whiskers as, for example, carbon nanotubes. The third type of nanocomposites is characterized by only one dimension in the nanometer range such as nanoclays [81,82]. The structures of these materials are given in Figure 2.10. [81].

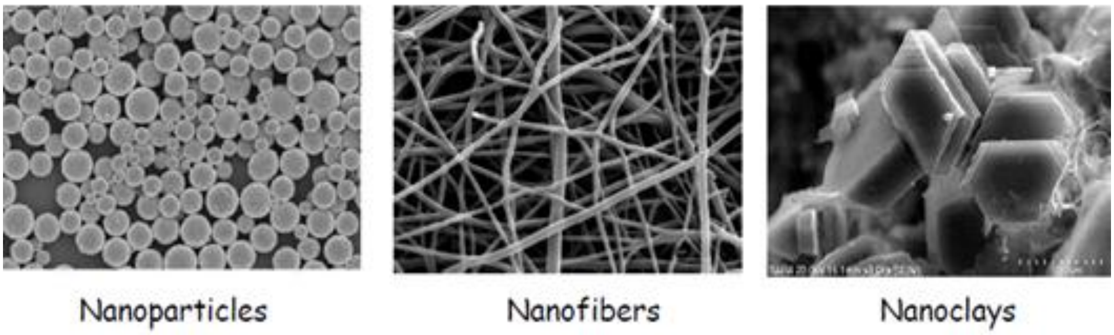

Figure 2.10 : Nanoparticles, nanofibers and nanoclays.

The another type of classification micro or nano composites depicted in Figure 2.10 are idealised cases, and intermediate situations are common.

i. When the polymer is unable to intercalate between the silicate sheets, a phase separated composite (Figure 2.11(a)) is obtained, whose properties stay in the same range as traditional microcomposites. Microcomposites are dispersions of fine, micro-sized clay mineral particles in the polymer matrix. This was, until recently, the traditional way of reinforcing polymers.

ii. Intercalated structure (Figure 2.11(b)) in which a single (and sometimes more than one) extended polymer chain is intercalated between the silicate layers resulting in a well ordered multilayer morphology built up with alternating polymeric and inorganic layersIn this case, the stacking of the layers is maintained, with ordering along the c-axis. Since the general term ‘delamination’ is used to designate the separation between the planar faces of two adjacent layers, in this case beginning of delamination occurs.

iii. Exfoliated nanocomposites are formed by the complete separation of the individual layers of the clay mineral, resulting in a disordered dispersion of the individual clay mineral layers in the polymer matrix. The layers become completely independent from one another, and an exfoliated or delaminated structure is obtained (Figure 2.11(c)) [82,84,85].

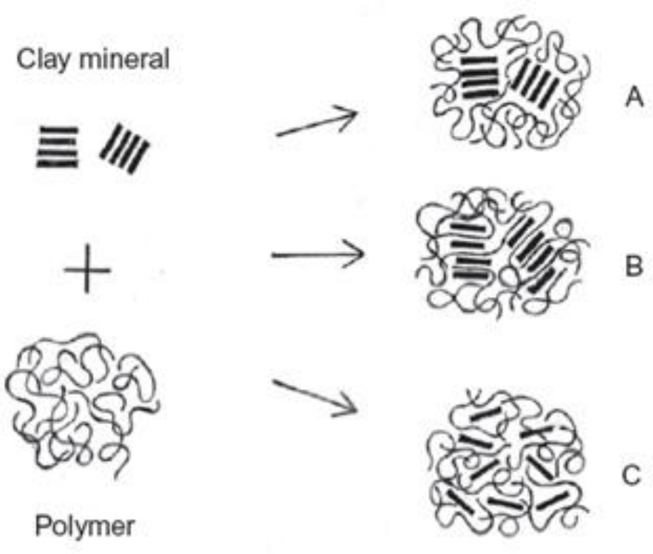

Figure 2.11 : Different types of composite materials: A. convectional composite or microcomposite, B. intercalated nanocomposite, C. exfoliated nanocomposite

Clay minerals have recently been adapted to the field of organic-inorganic nanocomposites because of their small particle size and intercalation properties, especially in the application of reinforcement materials with polymers [86-88]. Recently, special attention is being paid to the application of clay minerals in the formulation of clay–polymer nanocomposites [89-90].

What makes these materials interesting is that their properties can be significantly different from the properties of the individual components, resulting in some cases in dramatic synergistic properties [91].

In *in situ polymerization method* this method, the layered silicate is swollen within the liquid monomer or a monomer solution so the polymer formation can occur between the intercalated sheets. Polymerization can be initiated either by heat or radiation, by the diffusion of a suitable initiator, or by an organic initiator or catalyst fixed through cation exchange inside the interlayer before the swelling step [92].

At present, clay polymer nanocomposites are still under development with very little commercialization. Nevertheless, their wide-scale introduction in the market is highly awaited as they fulfil several market needs, the most relevant of which are reinforcing the elastic properties of polymeric matrices, fire retardancy and enhanced resistance to thermal oxidation. These materials are expected to be marketed at a reasonable cost [93].

2.6 Sepiolite

The name ‘sepiolite’ is derived from Greek sepion (squid, cuttlefish) and lithos (stone). It has found firstly in the locality of Baldissero Canavese, Piemont, Italy. ‘Sepiolite’ and ‘meerschaum’ were long considered synonymous. Werner was apparently the first to use the name meerschaum (German, meaning sea froth) in allusion to the lightness and colour of the material. The term ‘sepiolite’ was first used in 1847 by Ernst Friedrich Glocker (1793–1858) because the mineral was light and porous like the bone of cuttlefish [94-96]. Sepiolite is one of the least common clay around the world. The deposits are located in United States, Spain, Turkey, and Somalia. In Turkey, sepiolite clay occurances are seen in Western and Central Anatolian Regions, especially Eskişehir, Konya, Denizli, Ankara and Sivas [97].

Sepiolite is a hydrated magnesium silicate which has fibrous morphology resulting as an ideal unit formula: $Si_{12}O_{30}Mg_8(OH)_4 .(H_2O)_4 . 8H_2O$, shown in Figure 2.12. Sepiolite structure is established by a magnesium octahedral sheet in between two layers of silica tetrahedrons. This continues with an inversion of the apical ends every six units. Therefore, sepiolite has discontinuous octahedral sheet that provides rectangular tunnel, along the fibre axis. In cross section, these nanostructured tunnels have approximately 3.5 x 10.6 $A^{\circ 2}$ area. Also, these tunnels completely filled by zeolitic water $[H_2O]_{zeol}$ under ambient conditions. The Mg^{2+} cations placed at the edges of the octahedral sheets complete their coordination, bound with two molecules of structural water $[H_2O]_{coord}$.[98-99].

Sepiolite exhibits nano-needle morphology with particle size over a wide range, however the dimensions of the fibres are generally 100–5000 nm length, 10–30 nm width, and 5–10 nm thickness. Furthermore, sepiolite has high surface area at the range of 200-300 m^2/g due to the presence of blocks and tunnels along the needle direction [100-101].

In sepiolite structure blocks are linked together along their longitudinal edges by Si-O-Si bonds only in one direction**.** It is assumed that needle like clays can be more easily dispersed in polymeric matrices because it has lower specific surface area compared with platelet-like clays with the same aspect ratio. The relatively small contact surface thus the reduced tendencies to agglomerate, leads to better mechanical reinforcement of needle-like clays [16,17].

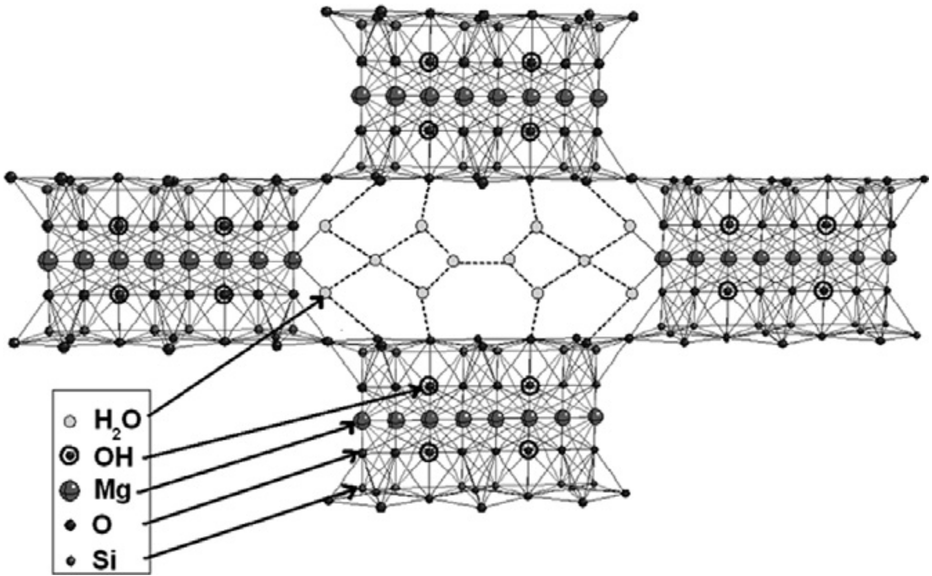

Figure 2.12 : Structure of sepiolite.

The discontinuity of the silica sheets provides increasing of the silanol groups (Si-OH) at external surface of the sepiolite particles which improves the interfacial interaction of sepiolite with organic solvent and polymers. As the presence of the tunnels and Si-OH, sepiolite can dispersed well in polymer matrix and thereby improve the mechanical properties, thermal stability, flame retardancy and barrier properties of polymers [17,23,102].

Additionally, in some cases, polymers not only interact with the external surface of sepiolite, but also penetrate into the structural tunnels of the mineral [103-105]. Since these cavities are organized as nano-structured pores, the resulting materials are considered as clay polymer nanocomposites. There are other cavities of nanometric dimensions along the fibre axis, mainly attributed to defects formed during the particle growth, that are accessible to organic species [92,106].

Today, usage of sepiolite can be applied for polymer functionalization and/or modification[13-23]. Sepiolite has been used for the preparation of nanocomposites using different polymers such as epoxy [13], polypropylene [14-16], polyimide [17], polyethylene [18], ethylene vinyl acetate [19], chitosan [20], polyvinylalcohol [21], polyhydroxyethyl acrylate [22] and polyamid [23]. However, sepiolite effects of resol resins has not been studied before. The reason could be the three-dimensional structure of the phenolics, even before cure.

2.7 Alendronic Acid

Bisphosphonates (BP)s are synthetic compounds ,which includes P-C-P bridge. The versatility of bisphosphonates is ascertained as they found applications such as osteoporosis, tumor-induced hypercalcemia, Paget's disease, parasitic diseases, hypercholesterolemia and atherosclerosis [24,107-110].

(1-Hydroxy-4-aminobutylidene)-1,1-bisphosphonic acid, an amino bisphosphonate commercially known as alendronic acid and sold as Fosamax by Merck, is a bisphosphonate drug that is used to treat several bone diseases (Figure 2.13) [111]. Some of the properties of alendronic acid is given in Table 2.2 [112].

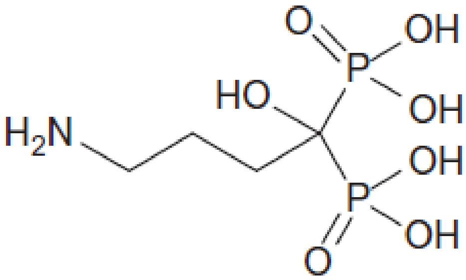

Figure 2.13 : Structure of alendronic acid.

Phosphorus-containing compounds cover a wide range of inorganic and organic compounds and also used as flame retardant materials. They have a broad range of applications, and a good fire safety performance. One of the most important phosphorus-containing flame retardant is phosphonates. Phosphorus-containing flame retardants are widely used in standard and engineering plastics, polyurethane foams, phenolic resins, polyamides, coatings, and textiles [113].

In literature, generally alendronic acid was used for development of drugs, however a few of studies has been investigated thermal stability of this compound. Ochiuz et al. investigated thermal stability of sodium alendronate (which is a monosodium salt of alendronic acid [112]) in a mixture with cross-linked acrylic acid polymers and chitosan [114]. Önen et al. prepared ketonic resins that include alendronic acid, and used for synthesis of fire retardant polyurethane [115].

Table 2.2 : Properties of alendronic acid.

Properties	**Values**
Molecular Formula	$C_4H_{13}NO_7P_2$
Molecular Weight (g)	249.10
Carbon %	19.29
Hydrogen %	5.26
Nitrogen %	5.62
Oxygen %	44.96
Phosphorus %	24.87

2.8 Glass Wool

The basic raw materials for glasswool products are a variety of natural minerals and manufactured chemicals. The major ingredients are silica sand, limestone, and soda ash. Other ingredients may include calcined alumina, borax, feldspar, syenite, and magnesite among others. Silica sand is used as the glass former, and soda ash and limestone help primarily to lower the melting temperature. Other ingredients are used to improve certain properties, such as borax for chemical resistance. Waste glass, also called cullet, is also used as a raw material [10,12].

Though commercial use of glass fiber is relatively recent, artisans created glass strands for decorating goblets and vases during the Renaissance. A French physicist, Rene-Antoine Ferchault de Reaumur, produced textiles decorated with fine glass strands in 1713. Glass wool, a fluffy mass of discontinuous fiber in random lengths, was first produced in Europe in 1900, using a process that involved drawing fibers from rods horizontally to a revolving drum [116].

The raw materials are blended in a batch mixer, from which the blend is transported to the smelter. Here, the temperature is adjusted to around 1100 ^{o}C – just sufficient to melt the blend into hot lava that is homogenized by stirring. Sand is introduced from the top of the smelter onto the surface of the lava to create a protective crust. This prevents excessive cooling. From the smelter, the molten glass is poured into a spinner where the fiberizing takes place. The spinner is a rapidly rotating flywheel with more than 2.000 small holes from which the fluid is constrained. Due to centrifugal force, the molten material is spun out of the flywheel.

Since the spinner aperture diameters are in micrometers, only fine fibers are produced. Outside the flywheel, airflow is applied from above to direct the fibers downward to cool them. As the fibers descend, the resol binder is applied by spraying. The binder joins the non-woven fibers together at their junction points.

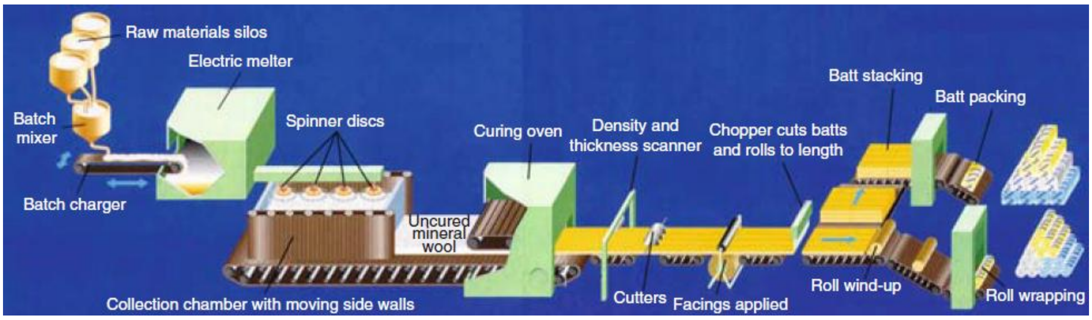

Figure 2.14 : The manufacturing process of glass wool.

The amount of binder or solid adhesive is adjusted to achieve the required mineral wool criteria. For example, the amount of binder provides the mineral wool with its characteristic mechanical properties such as compressive, tensile, and bending strengths. Therefore, flexible glass wool blankets need less binder than rigid slabs. The binder-sprayed glass fibers are white in color, and at this stage, form soft, easily ruptured wool. The wool is then moved along the conveyor belt into the collecting chamber, where most of the water is evaporated at around 80 ^{o}C. This pre-dried wool then moves into a curing oven equipped with specially arranged conveyor belts. This procedure compresses the soft mineral wool: the distance between the belts controls the mineral wool thickness. In the curing oven (180–250 ^{o}C), the wool is completely dried, the binder is cured, and the glass wool gets its distinctive yellow color. The mineral wool exiting the curing oven is almost a complete product with its desired thickness and mechanical properties. As it moves further along the conveyor belt it cools, before being cut to the required size with length and width trimmers [10]. About 80% of phenolic resin insulation is glass wool-based [40].

3. EXPERIMENTAL PART

3.1 Materials

Phenol (P, C_6H_6O, Carlo Erba Reagents), Formaldehyde (F, CH_2O, 37% Solution, MERCK), Sepiolite (SEP, $Si_{12}O_{30}Mg_8(OH)_4 .(H_2O)_4 . 8H_2O$, Pangel S9, Tolsa Group, Spain) Alendronic Acid (AA, $C_4H_{13}NO_7P_2$, Chemos GmbH) Sodium Hydroxide (NaOH, Carlo Erba Reagents) were purchased for the experimental analysis. All chemicals were used without further purification.

3.2 Synthesis of Phenol-Formaldehyde Resol Resin

The desired P/F molar ratio was 1/2. Therefore, 18.8 g (0.2 mol) of phenol and 33 mL (12 g , 0.4 mol) of formaldehyde solution were added into a three-necked flask. To prevent the evaporation of mixture reflux condenser was set to the system. Experimental setup of the polymerization was showed in Figure 3.1. The mixture was stirred with mechanical stirrer for 4 hours. Throughout the reaction, pH was adjusted to 10 using the 20 wt% NaOH solution and the temperature of oil bath was set to 85^{o}C. After 4 hours, the yellowish liquid resin was transferred in a rotary evaporator under vacuum at 85^{o}C for 15 minutes to remove water which occured during the reaction. At the end of rotary evaporation process, like a gel very viscous resin was obtained. For drying, the resin was put in an aluminum utensil under vacuum oven for 2 hours at 100^{o}C hence solid resin was synthesized. Finally, the solid resin was pulverized in a mortar. In Figure 3.2. the resol resin (PFR) before drying and after drying process was showed.

3.3 Synthesis of Sepiolite Modified Resol Resins (PFR-SEP)

PFR-SEPs were synthesized in eight different initial feed sepiolite content by phenol weight (3wt%, 5wt%, 8wt%, 10wt%, 15wt%, 20wt%, 30wt% and 50wt%). At each polymerizations, 0.2 mol (18.8 g) of phenol , 0.4 mol (33 mL) of formaldehyde solution were added into a three-necked flask. To prevent the evaporation of mixture reflux condenser was set to the system. pH was adjusted to 10 using the 20 wt% NaOH solution and the temperature of oil bath was set to 85^{o}C. The mixture was stirred with mechanical stirrer for 4 hours. For 3wt% and 5wt% sepiolite contents, the resins were liquid therefore rotary evaporator used for removing water to obtain viscous resin for 15 minutes at 85^{o}C. The other sepiolite samples were very viscous thus rotary evaporation process was not applied. The viscous resin was dried in an aluminum utensil under vacuum oven at 100^{o}C until the resin solidified. In the mortar, obtained reddish resin product was pulverized.

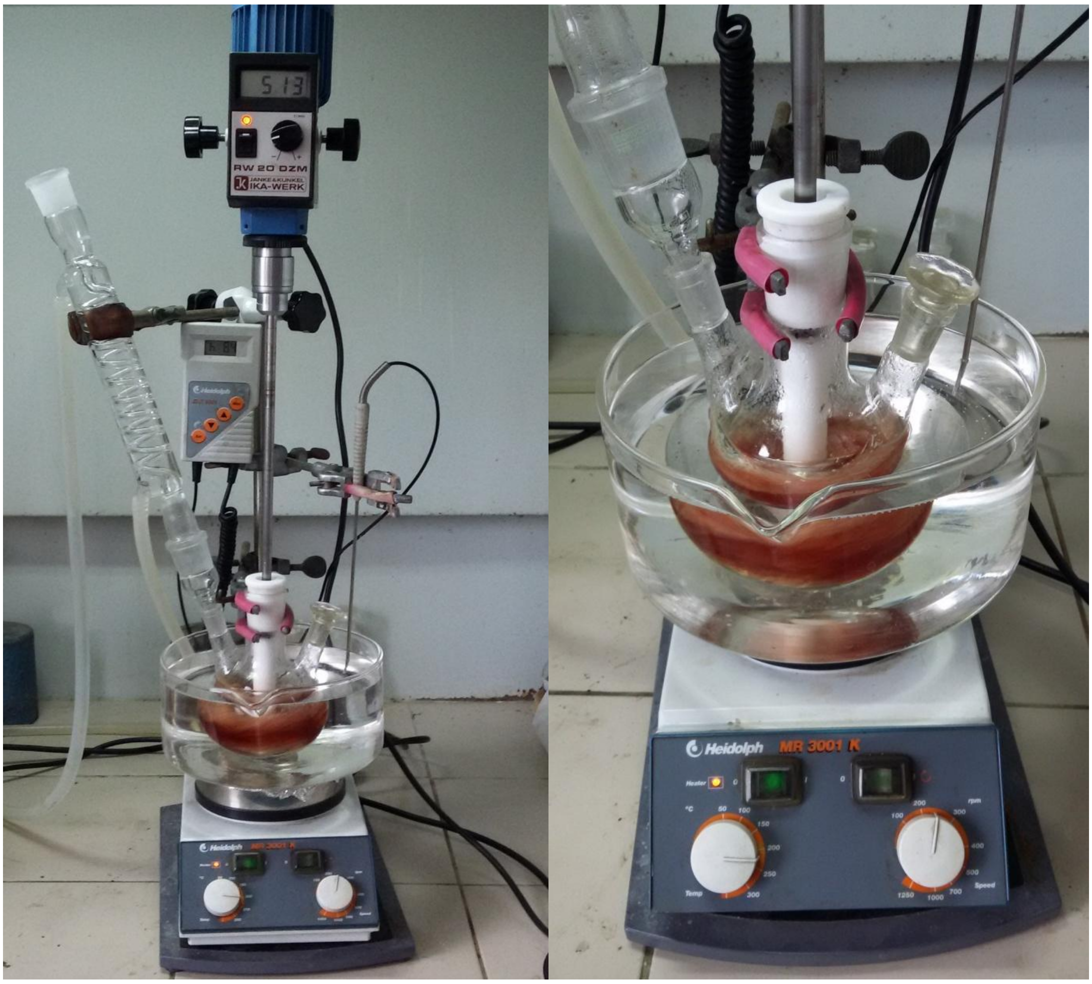

Figure 3.1 : Experimental setup of the polymerization.

3.4 Synthesis of Alendronic Acid Modified Resol Resins (PFR-AA)

Two different alendronic acid weight ratios as 5wt% and 10wt% of resol were synthesized. For the reaction, desired P/F molar ratio was 1/2 thus 0.2 mol (18.8 g) of phenol , 0.4 mol (33 mL) of formaldehyde solution were used. As a catalyst NaOH solution (20wt%) was added to the flask to fix the pH as 10. To prevent the evaporation, reflux condenser was set to the system and oil bath temperature was adjust to 85°C. With mechanical stirrer the reaction mixture was stirred for 4 hours to synthesize liquid resin. After this stage, rotary evaporator was used for removing water from the resin, which was formed during the reaction. Then, the obtained viscous resin was dried in the vacuum oven for 2 hours at 100°C and reddish resin was pulverized in a mortar.

Figure 3.2 : Resol resin (PFR) before drying and after drying process.

Figure 3.3 : Powdered resol nanocomposite resins.

3.5 Synthesis of Alendronic Acid and Sepiolite Modified Resol Resins (PFR-AA-SEP)

PFR-AA-SEP were synthesized by the same way and by the same experiment setup with PFR and PFR-AAs. 18.8 g (0.2 mol) of phenol and 33 mL (12 g , 0.4 mol) of formaldehyde solution and appropriate sepiolite(5wt%) and alendronic acid (5wt%) content by phenol weight were added into three necked flask.

In Figure 3.3 powder forms of resol nanocomposite samples were showed. Contents and drying time in vacuum oven of resin samples were showed in Table 3.1.

Table 3.1 : Contents and drying time of resin samples

Sample Name	**Sepiolite Content (g)**	**Alendronic Acid Content (g)**	**Drying Time (h)**
PFR	0	0	2
PFR-SEP3%	0.56	-	2
PFR-SEP5%	0.94	-	2
PFR-SEP8%	1.50	-	2
PFR-SEP10%	1.88	-	4
PFR-SEP15%	2.82	-	6
PFR-SEP20%	3.76	-	6
PFR-SEP30%	5.64	-	6
PFR-SEP50%	9.40	-	10
PFR-AA5%	-	0.94	2
PFR-AA10%	-	1.88	2
PFR-AA5%-SEP5%	0.94	0.94	3

3.6 Solubility of Solid State PFR, PFR-AA, PFR-SEP, and PFR-AA-SEP Samples

To determine the solvent behaviour of resins, acetone, methanol, tetrahydrofuran (THF), chloroform, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used. For this analysis, one flat spatule powdered resin and 1 mL of the solvent were added in a test tube at 25^{o}C. After 5 minutes, the observed solubility or dissolubility of resin sample was noted. To investigate temperature effect, same experiment was done at 50^{o}C in the water bath.

3.7 Blank Experiment of Phenol Formaldehyde Resol Resin

Blank experiment was done to prove the nanostructure of PFR-SEPs. Into a three necked flask 18.8 g (0.2 mol) of phenol and 33 mL (12 g , 0.4 mol) of formaldehyde solution were added. The mixture was stirred with mechanical stirrer for 4 hours. Throughout the reaction, pH was adjusted to 10 using the 20 wt% NaOH solution and the temperature of oil bath was set to 85^{o}C. After 4 hours, the liquid resin was cooled to room temperature. Then, 3wt% of sepiolite clay was added and mixed with resol resin. After mixing, the precipitation of sepiolite clay was seen in resol resin.

All of the *in situ* modified resol resins did not demonstrate phase separation that verify the nanostructure.

3.8 Characterization of PFR, PFR-AA, PFR-SEP and PFR-AA-SEP Samples

The structure of the specimens were studied using Fourier Transform Infrared (FTIR-ATR) spectroscopy. FTIR analyses of samples were carried out with Nicolet 6700 FTIR-ATR reflectance spectrophotometer using OMNIC as software.

Differential Scanning Calorimeter (DSC) measurements were performed with DSC 7020 Exstar. The cycle was heated from 30°C to 250°C with 10 °C/min heating rate. Thermogravimetric analysis (TGA) was operated under nitrogen atmosphere at a heating rate of 10 ^{o}C/min up 30^{o}C to 700^{o}C temperature TG/DTA 7200 Exstar.

X-ray diffraction patterns were recorded on a Rigaku D/Max-Ultima+/PC XRD instrument. Cu K α radiation with a wavelength of λ=0.15406 nm was applied in the range of 10^{o} to 70^{o}. Interlayer distance (d_{001}) of resins calculated with Bragg equation. ($n \cdot \lambda = 2 \cdot d \cdot \sin\theta$)

In order to investigate the morphology of resin samples, ESEM XL30 ESEM-FEG Philips model scanning electron microscope (SEM) was used and the samples for the SEM measurement were prepared by coating of gold.

3.9 PFR, PFR-AA, PFR-SEP and PFR-AA-SEP Application of Glass Wool Insulation Material

The synthesized resin samples were introduced to glass wool insulation sector. Silica sand, limestone, soda ash and waste glass were mixed in a furnace and the temperature adjusted around 1100^{o}C-1300^{o}C. From the reactor, the molten mixture was poured into a spinner which has more than 2000 small holes in micrometer scale. The fluid mixture were constrained and fibers were manufactured, owing to the centrifugal force of spinner.

After this step, glass wools were sprayed with our liquid sample resins that provide the junction of glass fibers. To cure the liquid resin samples, the glass wool was completely dried in the curing oven at 180-250^{o}C and the glass wool products gained the colour of resin samples. Length and width trimmers were cut the size of the composite glass wool insulation product. The steps of production process were shown in Figure 3.4.

Figure 3.4 : a) The furnace where the raw materials were melted. b) The spinner disc and glass wool. c) Glass wools were sprayed with resol resin samples. d) Curing oven. e) Edge trimmer. f) Composite glass wool insulation product.

4. RESULTS AND DISCUSSION

In this study, sepiolite and alendronic acid were used as filler to improve the thermal, spectroscopic and microscopic properties of *in situ* modified resol resins. The results were evaluated the different sepiolite and alendronic acid ratios. Furthermore, the synergist effect of sepiolite and alendronic acid was investigated. The predicted synthesis mechanisms of sepiolite and alendronic acid modified resol resins were given in Figure 4.1 and Figure 4.2.

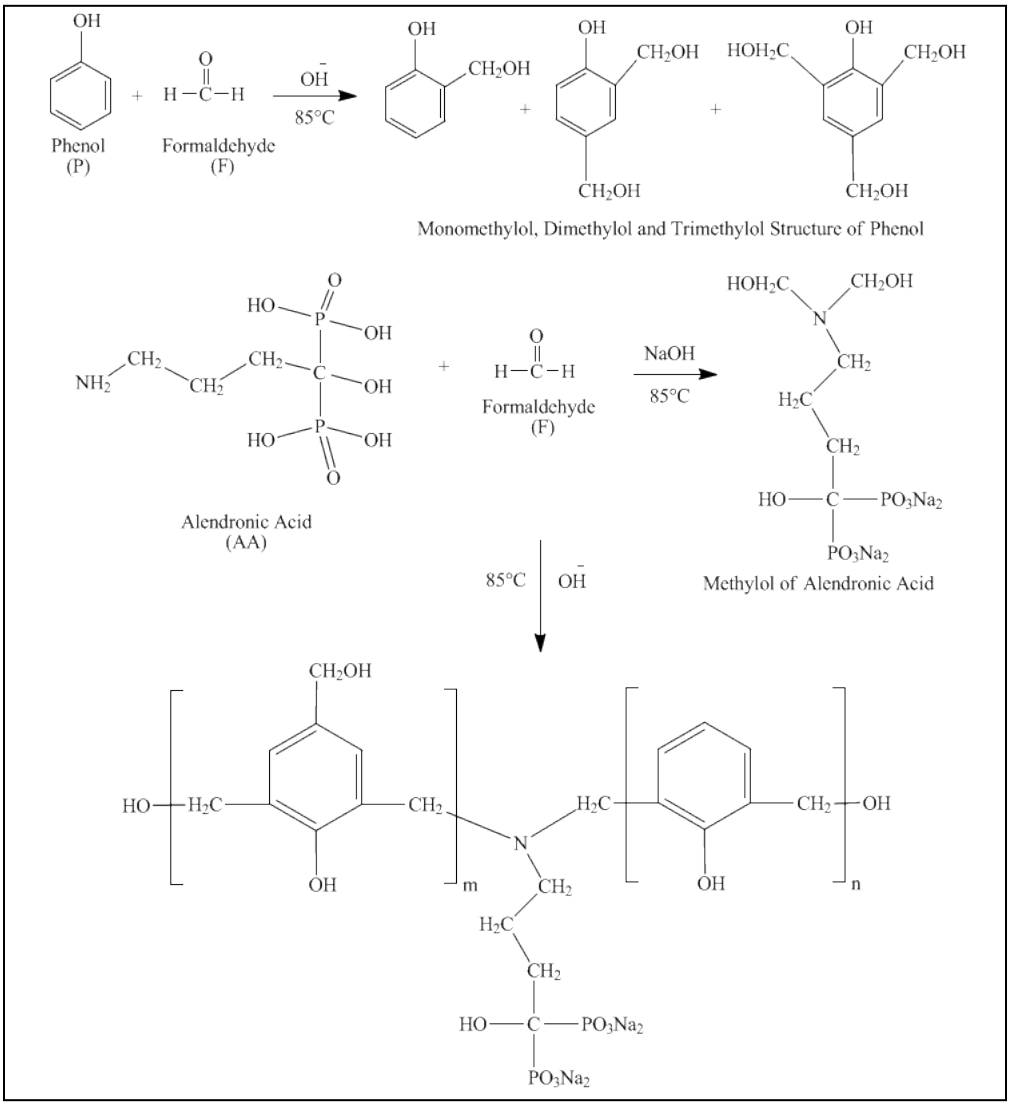

Figure 4.1 : Alendronic acid modified phenol formaldehyde resin (PFR-AA).

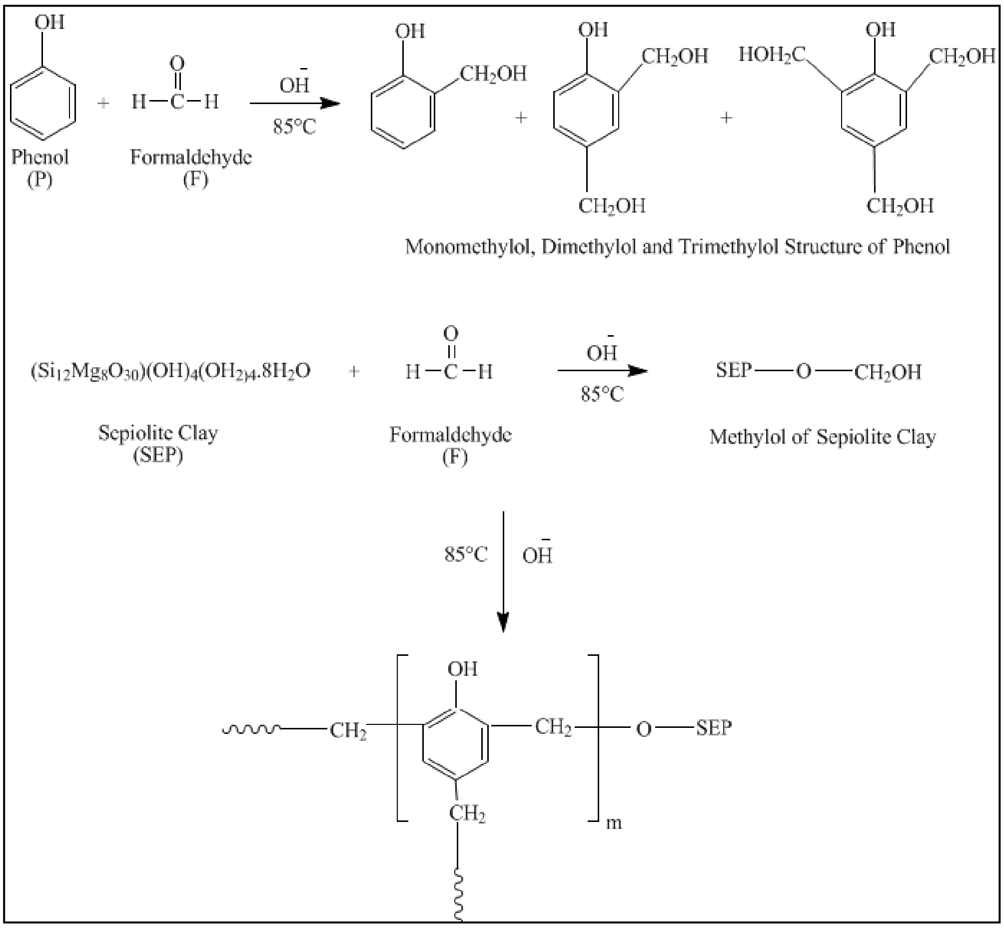

Figure 4.2 : Sepiolite modified phenol formaldehyde resin (PFR-SEP).

Acetone, methanol, tetrahydrofuran (THF), chloroform, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) used as solvents to determine the solubility attitude of nanocomposites. The solubility of samples were given and discussed in Section 4.1. The structures of the specimens were characterized by means of Fourier Transform Infrared (FTIR-ATR). FTIR fingerprints of sample results and characteristic peaks of nanocomposites were explained in Section 4.2. In resol resins curing is an important factor so that, maximum cure temperatures and onset of cure temperatures of samples were determined via DSC in pure nitrogen that mentioned in Section 4.3. In this thesis, thermal decomposition behaviour of the nanocomposite samples were determined with TGA. Degradation was carried out in a static air atmosphere to the maximum temperature of 700°C. The explanations about TGA results were discussed in Section 4.4. X-ray Diffraction (XRD) is a rapid analytical technique primarily used for determining the arrangement of atoms within a crystal, in which a beam of X-rays strikes a crystal and scatters into many different directions. By using this technique, information on structures, phases and interlayer distances are determined. The dispersion of sepiolite in the resol nanocomposites were examined by X-ray Diffraction (XRD) and the results were given in Section 4.5. The Scanning Electron Microscope (SEM) is a type of electron microscope which shows very detailed three dimensional images at much higher magnifications than is possible with a light microscope. SEM creates the magnified images by using electrons which interact with the atoms instead of light waves. The morphologic structure and distribution of PFR-SEPs were illustrated in Section 4.6.

4.1 Solubility in Solvents

The solvent resistance of the resins were tested with six different solvents that are acetone, methanol, tetrahydrofuran(THF), chloroform, dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) were chosen due to their common use in industry and ease to reach. Each tests were carried out at 25°C and 50°C. The results were shown in Table 4.1.Generally, PFRs are unsoluble in solvents with the exception of DMF and DMSO. The resol resins with alendronic acid (PFR-AA5% and PFR-AA10%) were slightly soluble in DMF, whereas the specimens that include same percent of sepiolite were not soluble (PFR-SEP5% and PFR-SEP10%). Similarly, PFR-AA5%-SEP5% was slightly soluble in DMF due to sepiolite presence. In DMSO, not only PFR-AAs but also most of PFR-SEPs and PFR-AA-SEP were soluble. However, increasing of sepiolite contents of PFR-SEPs reduce the solubility. As PFR-SEP15% and PFR-SEP 20% were slightly soluble, PFR-SEP30% and PFR-SEP50% were insoluble in DMSO. Temperature that is an important factor of solubility was investigated at 25°C and 50°C but in our experiments there was not found any evidence to improve solubility.

4.2 FTIR-ATR Spectrofotometric Analysis

FTIR spectra of resin samples were recorded in the transmittance mode. The FTIR spectrum of PFR resin was shown in Figure 4.3 and the characteristic peaks of PFR sample and literature values [10] were collected in Table 4.2. These signals were helpful in identifying the structure of PFR specimen.

Table 4.1: Solubility of solid state PFR, PFR-SEP, PFR-AA, and PFR-AA-SEP samples.

Resin Name	**Acetone**		**Methanol**		**THF**		**Chloroform**		**DMF**		**DMSO**	
	25°C	**50°C**	**25°C**	**50°C**	**25°C**	**50°C**	**25°C**	**50°C**	**25°C**	**50°C**	**25°C**	**50°C**
PFR	-	-	-	-	-	-	-	-	~	~	+	+
PFR-SEP3%	-	-	-	-	-	-	-	-	~	~	+	+
PFR-SEP5%	-	-	-	-	-	-	-	-	~	~	+	+
PFR-SEP8%	-	-	-	-	-	-	-	-	~	~	+	+
PFR-SEP10%	-	-	-	-	-	-	-	-	~	~	+	+
PFR-SEP15%	-	-	-	-	-	-	-	-	-	-	~	~
PFR-SEP20%	-	-	-	-	-	-	-	-	-	-	~	~
PFR-SEP30%	-	-	-	-	-	-	-	-	-	-	-	-
PFR-SEP50%	-	-	-	-	-	-	-	-	-	-	-	-
PFR-AA5%	-	-	-	-	-	-	-	-	+	+	+	+
PFR-AA10%	-	-	-	-	-	-	-	-	+	+	+	+
PFR-AA5%-SEP5%	-	-	-	-	-	-	-	-	+	+	+	+

+ : soluble, ~ : slightly soluble, - : insoluble

Table 4.2 : Functional groups and observed wavenumbers for resol type phenol-formaldehyde resin (PFR) and their literature values.

	PFR	
Literature data of wavenumber cm^{-1}	**Observed wavenumber cm^{-1}**	**Chemical functional group**
3600-3100	3284	-OH stretch of phenol
2980-2820	2880	Aliphatic C-H stretch
1610	1610	C=C stretch for phenolic ring
1480	1479	CH_2 bending
1370	1360	OH in plane deformation
1235	1208	Phenolic C-O stretch
1160	1149	Aromatic C-H in plane def.
1020	1014	Hydroxymethyl C-O stretch
880	883	o,p substituted phenol and o,o^1,p substituted phenol
820	823	Phenol with 2 adjacent free H atoms (p-substituted)
760	753	Phenol with 4 adjacent free H atoms (o-substituted)

According to previous study [10], it was observed that the most important peaks occurred at 3294 cm^{-1}, 1607 cm^{-1}, 1480 cm^{-1}, 1234 cm^{-1}, 1019 cm^{-1}, 824 cm^{-1}, 756 cm^{-1}. These peaks were attributed to –OH groups, C=C stretch of phenolic ring, CH_2 bending, phenolic C-O stretch, hydroxymethyl C-O stretch p-substitued phenol and o-substituted phenol respectively.

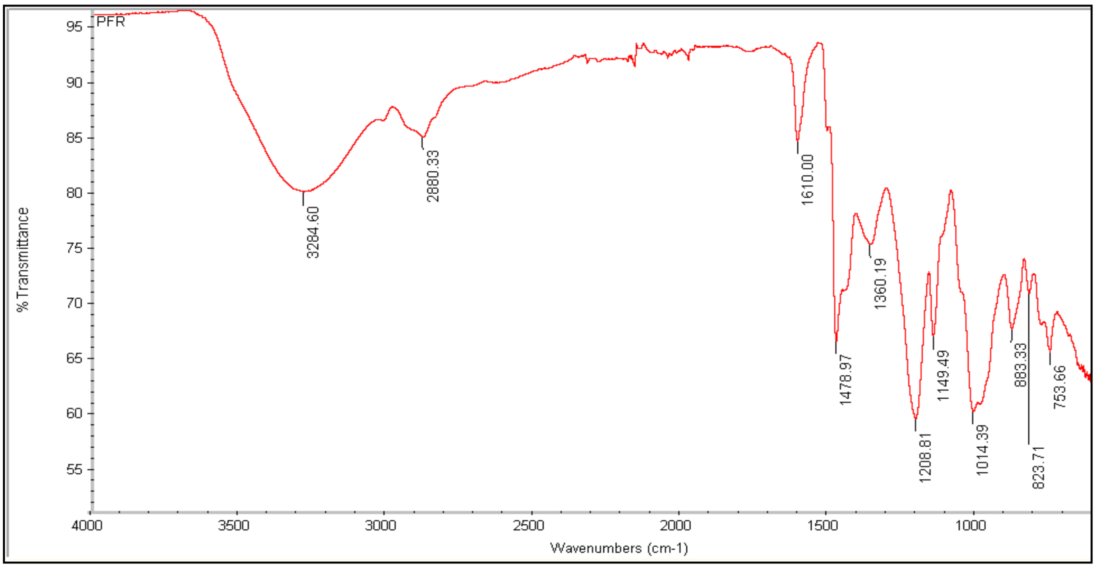

Figure 4.3 : FTIR spectrum of PFR.

In this study, the characteristic peaks of PFR were observed at 3284cm^{-1}, 2880 cm^{-1}, 1610 cm^{-1} and 1479 cm^{-1} corresponded to the –OH groups, aliphatic C-H stretch, C=C aromatic ring vibrations and CH_2 bending. Also, the absorbances at 1360 cm^{-1}, 1208 cm^{-1}, 1149 cm^{-1}, 1014 cm^{-1} and 883 cm^{-1} were belonged to the OH plane deformation, phenolic C-O stretch, aromatic C-H, hydroxymethyl C-O stretch, and o,p - o,o^{1},p substituted phenol respevtively, while the peaks at 823 cm^{-1} and 753 cm^{-1}, and 607 cm^{-1} corresponded to p-substituted and o-substituted phenol (Figure 4.3).To synthesize PFR-AA, PFR-SEP and PFR-AA-SEP modified resins, alendronic acid and sepiolite were added to the reaction mixture. Therefore, for comparison the FTIR spectrum of neat sepiolite and alendronic acid spectrums were given in Figure 4.4 and Figure 4.5.

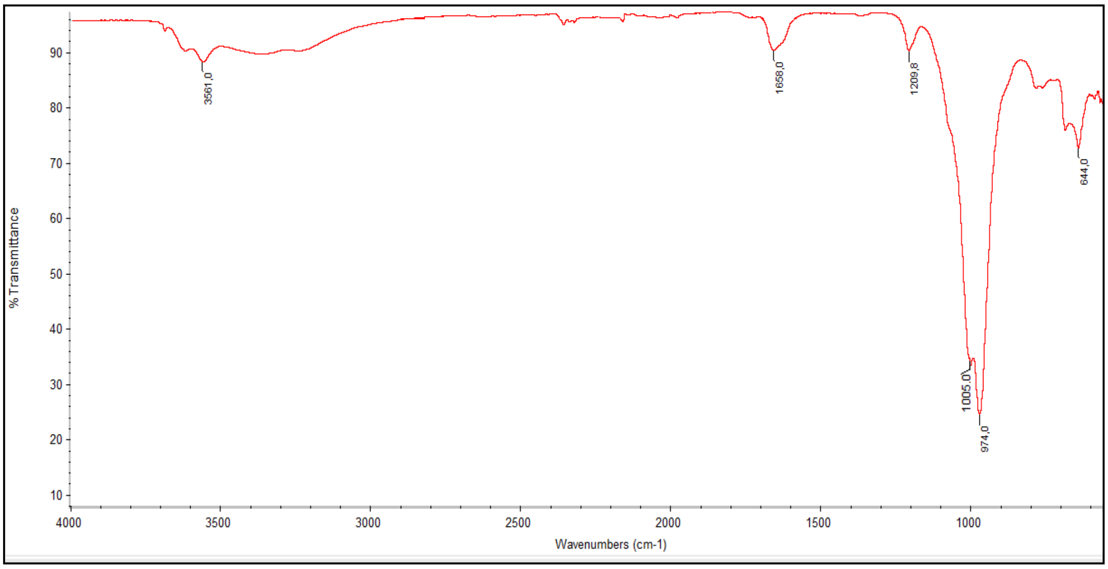

Figure 4.4 : FTIR of sepiolite clay.

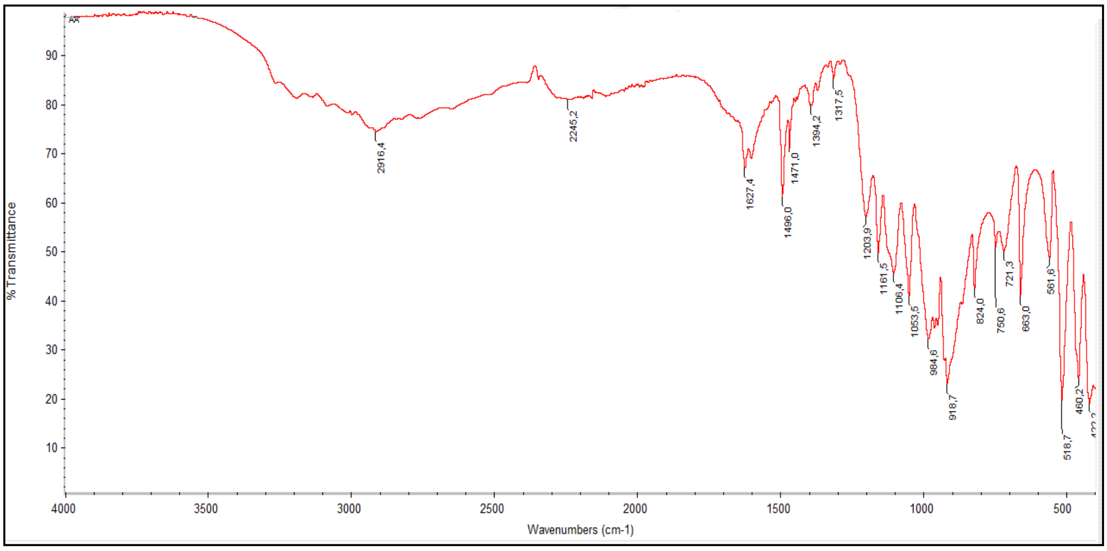

Figure 4.5 : FTIR of alendronic acid.

In the spectrum of sepiolite, the absorption peak at 3676 cm^{-1} is attributed to the Mg-OH stretching of sepiolite. The absorption peaks at 1076 cm^{-1}, 758 cm^{-1} and 470 cm^{-1} are ascribed to the Si-O vibrating and bending of sepiolite, and the peaks at 980 cm^{-1} and 689 cm^{-1} are the Si-O-Si vibrating characteristics of sepiolite [117].

From Figure 4.4, the peaks at 3561 cm^{-1} and 644 cm^{-1} are the Mg-OH stretching and Si-O-Si vibrating of sepiolite, and the biggest peaks at 1005 cm^{-1} and 974 cm^{-1} are the Si-O and Si-O-Si vibrating of neat clay.

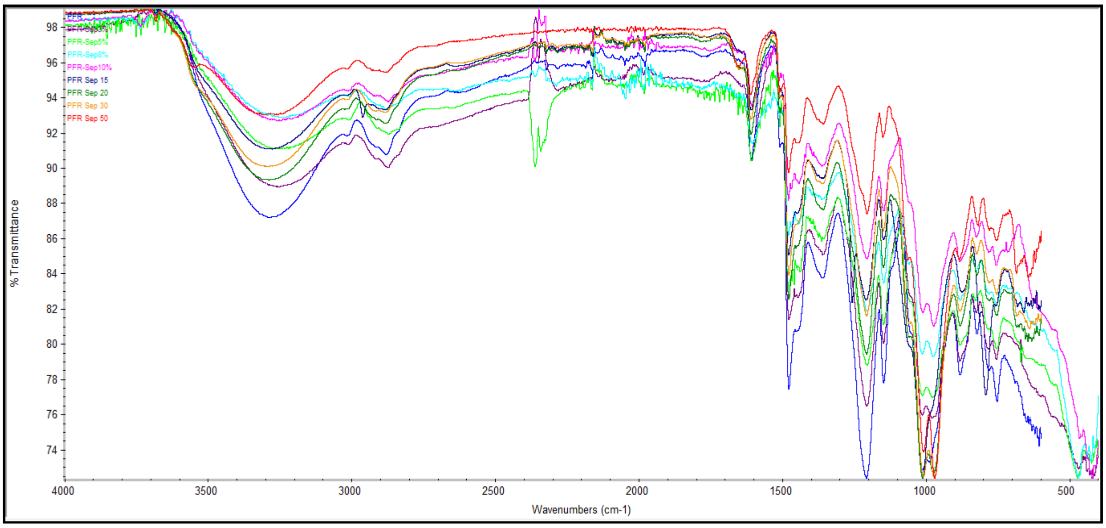

Figure 4.6 : FTIR of PFR-SEPs.

Strong bands in the region 1200–900 cm^{-1} correspond to C-O and P=O stretches [112]. Figure 4.5 verify the literature values.

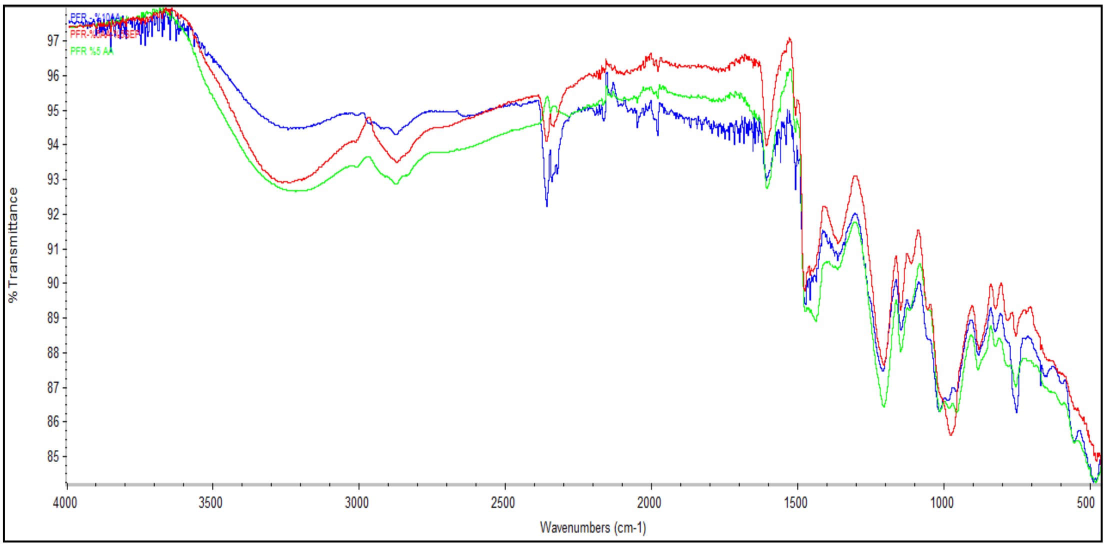

Figure 4.7 : FTIR of PFR-AAs and PFR-AA-SEP.

As shown in Figure 4.6 in addition to the characteristic peaks of PFR, Si-O-Si vibrating peak of sepiolite was also seen in samples. The intensity of sepiolite peaks strengthened with increasing amount of SEP in the nanocomposites and the intensity of resol peaks (-OH) decreased. Similar situation can be seen in PFR-AAs. As alendronic acid loading increased the resol –OH peaks decreased (Figure 4.7).

4.3 Differential Scanning Calorimeter (DSC)

In this work, differential scanning calorimetry (DSC) was used to measure the temperatures and heat flows associated with exothermic and/or endothermic changes that occur during thermal transitions in the samples. The measurements of PFR, PFR-SEP3%, PFR-SEP5%, PFR-SEP10%, PFR-SEP20%, PFR-SEP50%, PFR-AA5%, PFR-AA10% and PFR-AA5%SEP5% were operated with 1 cycle. The cycle was heated from 30°C to 200°C with 10 °C/min heating rate.

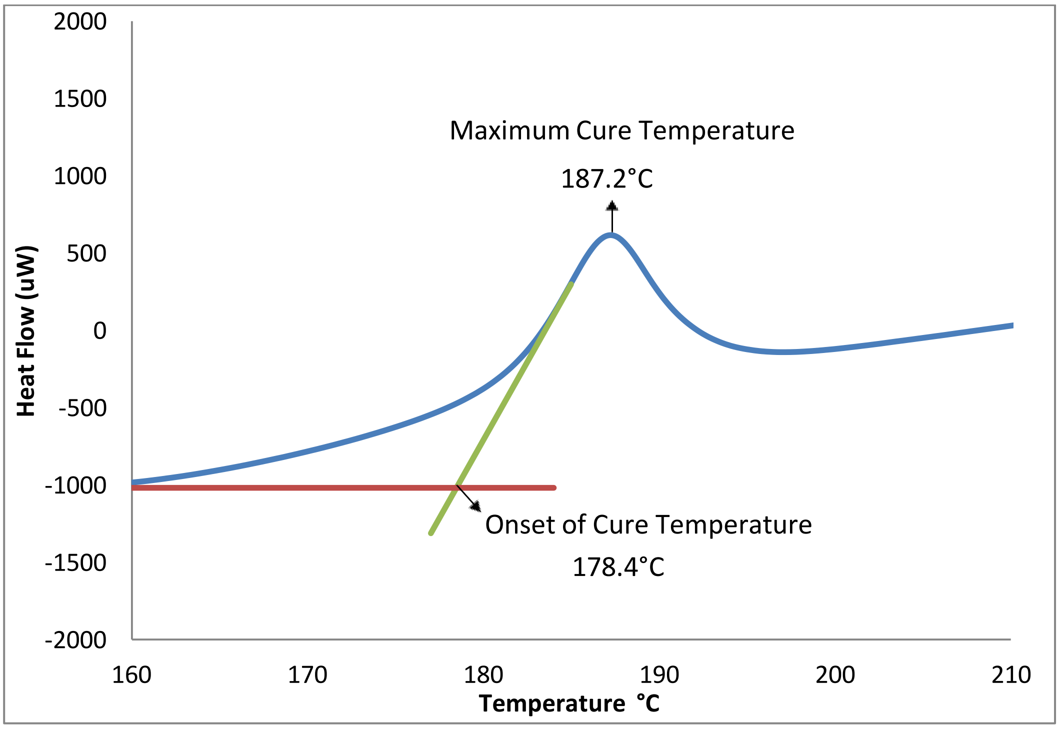

Figure 4.8 : Determination of the maximum cure temperature and onset of cure temperature for PFR-SEP5% from DSC plot.

The main application of DSC for phenolic resins is the specification of maximum cure temperatures and onset of cure temperatures. The technique is very useful when examining the effect of processing changes on cure. The determination of maximum cure temperatures and onset of cure temperatures of PFR-SEP5% and PFR-SEP20% samples were given in Figure 4.8 and Figure 4.9. The overall results of PFR, PFR-SEP3%, PFR-SEP5%, PFR-SEP10%, PFR-SEP20%, PFR-SEP50%, PFR-AA5%, PFR-AA10% and PFR-AA5%SEP5% were given in Table 4.3. Changes in the percent of sepiolite clay and alendronic acid affected the onset of cure temperature and maximum cure temperature. According to the results, the exothermic reaction was taken placed in the range of 160°C-210°C and the exothermic maximum cure temperature peak was found in between 171°C and 197°C.

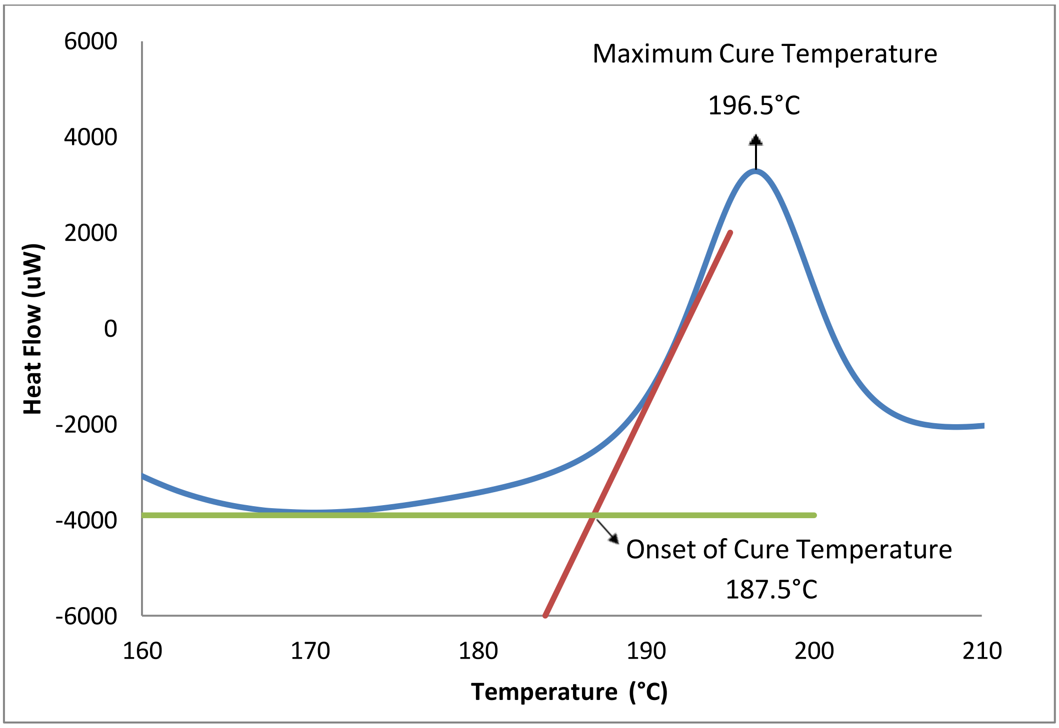

Figure 4.9 : Determination of the maximum cure temperature and onset of cure temperature for PFR-SEP20% from DSC plot.

With increasing sepiolite content and alendronic acid content, onset of cure temperature and maximum cure temperature were enhanced. To compare sepiolite clay and alendronic acid, the curing temperatures of nanocomposites that contain sepiolite were found better. The DSC results are important in industry because maximum cure temperature and onset of cure temperature determine the usage of resol resins.

On the other hand, the DSC results showed the synergist effect of alendronic acid and sepiolite clay. PFR-AA5%-SEP5% had higher temperature values than PFR-

AA5% and PFR-SEP5% that offers the combination of these materials. From all of the samples, PFR-SEP50% had the highest values.

Table 4.3 : DSC results of specimens.

Sample	Maximum Cure Temperature (^oC)	Onset of Cure Temperature (^oC)
PFR-SEP3%	185.1	176.0
PFR-SEP5%	187.2	178.4
PFR-SEP10%	196.1	185.2
PFR-SEP20%	196.5	187.5
PFR-SEP50%	197.0	189.1
PFR-AA5%	171.4	163.0
PFR-AA10%	187.3	178.0
PFR-AA5%SEP5%	192.7	182.4

4.4 Thermogravimetric Analysis (TGA)

TGA is one of the simplest of the thermal analysis technique that is used to determine thermal stability and the temperature of degradation for materials.

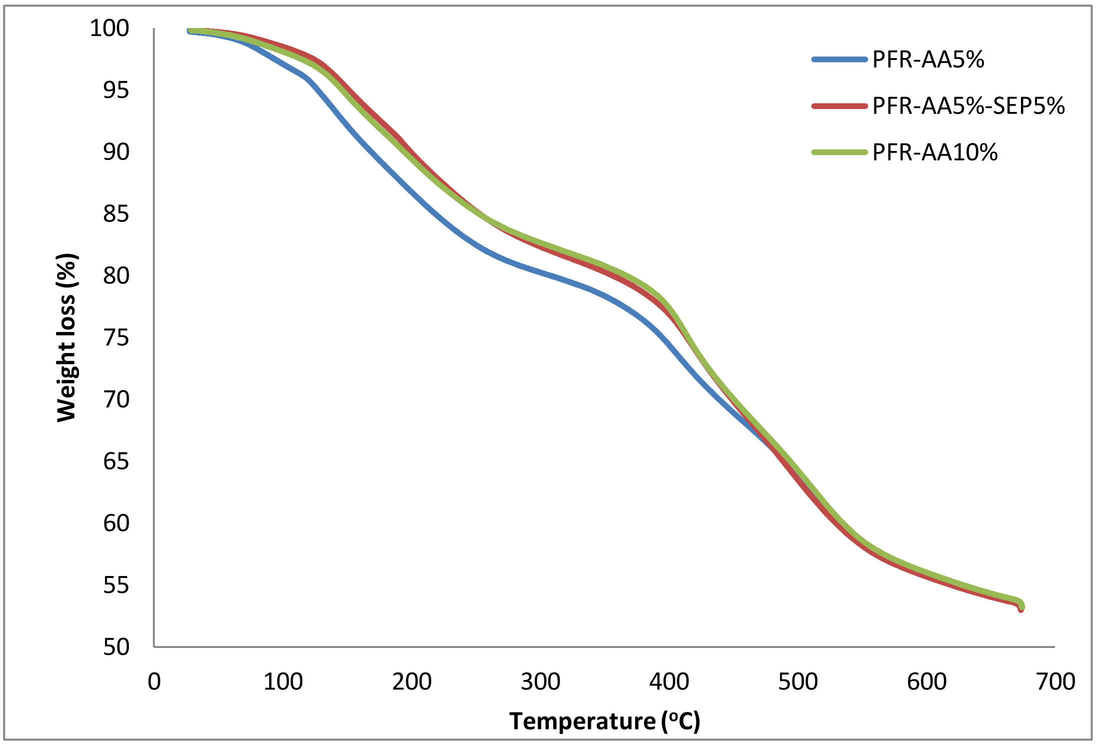

Figure 4.10 : TGA thermograms of PFR-AA5%, PFR-AA5%-SEP5% and PFR-AA10%.

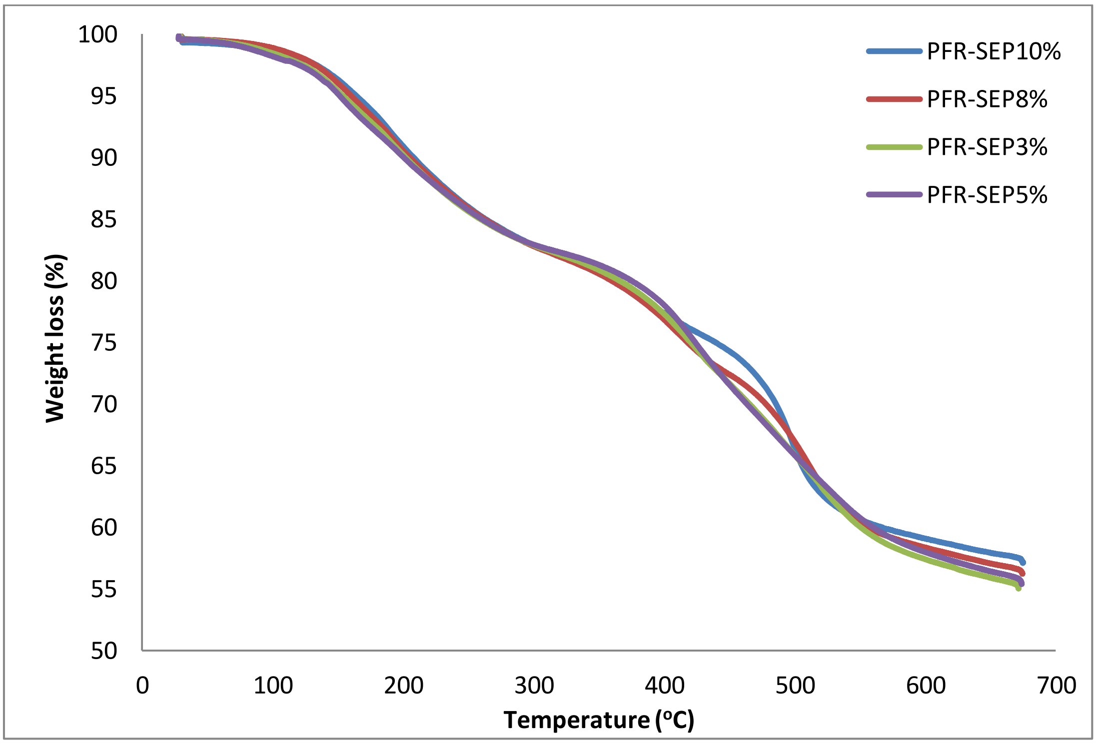

Figure 4.11 : TGA thermograms of PFR-SEP3%, PFR-SEP5%, PFR-SEP8% and PFR-SEP10%.

TGA can be used to evaluate phenolic resins in their pre-cured state or their fully cured state, both with and without other components.

Thermal decomposition behaviours of PFR, PFR-AAs, PFR-SEPs and PFR-AA-SEP samples were determined with TGA measurements. Degradation was carried out in nitrogen gas to the maximum temperature of 700°C. The weight loss (wt%) of the resins were calculated, the weight loss (%) rates were shown as a function of temperature in Figure 4.10 - 4.11 - 4.12 and Table 4.4.

Different stages of degradation were seen in the TGA thermogram: The first stage (until 100°C), the second stage (250-350°C) and the third stage (350°C-700°C). In the first stage, the water molecules left the sample . In the second stage the release of formaldehyde occured due to break of ether bridges. The last and third stage of thermal decomposition was lost of water from bound water from sepiolite clay and oxidation of network. At 700°C the all residues are upper the 50% ,so that the thermal stability of specimens were enhanced.

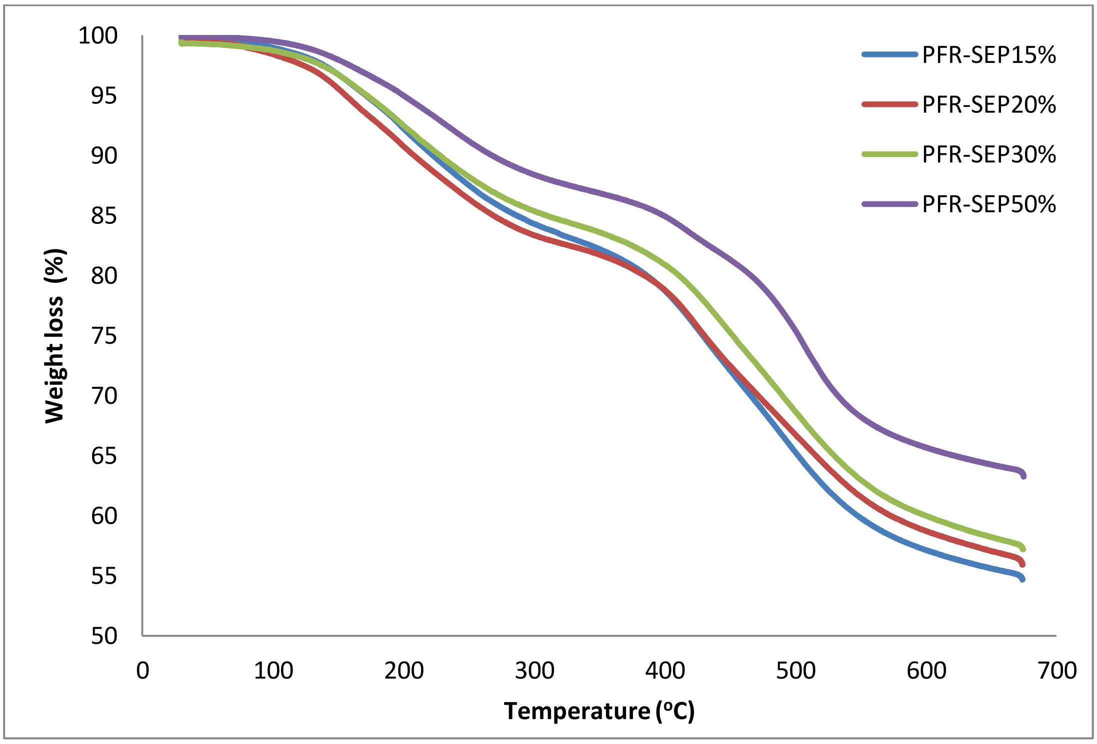

Figure 4.12 : TGA thermograms of PFR-SEP15%, PFR-SEP20%, PFR-SEP30% and PFR-SEP50%.

In Figure 4.10 and Table 4.4 as the percent of alendronic acid doubled the residue of alendronic acid containing was slightly increased (PFR-AA5% and PFR-AA10%). On the other hand, the thermal stability of PFR-SEP5% was found greater than PFR-AA5%. Therefore, sepiolite has better thermal effects than alendronic acid. Furthermore, PFR-AA5%-SEP5% had same residue with PFR-AA10%.

Table 4.4 : TGA results of specimens.

Sample	Residue (%) at 700°C
PFR-SEP3%	55
PFR-SEP5%	56
PFR-SEP8%	57
PFR-SEP10%	57
PFR-SEP15%	58
PFR-SEP20%	58
PFR-SEP30%	59
PFR-SEP50%	64
PFR-AA5%	53
PFR-AA10%	54
PFR-AA5%-SEP5%	54

The another comparasion can be done with PFR-SEP10% and PFR-AA10%. From the results PFR-SEP10% has better thermal stability than PFR-AA10%. Thus, clay loading is more useful to improve the thermal stability of resol resins. PFR-SEP50% was found the most stable sample because the highest residue value was obtained.

4.5 X-Ray Diffraction Analysis (XRD)

The structures and the variations of spacing of the neat resol, sepiolite clay and modified resol resins were detected by X-ray diffraction. In Table 4.4 d-spacings, which was calculated by Bragg's Equation ($n.\lambda=2.d.\sin\theta$), and 2θ angles were shown. 2θ measurements and d spacings (nm) (where d is interlayer distance in the direction of lattice plane diffraction peak) of the final samples are given in Table 4.5.

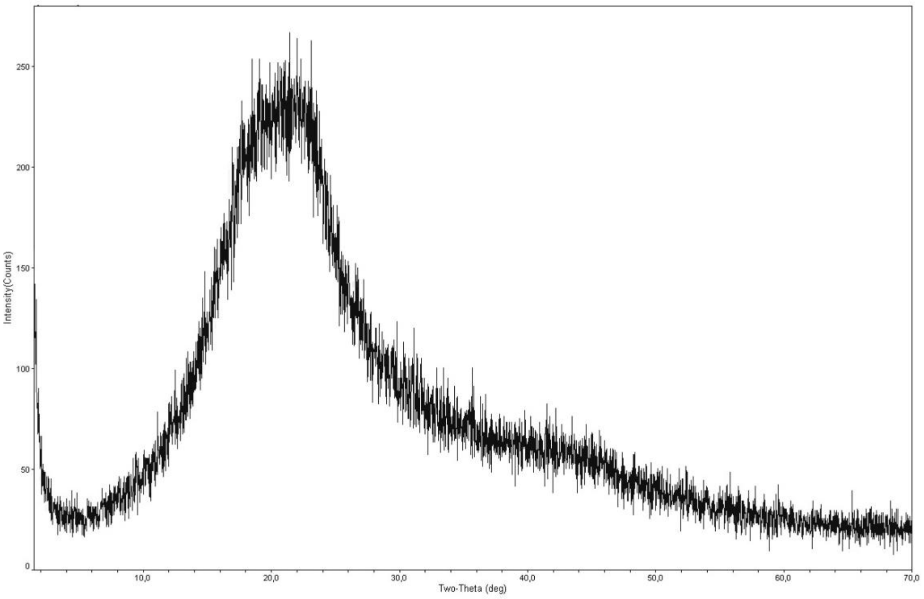

Figure 4.13 : XRD pattern of PFR.

The 2θ value and d-spacing of the neat PFR used were found to be 21.48^o and 0.413nm. (Figure 4.13 and Table 4.5). For sepiolite clay the values were determined as 7.46^o and 1.184nm respectively (Figure 4.14 and Table 4.5). The values of PFR and sepiolite compatible with the results of literature [102,118,119].

After adding the sepiolite, the intense diffraction peak is visible in the nanocomposites at corresponding to the channel reflections of the sepiolite structure that prove the intercalated structure. The relative intensity of the d peak increased with the percent of sepiolite loading (Figure 4.15). In addition, dispersion of sepiolite in resol was influenced by the amount of sepiolite; the more sepiolite in composites, the poorer dispersion.

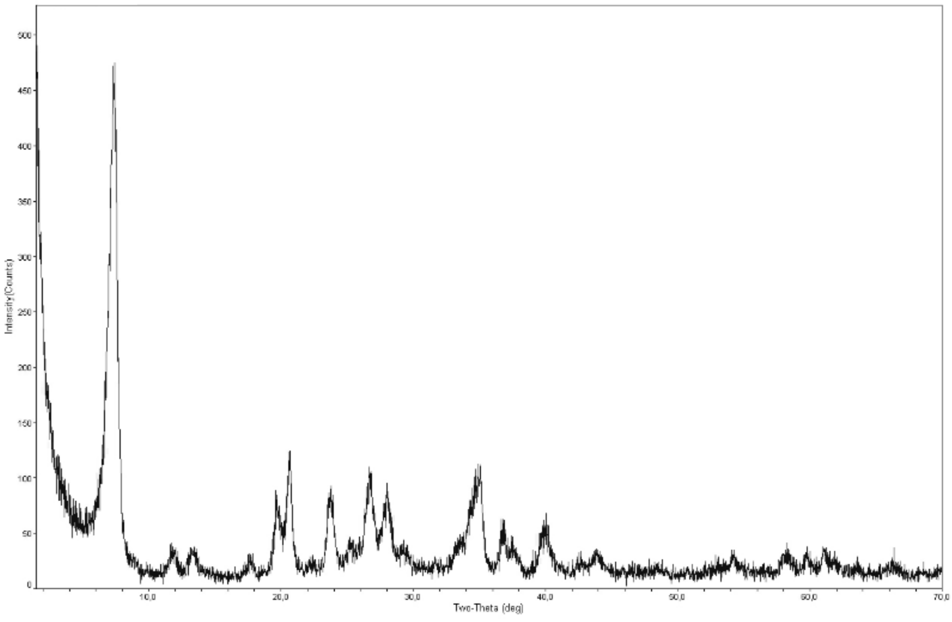

Figure 4.14 : XRD pattern of sepiolite clay.

XRD results showed the intercalated structure of PFR-SEPs due to the presence of sepiolite peaks. However, as the loading of sepiolite was increased, the interlayer distance did not change very much. Because, the layers of sepiolite are linked by covalent bonds (Si-O-Si), and resol has thermoset structure even before curing.

Table 4.5 : Diffraction characteristics of samples.

Sample	2θ (deg)	d-spacing (nm)
PFR	21.48	0.413
SEP	7.46	1.184
PFR-SEP3%	7.50	1.177
PFR-SEP5%	7.38	1.196
PFR-SEP8%	7.56	1.168
PFR-SEP10%	7.42	1.190
PFR-SEP15%	7.42	1.190
PFR-SEP20%	7.42	1.190
PFR-SEP30%	7.56	1.168
PFR-SEP50%	7.62	1.159
PFR-AA5%	19.62	0.452
PFR-AA5%-SEP5%	7.82	1.130
PFR-AA10%	3.28	2.693

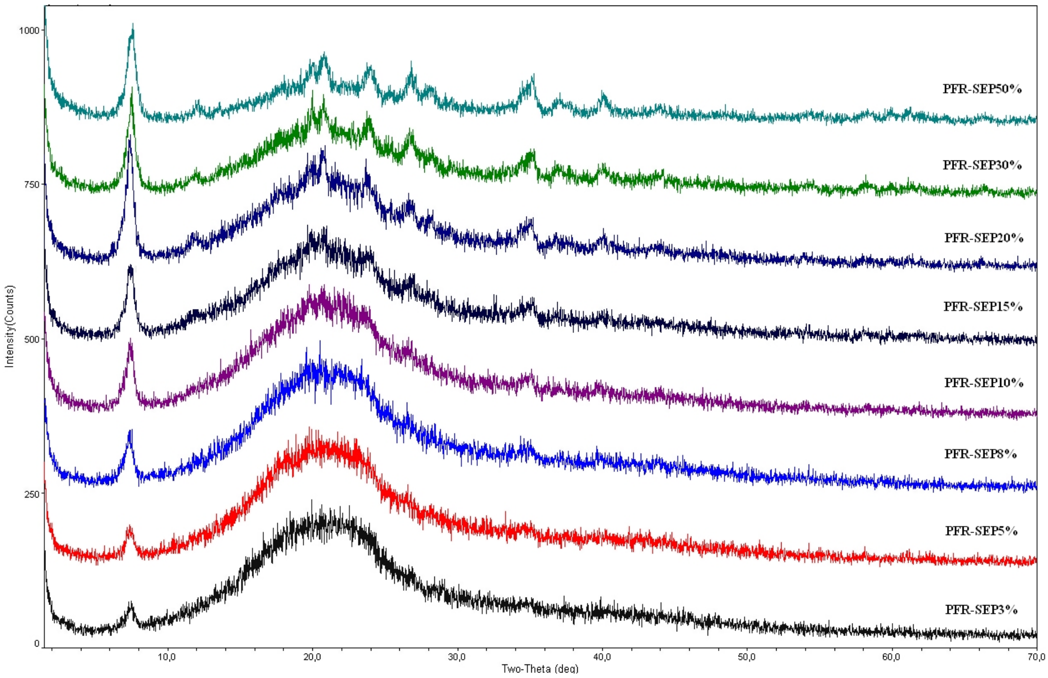

Figure 4.15 : XRD patterns of PFR-SEPs.

The XRD pattern of the PFR-AA5% had only one peak close to that of the pristine polymer (Figure 4.16). This suggests that alendronic acid particles were well exfoliated and dispersed uniformly in the polymer matrix. The d-spacing of PFR-AA5% was slightly increased compared to PFR (Table 4.5.).

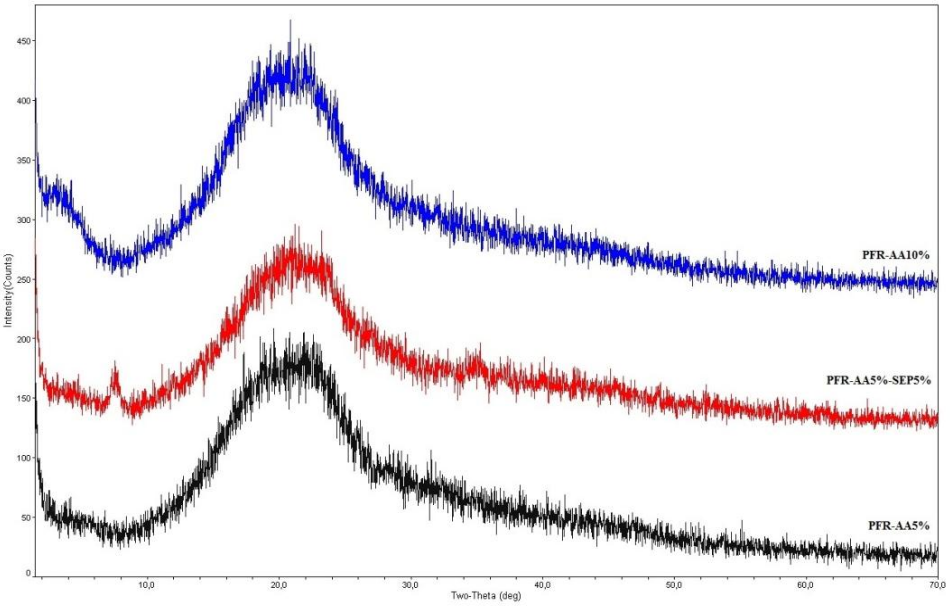

Figure 4.16 : XRD patterns of PFR-AAs and PFR-AA-SEP**.**

On the other hand, the nanocomposite PFR-AA10% had a slight of alendronic acid peak at 3.28^{o}. This result confirms that the alendronic acid dispersion at a higher content has a tendency of intercalated structure. The sample of PFR-AA5%-SEP5% has a sepiolite peak at 7.82^{o} and the interlayer distance was found as 1.130 nm. The value is lower than PFR-SEP5% because of the presence of alendronic acid.

4.6 Scanning Electron Microscope (SEM)

SEM analysis was performed to understand the distribution of clay particles in polymeric resol resin matrix and in order to gain an idea about the degree of intercalation and/or exfoliation of the clay layers. The SEM cross-sectional images of PFR-SEP10% nanocomposite are illustrated in Figure 4.17.

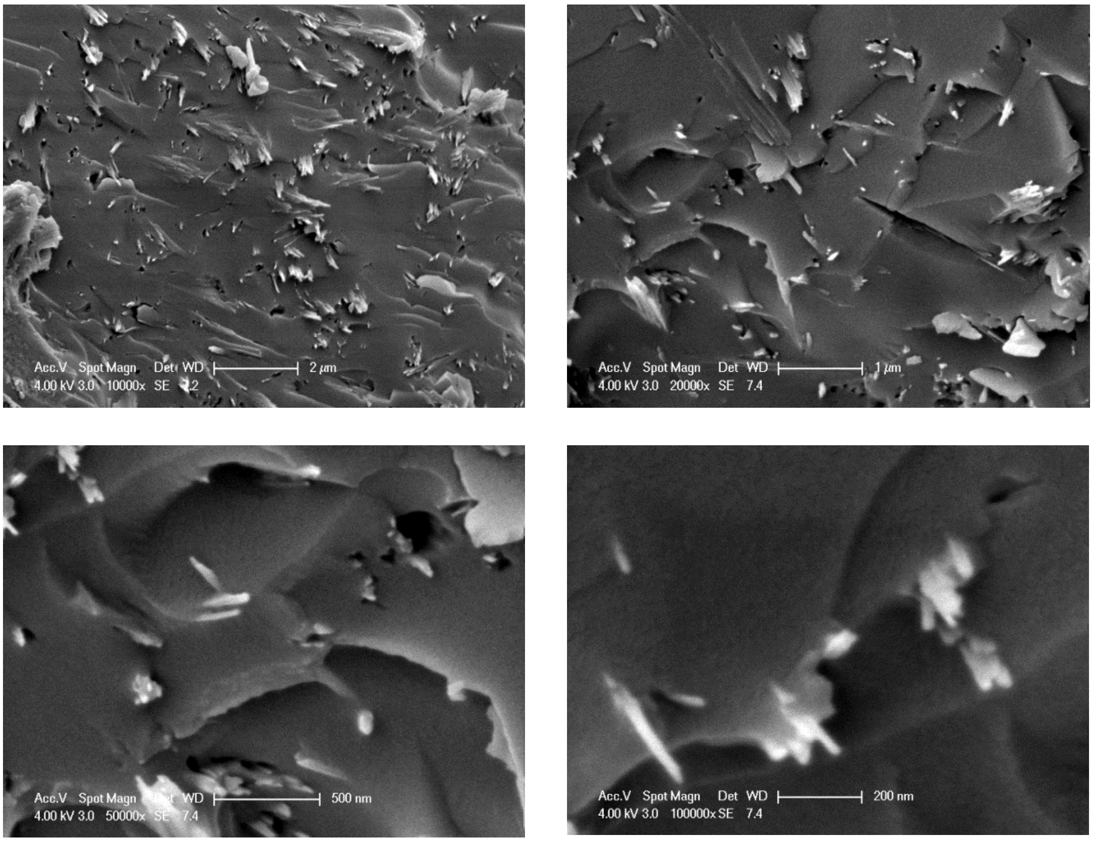

Figure 4.17 : SEM images of PFR-SEP10% at different magnifications.

It is obvious that the sepiolite has a fibrous and needle like morphology and sepiolite is uniformly dispersed in resol matrix. The resol covered with sepiolite suggesting interaction between the methylol groups (-CH_2OH) of resol and silanol groups (Si-OH) of sepiolite**.**

5. CONCLUSION

This is the first study that investigated and discussed the influence of the sepiolite clay and alendronic acid in the resol resin. This study can be divided into two parts. In the first part of this study, PFR, PFR-SEPs, PFR-AAs and PFR-AA-SEP were synthesized via *in situ* method. The obtained resin samples were characterized by FTIR, DSC, TGA, XRD, SEM and solubility tests. Solubility tests showed that the resol nanocomposites were resistant to solvents such as THF, methanol, acetone, and chloroform with the exception of DMSO and DMF. The specimens were better soluble in DMSO compared to DMF. In FTIR analysis the intensities of resol peaks were decreased and the intensities of sepiolite peaks and alendronic acid peaks due to loading. PFR-SEPs were synthesized with high clay percents up to 50% and the problem of clay precipitation did not occur due to needle like structure of sepiolite.

The determination of maximum cure temperatures and onset of cure temperatures of samples were done with DSC. The increasing of onset of cure temperature and maximum cure temperature were successed with the enhancement of sepiolite and alendronic acid percentages. Considerable thermal stability enhancement of resol matrix has been found by TGA analysis of PFR-SEPs, PFR-AAs and PFR-AA-SEP. In PFR-AAs the residue of resin increased 53-54% that is above the 50% resin at 700^{o}C. In PFR-SEPs the residues were found between 55-64%. When the influence of the alendronic acid and sepiolite was compared, sepiolite had better resistance definitely.

According to XRD results, PFR-AA5% had exfoliated structure and with increasing alendronic acid content the intercalated structure obtained with PFR-AA10%. Furthermore, the results showed the intercalated structure of PFR-SEPs. After modification, the characteristic diffraction peaks of sepiolite have not been very much changed that indicates the crystal structure of sepiolite has not been destroyed during the process. SEM measurements confirmed that the nanocomposite resins with the clay content of 10wt% had a good dispersion of sepiolite clay.

In second part of this study the synthesized resins were introduced the fabrication of glass wool insulation material. Nanocomposite resol samples were sprayed on the glass wool to enhance the thermal stability of finished glass wool product. The obtained glass wool-modified resol resin composites were found processable in insulation sector, due to improved thermal stability.

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